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Polymerization of Unsaturated Compounds by Photocycloaddition Reactions[1]

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Contents

Wendell L. Dilling was born in Bluffton, IN, in 1936 and received his B.A. degree in chemistry from Manchester College in 1958. His Ph.D. degree in organic chemistry was granted by Purdue University in 1962 where he worked with Dr. Earl T. McBee on reactions of dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane and related compounds. He joined The Dow Chemical Company in Midland, MI, in 1962 in their special assignments program, and from 1964 to 1974 worked in their E. C. Britton Research Laboratory on exploratory organic photochemistry. From 1974 to the present he has worked in Dow's Environmental Sciences Research Laboratory in the areas of atmospheric and aquatic environmental photochemistry. The major topics of his 45 publications are synthetic and mechanistic aspects of photocycloaddition reactions, carbenium ion rearrangements in the pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl system, pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane chemistry, monohalocarbenoid species formation and reactions, and the phototransformation of organic compounds in the atmosphere. He is active in the American Chemical Society, having served as a councilor from the Midland Section since 1976 and on the Society Committee on Publications since 1977. He was the general chairman of the 14th Central Regional ACS Meeting in 1982.

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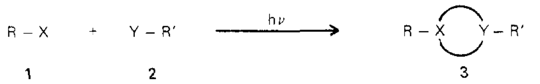
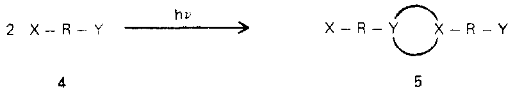
I. Introduction and Scope of the Review

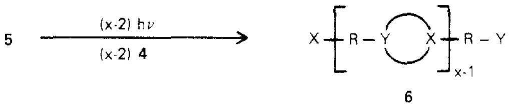
Cycloaddition (ring-forming)[2] reactions (eq 1) of unsaturated molecules **1** and **2** brought about by ultraviolet or visible radiation, although not well-understood as to some mechanistic details and controlling parameters, are useful for various synthetic and other applications.[3-5] For example, in polymerization reactions a molecule containing two or more reactive moieties, X, Y, etc., can form polymer chains **6** containing numerous (x) monomer units **4** linked together (eq 2 and 3).



1 2 3 (1)



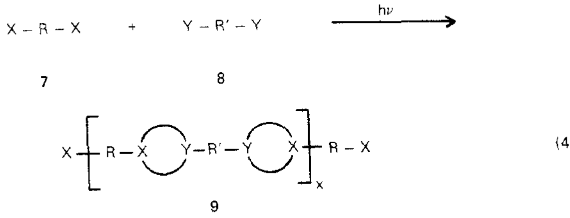
4 5 (2)



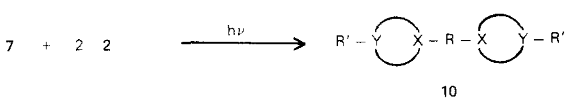
6 (3)

Numerous noncomprehensive reviews and research summaries have been published on these photocycloaddition polymerizations.[6-41] This review covers all such polymerizations, as defined below, that have been published through 1980 and part of 1981. For the purpose of this review, polymerization is defined as a process in which more than two monomer units join together, i.e., x (degree of polymerization, DP) > 2 in eq 3.

Most photocycloaddition polymerizations reported in the literature are homopolymerizations in which X and Y in the monomer **4** are the same. In a few examples X and Y are dissimilar. Copolymerizations of two unlike monomers such as **7** and **8** to give alternating copolymers **9** have been reported (eq 4). To fall within the scope of this review both monomers in a copolymerization must be bifunctional and the process must have incorporated more than three monomer molecules. Not included are crossed photocycloadditions of two dissimilar unsaturated molecules, one of which is bifunctional **7** and the other monofunctional **2** so that three molecules are incorporated into the 2:1 biscycloadduct **10** (eq 5).



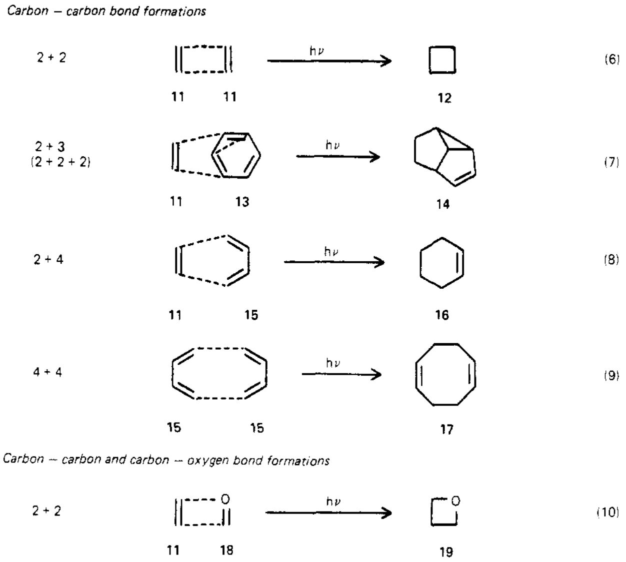
7 8 9 (4)



10 (5)

In contrast to photoinitiated polymerizations, which are chain reactions,[6] photocycloaddition polymerizations require absorption of a photon in each propagation step (eq 3). When the various excited state deactivation processes are included, the quantum yield (Φ) for the disappearance of monomer is ≤ 1.0 except for very low DP's. For a low DP, Φ could be > 1.0; e.g., in trimerization, $\Phi \leq 1.5$.

Scheme I

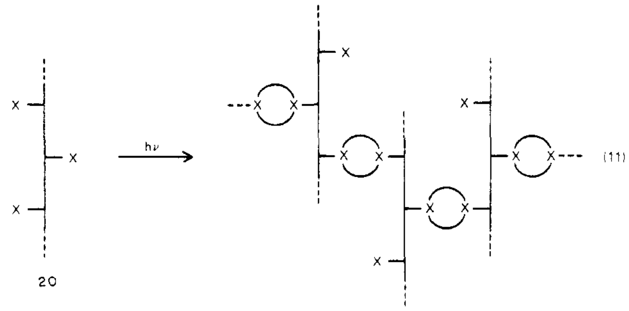


11 11 12; 11 13 14; 11 15 16; 15 15 17; 11 18 19

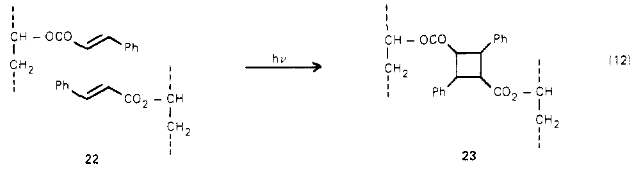
Many photocycloaddition polymerizations probably have been performed unintentionally, usually during studies of the intramolecular reactions. The resulting polymers were generally not characterized. A few examples from the literature were found, e.g., ref 43, and included in this review. Frequently, alternate polymerization mechanisms were possible so that one can not be certain the reactions occurred via a photocycloaddition.

This review is organized primarily according to the type of photocycloaddition reaction (Scheme I) that led to the polymerization, and secondarily according to the structure of the monomer. Other aspects of the reactions, such as the physical phase (solid, solution) of the monomer and the mechanism, are discussed with the individual processes.

The cross-linking of polymers, e.g., **20**, that contain unsaturated groups, by photocycloaddition reactions (eq 11) is not included in this review. These reactions are polymerizations in which the polymer **20** serves as the monomer. The cross-linking of polyvinyl cinnamate (**22**) is an example of such a reaction (eq 12). These



20 21 (11)

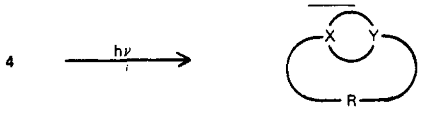


22 23 (12)

reactions have been reviewed previously.[8,44-47]

Some side reactions that occur during the polymerizations are considered briefly in this review. These side reactions reduce the achievable molecular weight and can severely limit the applicability of these polymerizations.

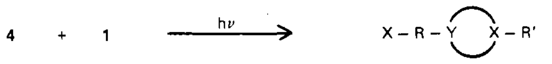
Intramolecular cycloaddition (eq 13) destroys both end groups X and Y. This process is highly dependent on the length and flexibility of the linkage R. Intramolecular cycloaddition can occur at any stage of the polymerization, and can involve the polymer as well as the monomer.



24

(13)

The presence of monofunctional impurities 1 (eq 14) or other reactive impurities 26 (eq 15) can terminate the chain growth on one end of the growing polymer. Thus, as in other polymerization processes, the monomer purity is a critical factor.



25

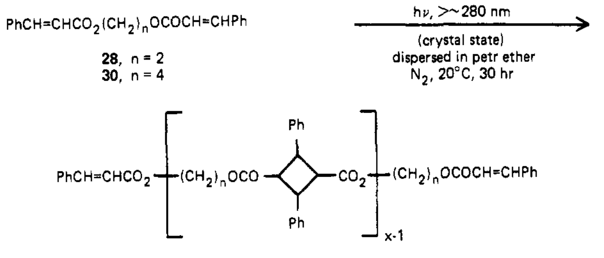
(14)

$$4 \quad + \quad \underset{26}{Z} \quad \xrightarrow{h\nu} \quad \underset{27}{X-R-Y-Z} \qquad (15)$$

II. Cycloadditions Involving Carbon 2 + 2 Addition

A. Acyclic Bis- and Poly(cinnamic acid) Derivatives

The dicinnamate esters 28 and 30 of ethylene glycol and 1,4-butanediol gave polymers 29 and 31, respectively, with undetermined DP's, on irradiation of the crystalline monomers either dispersed in petroleum ether (bp 40–60 °C) (eq 16) or in a solid KBr disk (eq 17).[48,49]

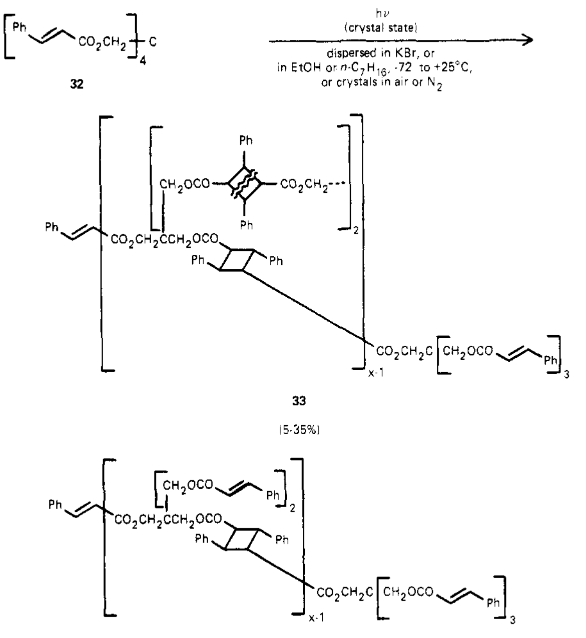


28, n = 2
30, n = 4

29, n = 2 (7%)
31, n = 4

(16)

$$\underset{}{28} \quad \xrightarrow[\substack{\text{(crystal state)} \\ \text{dispersed in KBr} \\ \sim 25^\circ\text{C, 30 hr}}]{h\nu,\ >\sim 280\ \text{nm}} \quad \underset{(100\%)}{29} \qquad (17)$$



32

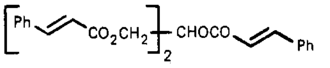
33
(5-35%)

34

(18)

Irradiation of several different crystal forms of the tetracinnamate ester 32 of pentaerythritol in the solid state gave an amorphous oligomer or polymer, the structure of which probably was 33 (eq 18).[50,51] The reaction presumably occurred via 2 + 2 cycloadditions, although this mechanism has not been established.[50,51] A crystal structure determination of the α crystal form of monomer 32 showed the two nearest intermolecular double bond separations were 3.78 Å and 4.79 Å.[50] The first polymerization stage was viewed as cycloaddition of these double bond pairs, forming the linear polymer 34 in a crystal lattice controlled process.[50] This linear polymer then probably cross-linked via intermolecular cycloaddition of the pendant cinnamyl groups.[50] The next shortest double bond separation, after the two noted above, was 8.14 Å.[50] This separation may have decreased following the initial linear polymerization, thus allowing the cross-linking. Alternately, local melting may have occurred leading to random conformations of the side chains, which then were able to undergo photocycloaddition giving 33.[50]

The tri-, 35, or tetraesters, 32 and 36, of cinnamic or cinnamylideneacetic acids were patented as monomers for photoresists.[52] These polymerizations, followed by cross-linking, may proceed via photocycloaddition reactions of the cinnamate double bonds.

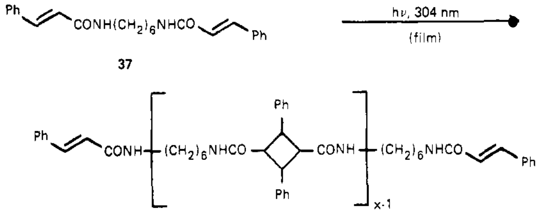


35

$$[PhCH{=}CHCH{=}CHCO_2CH_2]_4C$$

36

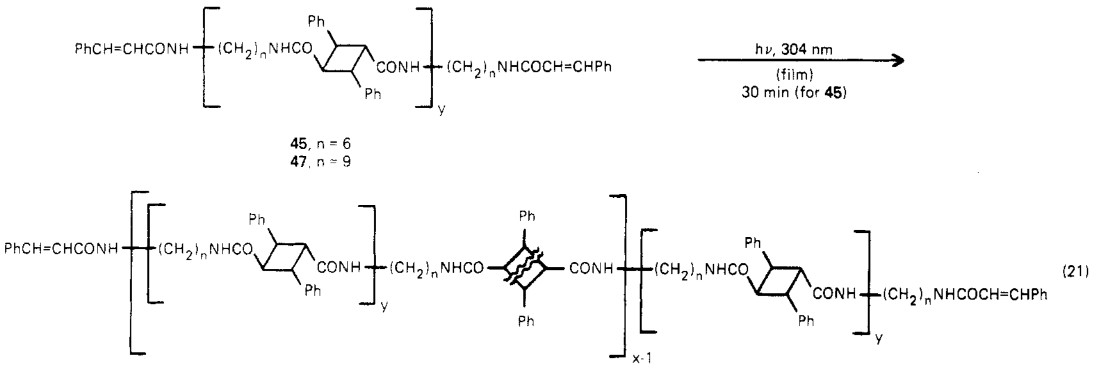
The bis(cinnamide) 37, which was formed in a film by photolysis of the polyamide 38 at 224 nm, re-formed the polymer 38 on photolysis at longer wavelength (eq 19).[49,53] The original polyamide 38 was prepared by a nonphotochemical polymerization.[53] The method of forming monomer 37 produced it in an oriented manner such that the double bonds were in the correct positions for undergoing cycloaddition (eq 19). This polymerization occurred only in the polymer matrix of 38.[23]



37

38

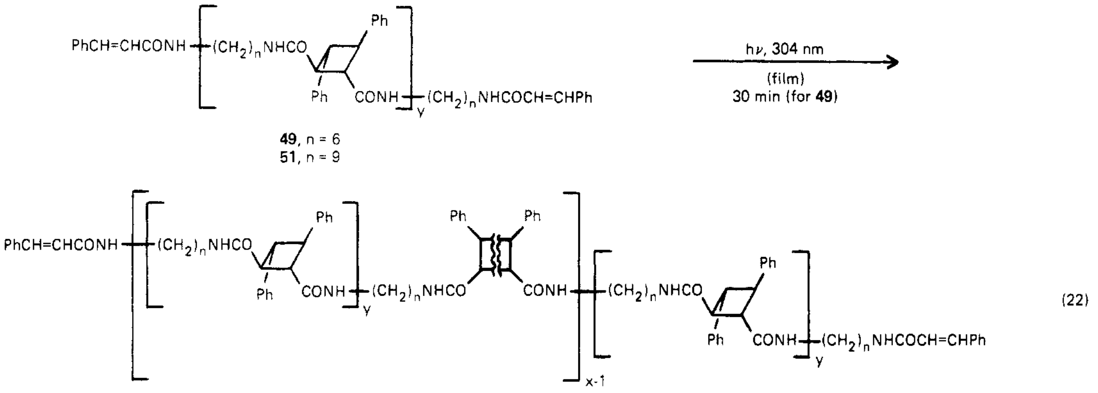
(19)



45, n = 6
47, n = 9

46, n = 6
48, n = 9

(21)



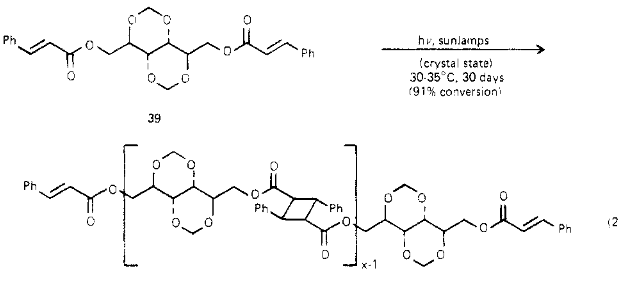
49, n = 6
51, n = 9

50, n = 6
52, n = 9

(22)

B. Alicyclic Bis(cinnamic acid) Derivatives

Irradiation of crystalline (+)-dimethylene-D-mannitol dicinnamate 39 gave the oligomers 41–44 in addition to higher molecular weight products 40 in which the probable values of x (DP's) were 6, 7, 8, and ≥10 (eq 20).[54] The smaller oligomers were favored at shorter reaction times and the larger ones at longer reaction times.[54]



39

40 (39%)

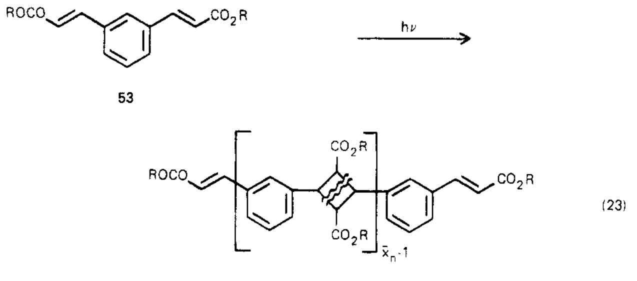
(20)

41, x = 5 (> 5%)
42, x = 4 (> 2%)
43, x = 3 (> 5%)
44, x = 2 (> 11%)

In reactions similar to that shown in eq 19, the partially photodepolymerized α-truxillates 45 and 47 gave polymers 46 and 48, respectively, on irradiation (eq 21).[55] Cis–trans isomerization about the carbon–carbon double bonds also occurred. In a similar manner the partially photodepolymerized δ-truxinates 49 and 51 produced polymers 50 and 52 and underwent cis–trans isomerization (eq 22).[55] A re-formation of the cyclobutane rings in these polymerizations (eq 21 and 22) has not been proven. These polymerizations initially were rapid and then decreased in rate. Most of the carbon–carbon double bonds reacted in 30 min, and all four polymerizations occurred at about the same rate.[55]

C. *m*-Phenylenediacrylic Acid and Esters

Irradiation of the diacid or diesters 53 in the crystal state or in solution (eq 23) gave low molecular weight oligomers 54 (Table I).[56-60] The products 54 formed in the crystal state had either undetermined or mixed regiochemistries,[56,60] or head-to-tail structures.[57,58]



53

54

(23)

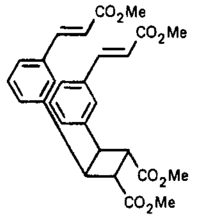
The product 56 formed in the presence of picramide (57) was presumably the same as that formed in the absence of 57,[58] but no data were presented to substantiate this assumption. The trinitro amine 57 was added as a spectral sensitizer for the oligomerization of 55, which was used for preparing holographic gratings.[58,59] The mechanism of the sensitization by 57 probably was the usual triplet energy-transfer process, followed by cycloaddition of 55*[3] to the ground state monomer 55.[58] The energy transfer was postulated to occur at the contact points of the crystals of 55 and 57.[58] The diacid 55 photopolymerized with a high quantum yield.[58]

TABLE I. Photopolymerization of *m*-Phenylenediacrylic Acid and Esters 53 (Eq 23)

R of monomer 53	physical state of monomer 53	λ, nm	temp, °C	time, h	product 54	yield of 54, %[a]	ref
H, 55	crystal dispersed in H_2O or H_2O-EtOH	b	~25	72	56, probably oligomer	100	56, 57
55	film of mixed microcrystals of 55 and picramide 57[c]	442[d]		0.0014–0.015	56		58, 59
Me, 58	crystal dispersed in H_2O	b	−20 to −10	30	59, $\overline{M}_n = 740, \overline{x}_n = 3.0$		60
58	crystal dispersed in H_2O	b	−10[e]	15[f]	59, $\overline{M}_n = 740, \overline{x}_n = 3.0$		60
58	crystal dispersed in H_2O	b	15	20	59, $\overline{M}_n = 1060, \overline{x}_n = 4.3$	~97	60
58	crystal dispersed in H_2O	b	25[e]	30	59, $\overline{M}_n = 1053, \overline{x}_n = 4.3$		60
58	crystal dispersed in H_2O or H_2O-EtOH	b	~25	30	59, $\overline{M}_n = 1040, \overline{x}_n = 4.2$	100	56, 57
58	0.42 M solution in $CHCl_3$	b		15	59	low[g]	60
58	0.42 M solution in $CHCl_3$	>300		~38[h]	59, $\overline{M}_n = 600, \overline{x}_n = 2.4$	~75[i]	60
Ph, 60	crystal in KBr	b			61, probably oligomer		56, 57

[a] Chemical yield. [b] Irradiated through quartz. [c] 1:0.8 (55:57) by weight. [d] Laser light source, 4–60 mJ cm^{-2}. [e] Conversion of double bonds given as a function of time. [f] Prolonged irradiation did not increase $\overline{M}_n$. [g] Cis-trans isomerization about the double bond occurred. [h] Conversion was ~75% in 10 h. [i] Conversion of 58.

The amorphous methyl ester oligomer **59**, formed by irradiation of the monomer **58** in the crystal state at 15 °C, probably contained a mixture of at least three stereoisomeric cyclobutanes that included both head-to-head and head-to-tail units.[60–62] The head-to-head dimer **62** of **58** was formed topochemically in the ordered crystal at −10 °C during the first few hours of irradiation.[60,62] The crystal structure of monomer **58**, determined by X-ray crystallography, supported the structural assignment of the dimer **62**.[62] The double bonds of **58** that became part of the cyclobutane ring of **62** were separated by 3.960 Å.[62] Dimerization of **58** increased the separation of the two remaining double bonds and destroyed the regular arrangement of the surrounding monomers.[62] The crystal thus became disordered, and subsequent random photocycloaddition occurred with the formation of an amorphous oligomer that contained cyclobutane rings having variable configurations.[60,62] The rate of this random cycloaddition in the disordered lattice was expected to be slower than that of the initial dimerization and faster at higher temperatures.[62] Monomer **58** disappeared slightly faster at 25 °C than at −10 °C.[60] At −30 °C molecular movement was suppressed to where topochemical dimerization was the only significant reaction.[60]



62

In contrast to oligomerization of the methyl ester **58** in concentrated solution (0.42 M, Table I), irradiation of **58** as a 0.042 M solution in $CHCl_3$ produced only trans–cis isomerization.[60] In concentrated $CHCl_3$ solution, oligomerization of **58** probably occurred via isomerization of *trans,trans*-**58** to *trans,cis*-**58** and *cis,cis*-**58**, and photocycloadditions of all three isomers to produce various regioisomeric cyclobutane rings in the oligomer **59**.[60]

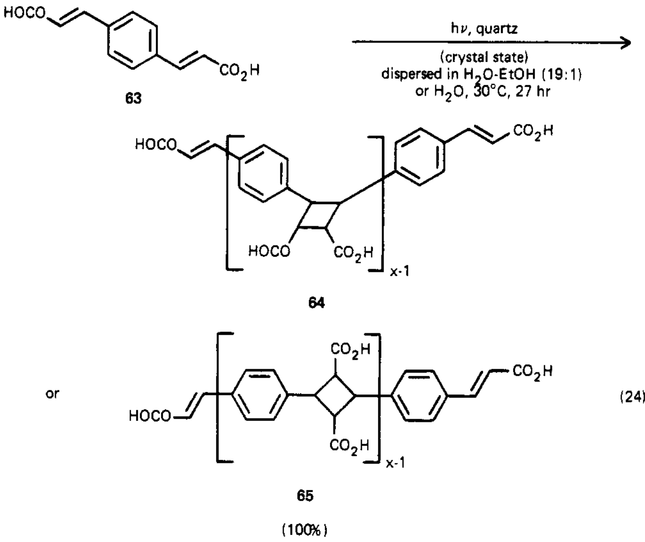
X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photo-oligomerization (λ >410 nm) of **58** showed that nucleation began and propagation proceeded within the defect-free structure.[51] In comparison to other related reactions studied, **58** had a medium reactivity.[51]

A study of the morphological changes in the solid state photopolymerization of **58** showed the oligomer **59** was amorphous and the crystal did not change shape during the reaction.[61] In this study the oligomer **59** was indicated to contain the head-to-head cyclobutane structure.[61]

D. *p*-Bis(monosubstituted vinyl)benzenes

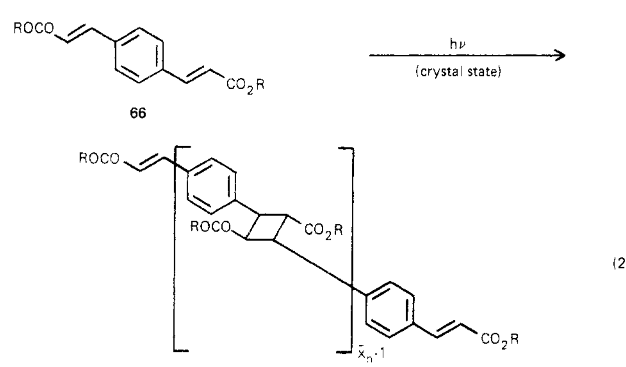
1. *p*-Phenylenediacrylic Acid, Esters, and Amides

Irradiation of the diacid **63** in the crystal state (eq 24) at 30 °C gave a low molecular weight polymer with structures suggested as either **64**[56] or **65**.[22,57,63] Irradiation at −25 °C gave a high (unspecified) molecular weight polymer.[56]



(24)

X-ray crystal structure determinations of the methyl,[64] ethyl,[65] and phenyl[66] esters **66** of the diacid **63** indicated the stereochemistry of the polymers **67** that resulted from the crystal state irradiations of the monomers **66** (eq 25) (Table II).[24,56,57,63,67–73] These polymerizations occurred only in the crystal state. Little reaction was observed on irradiation of the ethyl ester **70** in the molten state at 110 °C[63,71] or in solution;[56] a low molecular weight oligomer was isolated from the



66

67

(25)

irradiation in solution as described later (eq 32). The monomer crystals were transformed directly into polymer crystals, conversions typical of topochemical processes.[67]

Irradiation of the esters **68** (eq 26) and **70** at 360 nm gave low molecular weight oligomers because only the monomers absorbed light having this wavelength.[68,71] Polymerization ceased after all monomer molecules were incorporated into the numerous oligomer units. The formation of each oligomer was initiated by the random absorption of light or localization of excitation throughout the monomer crystal. Shorter wavelength light, e.g., 310 nm, which was absorbed by both the monomers (eq 26) and the growing polymer chains (eq 29) gave higher molecular weight polymers. These processes are shown in Scheme II for the methyl ester **68** where $\bar{x}_n$ represents here, the actual, not the average, degree of polymerization.[68,71] In agreement with this mechanism, the molecular weight of the ethyl ester polymer **71** continued to increase after the monomer **70** had been consumed.[71]

In contrast to these results, the intrinsic viscosity of the methyl ester polymer **69** solutions did not increase significantly on irradiation after the monomer **68** had completely reacted.[67] The similar shapes of the conversion–time and viscosity–time curves was cited as supporting evidence for the 2 + 2 photocycloaddition mechanism.[67] Clarification of this apparent inconsistency is needed.

At −269 to −103 °C with unfiltered UV radiation and at 30–60% conversion of the ethyl ester **70**, the major reactions were dimerization[74] and addition of **70** to the dimer and low molecular weight oligomers.[69] At ~50% conversion of **70** the DP was 3–5.[69] At higher conversions the molecular weights reached ~3000 (DP ≈ 11).[69]

Variable induction periods were noted in the photopolymerization of the ethyl ester **70** at −269 to −103 °C.[69] The cycloaddition probably occurred close to crystal defect sites,[74] and the rate probably depended on the number and kind of such sites.[69] The variability in the quality of different crystal samples presumably caused the variation in induction periods.[69] Microcracks developed during the induction period; these served as new defect sites.[69] The induction period disappeared after 10–15% conversion of the double bonds.[69] Other results, described later in this section indicate that photocycloaddition did not occur at defect sites.

The low temperature dependence of the polymerization of **70** was determined after 30–40% reaction had occurred.[69] An example of such data at −125 °C is given in Table II. The relative rates of disappearance of double bonds from **70** were 1.0, 2.1, 4.1, and 65 at −269, −196, −173, and −105 °C, respectively.[69] From these and other data the activation energy was found to be <20 cal mol^{-1} at −269 to −183 °C,[69,74] 1 kcal mol^{-1} at −190 to −180 °C,[70] 3 kcal mol^{-1} at −180 to −170 °C,[70] and 1.6 ± 0.3 kcal mol^{-1} at −173 to −103 °C.[69,74]

Scheme II

$$68 \xrightarrow[360 \text{ or } 310 \text{ nm}]{h\nu} 68^* \qquad (26)$$

$$68^* + 68 \longrightarrow 69\ (\bar{x}_n = 2) \qquad (27)$$

$$68^* + 69\ (\bar{x}_n = n) \longrightarrow 69\ (\bar{x}_n = n + 1) \qquad (28)$$

$$69\ (\bar{x}_n = n) \xrightarrow[310 \text{ nm}]{h\nu} 69^*\ (\bar{x}_n = n) \qquad (29)$$

$$69^*\ (\bar{x}_n = n) + 68 \longrightarrow 69\ (\bar{x}_n = n + 1) \qquad (30)$$

$$69^*\ (\bar{x}_n = n) + 69\ (\bar{x}_n = m) \longrightarrow 69\ (\bar{x}_n = m + n) \qquad (31)$$

The following explanation was offered for these results at low temperatures. Usually no potential barrier exists to the photocycloaddition of two isolated ethylenic bonds.[69] In a crystal, however, lattice forces evidently produce a barrier that can be overcome by the energy of local vibrations close to the electronic excited molecule.[69] At very low temperatures, the amplitude of the zero vibration, ~0.1 Å, is insufficient to cause reaction in the lattice; ~1–1.5 Å is necessary.[69] The probability of photocycloaddition is proportional to the probability of a deformed region forming in the crystal and does not depend on the temperature near absolute zero.[69] An increase in rate with an increase in temperature begins in the temperature range where the population of higher vibrational levels becomes possible.[69] However, if the quantum yield for the loss of double bonds in the ethyl ester **70** was ≤2, then the low temperature of the crystal environment may not have been pertinent to the specificity of the reaction.[26] The quantum yield for the loss of double bonds in the methyl ester **68** at higher temperature was ≤2, i.e., a new photon was required for each cycloaddition step.

The polymerization rate of the ethyl ester **70**, as measured by the disappearance of **70**, increased slightly as the temperature increased from −50 °C to −20 °C.[71] At −20 °C, 50% conversion occurred in ~5 min and 95% in ~40 min. At higher temperatures, −20 °C to 15 °C, the rate decreased with increasing temperature, especially at conversions >~75% of **70**.[71] The rate decreased even further near the melting point of **70**, 100 °C.[14,49,74] At 30–96 °C only low conversions could be achieved.[49]

At 50% conversion of **70**, the molecular weight of polymer **71** decreased with increasing reaction temperature (−50 °C to +15 °C).[71] At 30–96 °C only oligomers were formed.[49] A later reference stated that only dimer was formed, in low yield, at 56–96 °C.[75] At <25 °C, quantitative yields of crystalline high polymer **71** were formed; at >25 °C poor yields of amorphous, partially cross-linked polymer were produced.[14] In the presence of 360 nm radiation in the KBr matrix, the oligomer **71** formed at −28 °C contained 10% fewer end groups than that formed at 20 °C; thus a higher degree of oligomerization occurred at the lower temperature.[71]

A crystal transition at 56 °C for **70** did not significantly alter the arrangement of the monomer in the crystal,[71,75] and the double-bond separation actually contracted slightly.[75] The selective dimerization above 56 °C was attributed to a topochemically controlled photocycloaddition followed by local melting, which was

TABLE II. Photopolymerization of *p*-Phenylenediacrylate Esters **66** in the Crystal State (Eq 25)

R of monomer **66**	dispersion medium for monomer **66**	λ, nm	temp, °C	time, h	product **67**	yield of **67**, %	$\Phi_{-(C=C)}$[a]	ref
Me, **68**	H_2O	*b*	3	5	**69**[c]	93.2[d]		67
68	H_2O	*b*	19	5	**69**[e]	90.6[f]		67
68	H_2O	*b*	~25	0.17-5	**69**[g]	~90[h]	0.7-1.2	67
68	H_2O or H_2O-EtOH	quartz[i]	30	1.5	**69**	55, 100		56
68	H_2O-EtOH (19:1)		0-5	7	**69**			63
68	KBr	365			**69**, oligomer		1.2-~2	68
68	KBr	360			**69**, oligomer			68
68	KBr	313			**69**, high polymer			68
68	KBr	310			**69**, high polymer			68
68	KBr			0.17	**69**			56
68			~25	30	**69**, $\overline{M}_n = 1040$, $\overline{x}_n = 4.2$	100		57
Et, **70**	none[j]	*b*	−269 to −103		**71**, $\overline{M}_n = 3000$, $\overline{x}_n = 11$			69
70	none[j]	*b*	−145	0.21	**71**	4[k]		69
70	none[j]	*b*	−145	0.21	**71**	23[k,l]		69
70	none[j]	*b*	−145	0.77	**71**	34[k]		69
70	none[j]	*b*	−125	0.12	**71**	27[k,m]		69
70	He(l)	*b*	−269.0	0.83	**71**	*n*		69
70		*b*	−190	1	**71**	~30-40		70
70	H_2O	360	20		**71**, $\overline{x}_n = 3.0$,[o] **72**	100		71
72	H_2O	310	20		**71**, nearly amorphous polymer			71
70	H_2O	>~280[p]	32		**71**, $\overline{x}_n = 3.4$	67		71
70	H_2O	>~280[p]	45		**71**, $\overline{x}_n = 2.3$	18		71
70	H_2O	>~280[p]	62	20	**71**, ~30% dimer, $\overline{x}_n = 2$	40		71
70	H_2O		60-65	6	**71**, dimer, $\overline{x}_n = 2$	~30		72
70	H_2O or H_2O-EtOH	quartz	−25	1.5	**71**, crystalline polymer[q]	100		56, 57
70	H_2O or H_2O-EtOH	quartz	30	50	**71**, amorphous polymer[r]	100		56, 57
70	H_2O or H_2O-EtOH	quartz			**71**, $\overline{M}_n = 2200$, $\overline{x}_n = 8.0$, **73**[s]			72
73	film	277			**71**			72
73	film	>280			**71**, $\overline{M}_n = 3000$, $\overline{x}_n = 11$			72
70	H_2O-MeOH (2:3)[t]	>~280[p]	−50	*u*	**71**, crystalline high polymer	100		71
70	H_2O-MeOH (2:3)[t]	>~280[p]	−35	*u*	**71**	100		71
70	H_2O-MeOH (1:1)[t]	>~280[p]	−20		**71**, $\overline{x}_n = 3.0$[v]	~70		71
70	H_2O-MeOH (1:1)[t]	>~280[p]	−20	1-3[w]	**71**, crystalline high polymer	100		71
70	H_2O-MeOH (3:2)[t]	>~280[p]	0	*u*	**71**	100		71
70	H_2O-MeOH (65:35)[t]	>~280[p]	15	*u*	**71**	100		71
70	H_2O-EtOH (19:1)		0-5	7	**71**	94		63
70	KBr	360	−28		**71**, oligomer			71
70	KBr	360	20		**71**			71
70	KBr	310	20		**71**, polymer			71
70			<15		**71**, high $\overline{M}_n$	100		24
70			30		**71**, $\overline{x}_n = 2-5$			24
C_2D_5, **74**	H_2O-MeOH (1:1)	>~280[p]	−20		**75**			71
Ph, **76**	H_2O or H_2O-EtOH	quartz	30	10	**77**, high polymer	85		56, 57, 73
76	H_2O-EtOH (19:1)		0-5	7	**77**			63

[a] Quantum yield for reaction of monomer or polymer double bonds. [b] Unfiltered mercury arc lamp. [c] Intrinsic viscosity = 4.5 dl g^{-1} at 0.5 h and 5.6 dl g^{-1} at 5 h. [d] 80.0% conversion at 0.5 h. [e] Intrinsic viscosity = 2.7 dl g^{-1} at 0.5 h and 5.7 dl g^{-1} at 5 h. [f] 68.0% at 0.5 h. [g] Intrinsic viscosity as a function of time given. [h] At ~4.9 h analysis by IR showed the conversion was ~100%. Conversions at shorter reaction times also given. [i] All wavelengths from high pressure mercury arc that are transmitted by quartz. [j] Thin film of crystals. [k] Conversion of double bonds of monomer. [l] 13% of monomer double bonds were converted to polymer bonds prior to this reaction. [m] 39% of monomer double bonds were converted to polymer bonds prior to this reaction. [n] Almost all of monomer **70** reacted, 20% of monomer double bonds were converted to polymer bonds prior to this reaction by irradiation at ~25 °C. [o] Oligomer contained dimer. [p] Pyrex glass filter. [q] Reduced viscosity = 1.41. [r] Reduced viscosity = 0.16. [s] $CHCl_3$ soluble fraction: $\overline{M}_n \approx 1000$, $\overline{x}_n \approx 3.6$. [t] <1% of **70** dissolved. [u] Conversion of monomer as a function of time given. [v] Extracted from product (23% yield). [w] Conversion of monomer and formation of polymer as a function of time given.

caused by the melting point depression of the mixture of dimer and monomer.[75] Because the cycloaddition did not occur in the molten state, the reaction stopped at the dimer stage.[75]

The conversion and chain growth of the methyl ester **68** both decreased with increasing temperature.[67]

The effect of temperature on the photocycloaddition polymerization of these esters **66** has been discussed for three temperature regions.[71] At the lowest temperatures studied, the crystal system was rigid and the polymerization proceeded until all the double bonds had reacted. At increased temperatures the polymerization rate increased, and the degree of polymerization decreased. This behavior was consistent with a temperature dependence of the reactions (Scheme II) that decreased in the order (27) > (28) > (30).[71]

In the intermediate temperature range the crystal system was rigid, but the molecules were disordered.[71] Again all of the monomer **66** was consumed, but a small amount of functional groups remained even after prolonged irradiation. An increase in temperature in this region initially increased the rate of polymerization, but

TABLE III. Photopolymerization of *p*-Phenylenediacrylate Esters **66** in the Crystal State (Eq 33)

R of monomer **66**	dispersion medium for monomer **66**	wave-length filter	temp, °C	time, h	product **79**	yield of **79**, %	ref
n-Pr, **80**	H_2O or H_2O-EtOH	quartz	0–5	50	**81**, oligomer	42	56, 57, 71
i-Pr, **82**	H_2O or H_2O-EtOH	quartz	30	49	**83**, oligomer	65	56, 57, 71
n-Bu, **84**	KBr	quartz		10	**85**, oligomer		56, 57
C_8H_{17}, **86**					**87**		61
$PhCH_2$, **88**	KBr	quartz		10	**89**, oligomer		56, 57
p-MeC_6H_4, **90**	KBr	quartz			**91**, oligomer		56, 57
p-$O_2NC_6H_4$, **92**	H_2O or H_2O-EtOH	quartz	30	50	**93**, oligomer	89	56, 57

in the later stages decreased this rate. Again the degree of polymerization decreased with increased temperature. Apparently, disordering of the crystal occurred during the polymerization, which decreased the rates of reactions 28 and 30 (Scheme II).[71,74]

At the highest temperatures studied the crystal system was considerably disordered.[71] The polymerization was suppressed at the oligomer stage with low conversions of the monomer **66**. An increase in temperature decreased the conversion and the degree of polymerization. The heat generated by the reaction and by absorption of light caused partial melting so that the crystal became sticky.[71]

The double bonds that reacted to form cyclobutane rings in the crystal had separations of 3.937 Å,[14,64,76] 3.970 Å (at 25 °C),[65,76] and 3.928 Å[66,76] in the methyl **68**, ethyl **70**, and phenyl **76** esters, respectively. The separation in the ethyl ester **70** at 70 °C was 3.87 Å.[75]

Polymerization of the methyl ester **68** resulted in movement of the monomeric unit in the chain growth direction with an elongation of 8.8%. The direction of the crystal axes was not retained.[67]

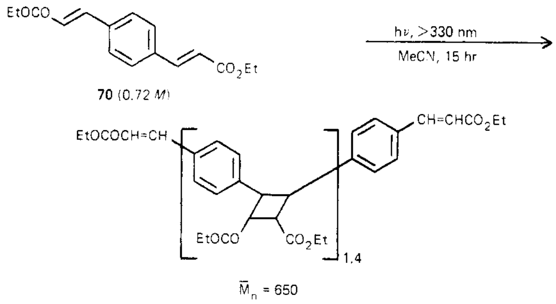
X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photopolymerizations (λ >365 nm) of **68**, **70**, and **76** showed that nucleation began and propagation proceeded within the defect-free structures.[51] In comparison to other related compounds studied, the methyl ester **68** had a high reactivity, and the ethyl **70** and phenyl **76** esters had medium reactivities.[51]

A study of the morphological changes during the solid state polymerizations of the methyl **68**, ethyl **70**, and phenyl **76** esters showed that although the polymers were crystalline and crackfree, deformation did occur during the polymerizations.[61] Large molecular movements also occurred during the reaction.

These and some of the other solid state polymerizations discussed in later sections were believed to be homogeneous with the formation of a small amount of product dispersed in the monomer in the early stages.[61] The monomer crystal became strained by the accumulation of the product and cracked if the strain was sufficient. Crack formation during this initial stage depended on the cleavability of the monomer crystal. As the polymerization proceeded, this crystal was transformed into the polymer crystal containing a small amount of dispersed monomer. Phase separation of the polymer sometimes started at this stage. Finally, the monomer crystal was converted entirely to polymer.[61]

The molecular features favorable for forming polymerizable crystals have been generalized as those that produce rigid, rod-like, nearly planar shapes with the two functional groups having mutually opposite dipole directions.[65]

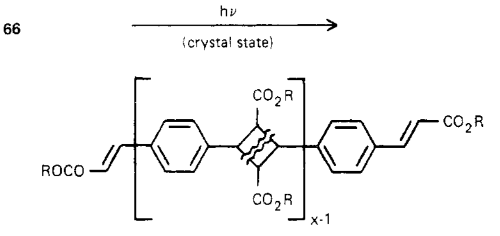
In contrast to the crystal state photopolymerization of the ethyl ester **70**, irradiation of a concentrated solution of **70** gave a low molecular weight oligomer **78** (eq 32).[77] The stereo- and regiochemistries of the photocycloaddition were different from those observed in the crystal state. Cis–trans isomerization about the double bonds was the only reaction observed in dilute solution (0.0018 M).[77] Evidence indicated photooligomerization occurred via an excimer of **70**.[77]



78

(32)

Several other esters **66** of *p*-phenylenediacrylic acid have been polymerized by photocycloaddition reactions of the monomers in the crystal state (eq 33) (Table III).[56,57,61,71] In these reactions the stereochemistries of the cycloadditions have not been determined although in some references[57,61] the cyclobutane rings are shown as head-to-tail adducts.



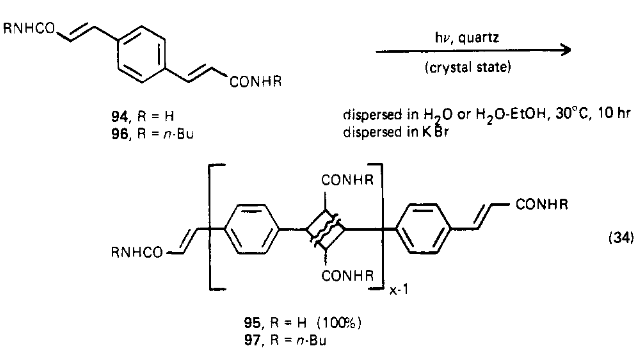
79

(33)

The relative rates of polymerization of the esters **66** were as follows:[78] Me (**68**) > Et (**70**) > *n*-Pr (**80**) > *i*-Pr (**82**) > *n*-Bu (**84**). The molecular weights of the two propyl ester polymers **81** and **83** decreased when the polymerization was performed at higher temperatures.[56]

Morphology studies on the isopropyl **83** and octyl **87** ester polymers showed they were amorphous and that they did not change shape during formation.[61]

On irradiation (eq 34), the amides **94** and **96** polymerized similarly to the esters described previously.[56,57,63] The unsubstituted amide **95** was reported to be a high molecular weight polymer while the N-substituted product **97** was suggested to be an oligomer.[56] No molecular weight data were reported. In some references the polymer structures **95** and **97** were shown as



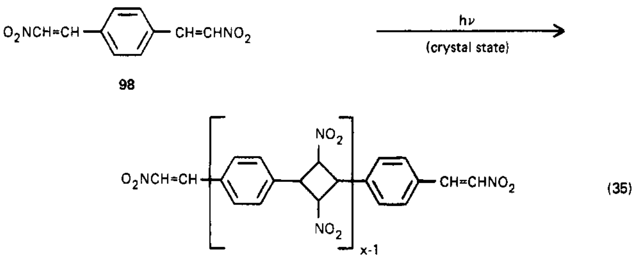
94, R = H
96, R = *n*-Bu

95, R = H (100%)
97, R = *n*-Bu

the head-to-tail cyclobutane structures.[57,63]

2. *p-Bis(β-nitro- and β-arylvinyl)benzenes*

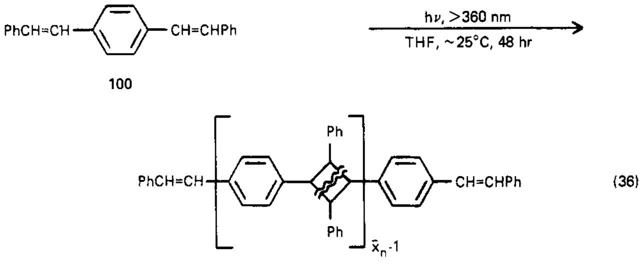
The bis(nitroethylene) derivative **98** was reported to polymerize by cycloaddition when irradiated in the crystal state (eq 35).[57] The polymer **99** was indicated to have the head-to-tail structure, but no evidence was presented.[57]



98

99

Irradiation of *p*-distyrylbenzene (**100**) in tetrahydrofuran solution (1.42 × 10^{-2} M) gave the oligomer **101** quantitatively (eq 36).[14,79] Cis–trans isomerization about the double bond occurred during the reaction.[14]



100

101

$\bar{M}_n = 634$, $\bar{x}_n = 2.25$

(100%)

Further irradiation of the oligomer **101** in $CHCl_3$ solution with light of wavelength longer than 340 nm decreased the molecular weight[79] rather than increasing it as might have been expected on the basis of related reactions shown in Table II. If only the monomer **100** was excited by the light, then only reactions 37 and 38 would have occurred (Scheme III) as took place on irradiation at wavelengths longer than 360 nm.[79] The average molecular weight depended on the ratio of rate constants, k_{38}/k_{37}. If $k_{38}/k_{37} = 0$, only dimer, **101** ($\bar{x}_n = 2$), would have been formed. If $k_{38}/k_{37} = \infty$, only higher molecular weight polymers, **101** $\bar{x}_n = n$), would have been formed. However, k_{38}/k_{37} was actually an intermediate value.[79] Under conditions where $k_{39} = 0$ and k_{38}/k_{37} was not extremely large, all of the monomer molecules **100** could not grow into high molecular weight polymers. This situation was in contrast to that where the growing polymer molecules absorbed light at the same wavelengths as the monomer, as occurred with the bis(maleimides) discussed in section IIK.

Scheme III

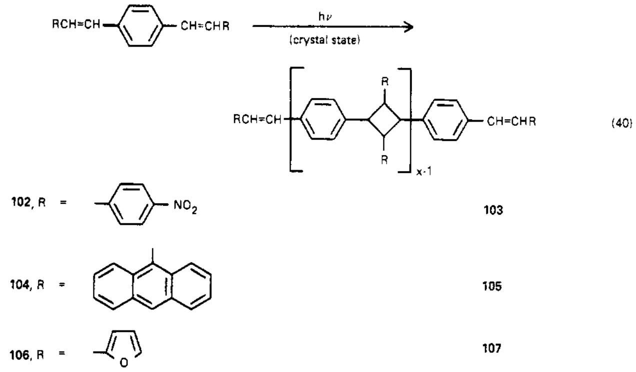
$$2\ \mathbf{100} \xrightarrow{h\nu} \mathbf{101}\ (\bar{x}_n = 2) \qquad (37)$$

$$\mathbf{100} + \mathbf{101}\ (\bar{x}_n = n) \xrightarrow{h\nu} \mathbf{101}\ (\bar{x}_n = n + 1) \qquad (38)$$

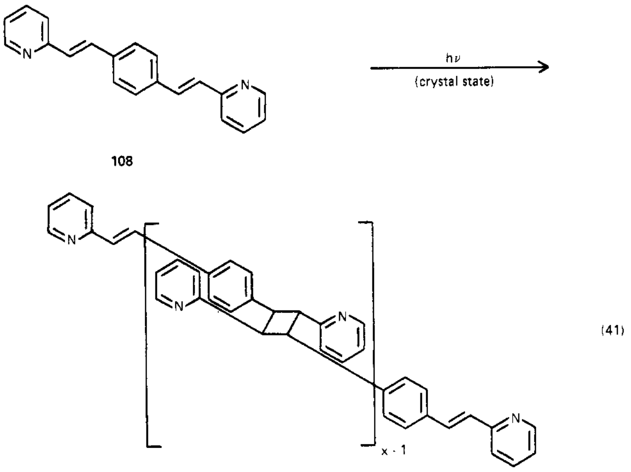
$$\mathbf{101}\ (\bar{x}_n = n) + \mathbf{101}\ (\bar{x}_n = m) \xrightarrow{h\nu} \mathbf{101}\ (\bar{x}_n = m + n) \qquad (39)$$

In contrast to many other reactions discussed in this review, the distyrylbenzene **100** did not polymerize when irradiated in the crystal state.[14,78] Presumably, unfavorable alignment of the molecules in the crystal lattice caused this behavior.

Several related (β-arylvinyl)benzenes, **102**, **104**, and **106**, were reported to polymerize via photocycloaddition in the crystal state to give the head-to-tail cyclobutane polymers (eq 40), but no evidence for these structures was given.[57] The bis(anthracene) derivative **104** could have polymerized via 4 + 4 cycloadditions of the anthracene moieties similarly to other anthracenes discussed in section VB. An appropriate arrangement of the monomer molecules **104** in the crystal lattice would have been required for this reaction.



X-ray diffraction studies[76,80,81] of the crystal state bis(pyridylvinyl)benzene **108** photopolymerization (eq 41) (Table IV)[14,57,68,80–83] established the *trans*-1,3-cyclobutane structure in the main chain. The monomer molecules **108** were aligned in the crystal so as to give the polymer **109**. The double bonds that underwent cycloaddition were separated by 3.910 Å.[76,81]



108

109

Single crystal X-ray diffraction studies showed that on conversion of the monomer **108** to polymer **109**, only a slight change in unit cell dimensions occurred, the unit

TABLE IV. Photopolymerization of *p*-Bis(β-2-pyridylvinyl)benzene (108) in the Crystal State (Eq 41)

dispersion medium for monomer **108**	λ, nm	temp, °C	time, h	product **109**	yield of **109**, %	$\Phi_{-(C=C)}$	ref
EtOH-H_2O (5:1)	>~280	~25	9	polymer	90		83
KBr	410			oligomer, **110**			68
KBr	405			oligomer		⩾0.04	14, 68
110, KBr	350			high polymer			68
	unfiltered[a]	~45	~100	polymer	>99		80
			9	polymer	>90		57
				polymer		0.04	81

[a] High pressure mercury vapor lamp.

cell symmetry probably did not change, and the average unit cell orientation remained unchanged.[80] These observations suggested that minimal molecular rearrangement occurred during the polymerization.[80] The polymer **109** was highly oriented along the *c* axis, which had elongated 2.7% from that of the monomer.[81] The divinylbenzene derivative **108** crystal had a unit cell and symmetry analogous to those of the divinylpyrazine derivative **192** (see section IIG1.).[82]

When a single spot on a crystal of the monomer **108** was irradiated, polymerization occurred only at that spot.[84] The polymerization may have proceeded from the surface to the interior of the monomer crystal.[76]

Polymerization of the bis(pyridylvinyl)benzene **108** in the crystal state was slower than that of the distyrylpyrazine **192** (see later section)[81,83] whereas oligomerizations of the two monomers in solution proceeded at approximately the same rate.[81] The difference in quantum yields for the two polymerizations in the crystal state therefore were probably not caused by properties of the isolated molecules. Rather it could have resulted from slight differences in the molecular packing arrangements in the two crystals or of differences in the overlap of the nitrogen atoms with the phenyl rings.[81] A molecular orbital treatment of these two reactions on the basis of the crystal structures has been used to explain the difference in quantum yields.[14,81]

Changes in temperature (30–70 °C) had little effect on the rate of polymerization of **108**, but the DP decreased markedly as the temperature increased, implying that the polymerization depended on the crystal state at the growing chain end.[73] Typical of stepwise polymerizations, the DP increased gradually with conversion of **108** in the early stages of the reaction.[73] At high conversions of **108** the DP increased sharply and continued to rise even after the monomer was completely consumed.[73]

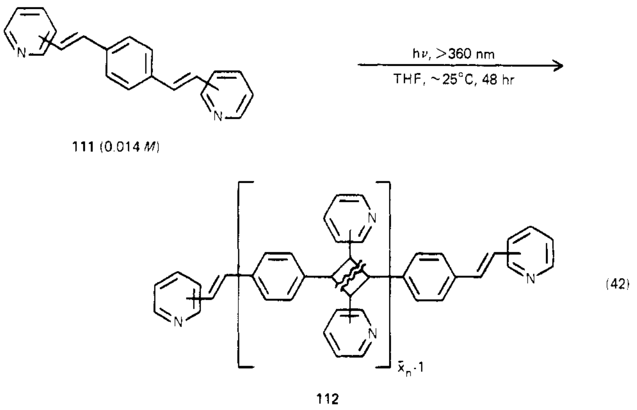
X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photopolymerization (λ >365 nm) of the bis(pyridylvinyl)benzene **108** showed that nucleation began and propagation proceeded within the defect-free structures.[51] No evidence was obtained for the occurrence of discrete nuclei of products.[51] Fissures, but no dislocations or planar faults, were introduced on polymerization.[51] In comparison to other related monomers studied, **108** had a low relativity.[51]

The polymer **109** was crystalline. Molecular movement during the reaction was small, but the crystal exhibited a large shape change and developed large cracks.[61]

The 3- and 4-pyridyl analogues of the bis(2-pyridylvinyl)benzene **108** did not photopolymerize in the crystal state,[82] but all three isomers underwent oligomerization in solution on irradiation (eq 42) (Table V).[14,79]

TABLE V. Photopolymerization of *p*-Bis(β-pyridylvinyl)benzenes 111 in THF Solution (Eq 42)[14,79]

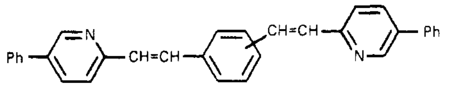
position of attachment of pyridyl group of **111**	product **112** number	product **112** $\overline{M}_n$	product **112** $\bar{x}_n$	yield of **112**, %
2, **108**	**113**	814	2.9	29
3, **114**	**115**	1074	3.8	94
4, **116**	**117**	682	2.4	73, 74



These results imply that the crystal lattices controlled the solid state reactions.[14]

The 2-pyridyl oligomer **113** was amorphous and differed from the crystalline oligomer **109** formed in the solid state.[79] The oligomers **113**, **115**, and **117** (Table V), formed in solution probably contained cyclobutane rings having various configurations.[79] Irradiation of the oligomers **112** in $CHCl_3$ solution with light of wavelength longer than 340 nm decreased the molecular weight.[79] Cis–trans isomerization of the monomers **111** accompanied the polymerization.[14]

A diphenyl derivative **118** related to the bis(2-pyridyl) monomer **108** was cited in a review as giving a cyclobutyl polymer when irradiated in the crystal state.[16] An original reference for this reaction was not found.



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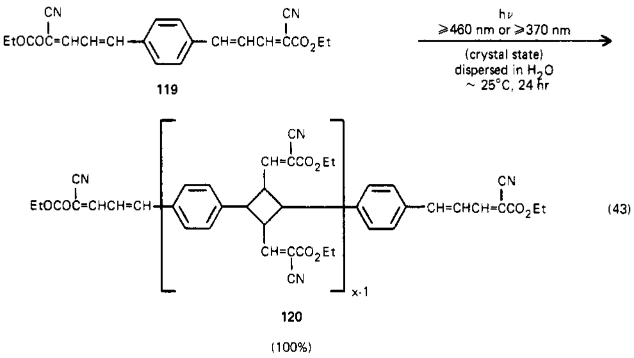
3. p-Di-1,3-butadienylbenzenes

The crystalline bis(diene ester) **119** gave a cyclobutyl polymer **120** on irradiation (eq 43).[65,85] Low and high



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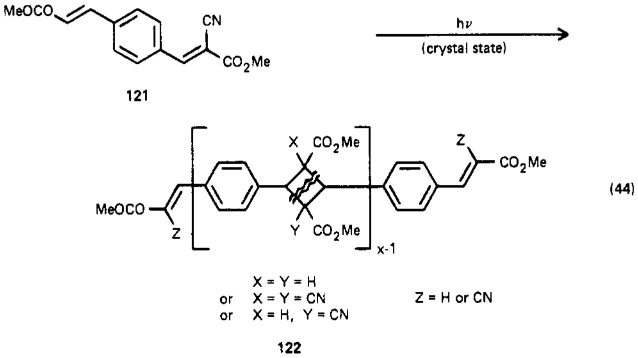
molecular weight polymers **120**, having intrinsic viscosities of 0.08 and 0.65, formed on irradiation with long (≥460 nm) and short wavelength (≥370 nm) light, respectively.[85] Irradiation of low molecular weight **120** at ≥370 nm produced high molecular weight polymer that contained *trans*-1,3-substituted cyclobutane rings.[85] The exact stereochemistry was not reported. The molecular weight dependence on the wavelength was presumably caused by the same factors discussed previously for the ester **68** and shown in Scheme II.

E. *p*-Bis(polysubstituted vinyl)benzenes

1. Cyano-*p*-phenylenediacrylate Esters

Irradiation of the crystalline cyano-*p*-phenylenediacrylate ester **121** gave an amorphous cyclobutyl oligomer **122** of undefined regiochemistry (eq 44).[51,86] An X-ray crystal structure determination showed monomer **121** had parallel stacks with both double bond separations of 3.956 Å.[86] The probable initiation reaction was formation of a mirror symmetric dimer, **123** or **124**.[86]



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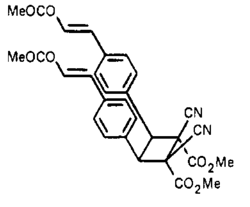
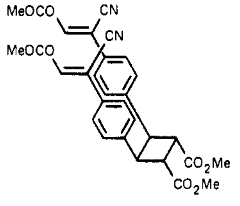


123

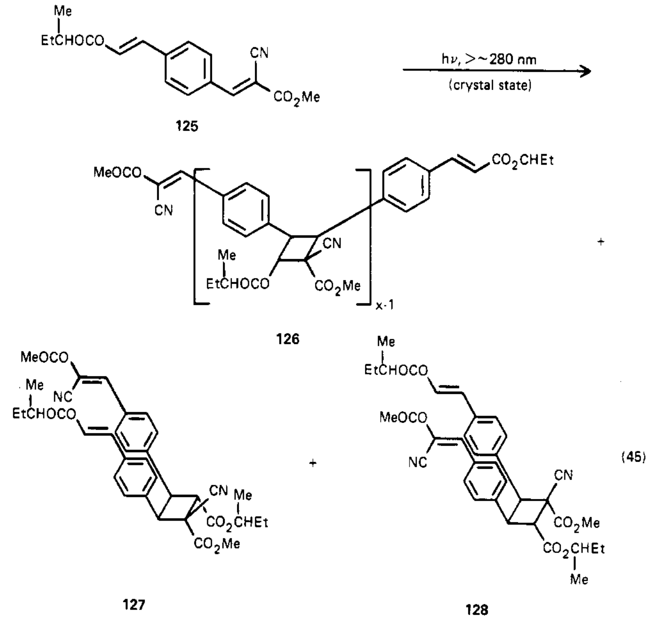


124

Formation of these dimers was expected to destroy the regular arrangement of the surrounding monomers and produce nonregiospecific cycloaddition to the olefinic bonds remaining in the dimers, **123** and **124**, or the oligomers formed therefrom.[86]

X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photooligomerization (>410 nm) of **121** showed that nucleation began and propagation proceeded within the defect-free structure.[51] In comparison to other related monomers studied, the cyano dimethyl ester **121** had a high reactivity.[51]

Irradiation of the racemic *sec*-butyl methyl diester **125** in one of its crystal forms gave a racemic polymer[87,88] or oligomer[89] **126** and racemic dimers **127** and **128** (eq 45). A second crystal form of **125** was stable to irradiation.[89] The structure of polymer **126** was inferred from the structure of the dimers and the crystal structure of monomer **125**.[89]



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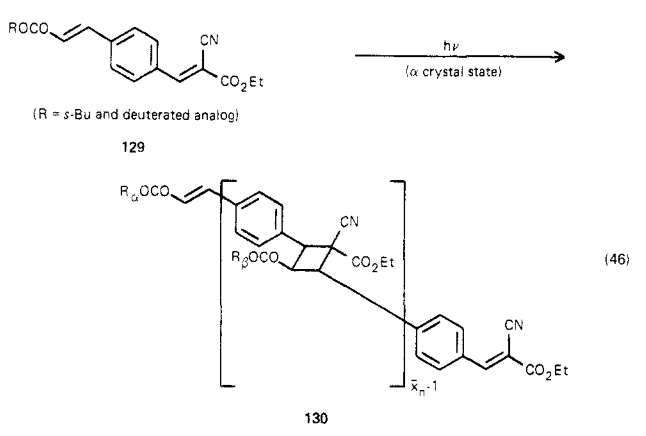
Irradiating the optically active (*S*)-(+) form (90% optically pure)[89] of the diester **125** gave a polymer [**126**, (*S*)-*s*-Bu] and two diastereomeric dimers [**127** and **128**, (*S*)-*s*-Bu] (1:1 ratio), all of which were optically active only because of the chiral *sec*-butyl group.[87,90] No asymmetric induction was induced during this cycloaddition in contrast to the reaction of the ethyl ester analogue **129** (see following section) where asymmetric induction occurred.

X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photooligomerization (>410 nm) of racemic **125** to give an amorphous product **126** showed that nucleation began and propagation proceeded within the defect-free structure.[51] No evidence was found for the occurrence of discrete nuclei of products.[51] In comparison to other related monomers studied, the monomer **125** had a medium reactivity.[51]

The two crystal forms of the *sec*-butyl ethyl diester **129** gave polymeric cycloadducts of different stereochemistries when irradiated in the solid state.[88] The α crystal form gave polymers of structure **130** (eq 46).[89] Trimers **131** and dimers **132** having structures analogous to that of polymer **130** were also isolated. A crystal structure determination of the α form of (*S*)-(+)-**129** (**134**) showed the monomer molecules aligned so that the adjacent double bonds, which were separated by 4.04 Å, could combine to give the cyclobutane rings indicated in structures **130**, **131**, and **132**.[89,91,92]

The products formed on irradiation of the separate optical isomers of **129** and their mixtures under a variety of conditions are shown in Table VI.[87-94]

The effect of irradiation wavelength on the DP of **134**[93] was similar to that noted previously for the ester **68** (Scheme II). Whereas the yield of dimer **132** was



$\sim$23% on irradiation of **134** with λ >300 nm (Table VI), it was 60% with λ >350 nm under otherwise comparable conditions.[89]

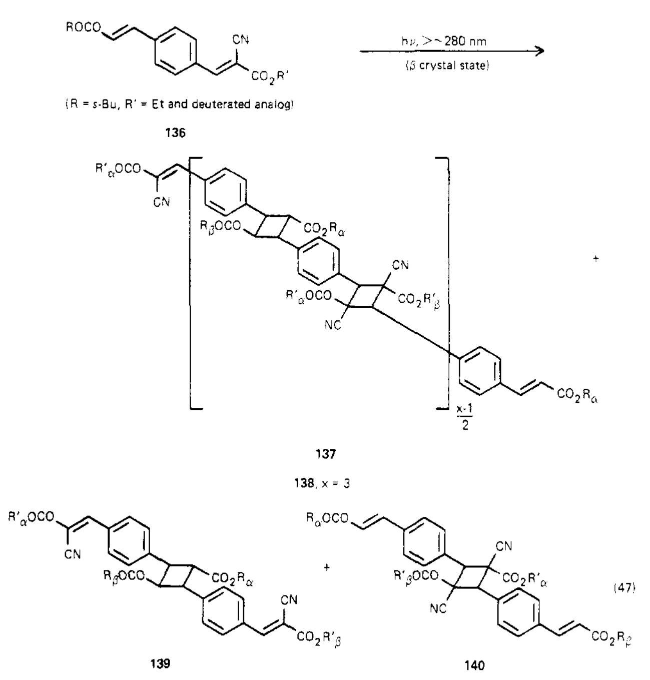
The (*R*)- and (*S*)-*sec*-butyl esters **133** and **134** each crystallized preferentially in one of two possible enantiomeric crystals because of the chiral handles.[93] Irradiating these crystals produced cycloadducts **130**, **131**, and **132** that were optically active after the *sec*-butyl groups were replaced by methyl groups.[89] The chiral environment of the reaction site, not the chiral *sec*-butyl handle, caused these asymmetric inductions.[87,89,91,93] The asymmetric inductions were quantitative in both the initiation and propagation steps.[89]

Crystals of racemic ester (**133**, **134**) that were grown from the melt by very slow cooling gave optically active oligomers in some experiments.[90-92,94] Enantiomeric excesses of up to 37% were achieved.[92] No net optical rotation of the monomer occurred either before or after irradiation.

Asymmetry was induced in the crystallization of racemic ester (**133**, **134**) by the addition of 3–15% of optically active dimer (*R*)- or (*S*)-**132**.[95] Irradiating these mixed crystals for 2 weeks at 5 °C gave oligomers **130**, trimers **131**, and dimers **132**.[95] Optical activity measurements on the newly formed dimers **132** indicated an excess of the configuration opposite to that of the originally added dimer.[95] The oligomers and trimers presumably had configurations analogous to those of the newly formed dimers.

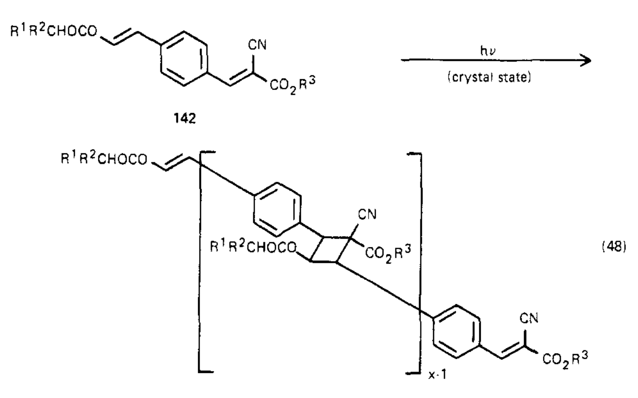
The β crystal form of **129** (**136**) gave polymer **137**, trimers **138**, and dimers **139** and **140** (eq 47).[88] Only the racemic form of the monomer **136** was studied (Table VII).[88] The structure of the polymer **137** was assigned by analogy to those of dimers **139** and **140**.

Photocycloaddition of the β crystal consisting of a 50:50 mixture of (*S*) and (*R*) *sec*-butyl esters **134** and **141** (Table VII) was studied to gain information on the microstructure of the racemic crystal.[88] Only the compositions of the dimers **139** and **140** were determined although oligomers also formed presumably had analogous structures. The β crystals of the mixture of **134** and **141** were grown from various solvents at −20 to $\sim$+40 °C. The ratio of dimers (*S*)-**139** (*SS*) plus (*R*-*d*)-**139** (*RR*) to (*S*-*R*-*d*)-**139** plus (*R*-*S*-*d*)-**139** (*RS*) formed from these mixed crystals varied from 1.00:0.93 to 1.00:2.56 whereas for the **140** type dimers the corresponding ratios [(*S*)-**140** + (*R*-*d*)-**140**:(*S*-*R*-*d*)-**140** + (*R*-*S*-*d*)-**140**] varied from 1.00:0.90 to 1.00:1.88.[88] Some order existed in the crystals as indicated by the excess of *RS* pairs under most conditions. No significant difference occurred in rates for the reactions of **134*** with **134** or **141** and for the reactions of **141*** with **134** or **141** as shown by the lack of a systematic variation of the product ratios with temperature.[88] The rate of monomer disappearance at 25 °C was approximately twice that at −20 °C. More contacts leading to the **139** type dimers were present than those leading to the **140** type.[88]



X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photooligomerization (>410 nm) of chiral **133** (or **134**) to give an amorphous oligomer **130**, $\bar{x}_n \approx 10$, showed that nucleation began and propagation proceeded within the defect-free structure.[51] No evidence was found for the occurrence of discrete nuclei of products.[51] In comparison to other monomers studied, the monomer **133** (or **134**) had a medium reactivity.[51]

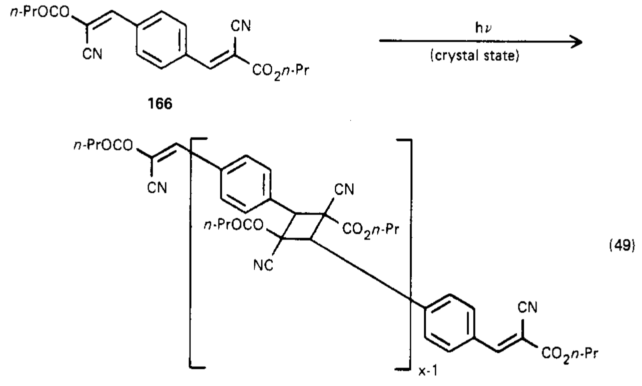
Several other esters **142** related to **129** gave cyclobutyl polymers, oligomers, trimers, and dimers **143** analogous to **130**–**132** (eq 48) (Table VIII).[91,95,96]



As in the reactions of the *sec*-butyl ethyl diester (**133**, **134**), the addition of optically active *sec*-butyl ethyl dimer (*R*)- or (*S*)-**132**, or trimer (*R*)- or (*S*)-**131**, or oligomer (*R*)- or (*S*)-**130** (Table VIII), gave optically active dimers **143** (x = 2) with an excess of the configuration opposite to that of the additives in all but one instance.[95] The oligomers and trimers presumably had configurations similar to those of the newly formed dimers. Similar results were obtained when the photocycloaddition products of **151** and **155** were used as additives.[95] These photocycloaddition reactions served as the method of determining the absolute configuration of the monomer crystals. Special techniques were employed for growing the crystals used in these studies.

2. Dicyano-p-phenylenediacrylate Esters

The bis(propyl cyanoacrylate ester) **166** polymerized rapidly when irradiated in the crystal state (eq 49) (Table IX).[76,78,97] X-ray crystal structure determination of monomer **166** showed the double bonds that reacted to form cyclobutane rings has an intermolecular separation of 3.931 Å.[76,98] Examination of the crystal structure of **166** led to the prediction of **167** as the structure of the polymer.



167

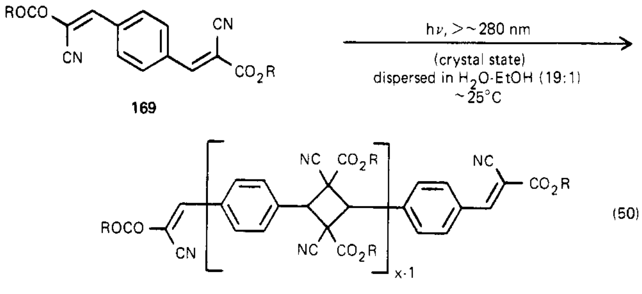
A mechanism analogous to that shown in Scheme II was proposed to account for the effect of wavelength on the DP (Table IX).[97] The incomplete oligomerization of **166** exposed to >360 nm light was attributed to disordering of the crystal during the reaction.[97] Thus some monomer molecules became isolated and could not add to neighboring monomers or oligomers. Irradiating the oligomer **168** at ∼300 nm gave high polymer. Excitation of the oligomer and its addition to another oligomer occurred in a manner analogous to reaction 31 in Scheme II.[97] This polymerization of **168** was not complete, possibly because the crystal became disordered during oligomerization.[97] Only the *as*-oligomerized crystal of **168** gave high polymer. Samples recrystallized from chloroform failed to polymerize, presumably because the crystal structure was altered.[97]

X-ray diffraction and low temperature electron microscopy studies of the crystal state photopolymerization (>365 nm) of the heavily faulted dicyano dipropyl ester **166** showed that nucleation began and propagation proceeded within the defect-free structure.[51] Discrete nuclei of products were not found.[51] The crystal imperfections present after polymerization showed no correlation with those present before irradiation.[51] In comparison to other monomers studied, the monomer **166** had a high reactivity.[51,99]

Polymerization of **166** produced a crystalline product containing fine cracks and fibrils; a large molecular movement occurred during the reaction.[61]

Irradiating **166** in solution with light of wavelength greater than 340 nm gave no polymer.[97]

Several other bis(cyanoacrylate) esters **169** polymerized when irradiated in the crystal state (eq 50) (Table X).[78] The stereochemistry of the photocycloaddition has not been determined for these esters.



170

The rates of polymerization of the cyano esters **169** decreased in the order *n*-Pr (**166**) > Me (**171**) > *i*-Pr (**175**) > *n*-Bu (**177**) > Et (**173**).[78] The *n*-Pr ester **166** polymerized as rapidly as distyrylpyrazine **192** (see section IIG1.).[78] The *i*-Pr and *n*-Bu cyano esters **175** and **177** polymerized faster than the corresponding *p*-phenylenediacrylate esters **82** and **84**.[78]

The poly(*n*-Pr ester) **167** had the highest reduced viscosity of all the poly(cyano esters) **170** whereas the Me polymer **172** had the lowest.[78] The low reduced viscosity, i.e., low DP, of the latter was attributed, at least partially, to cis–trans isomerization of the olefinic bond during the polymerization.[78]

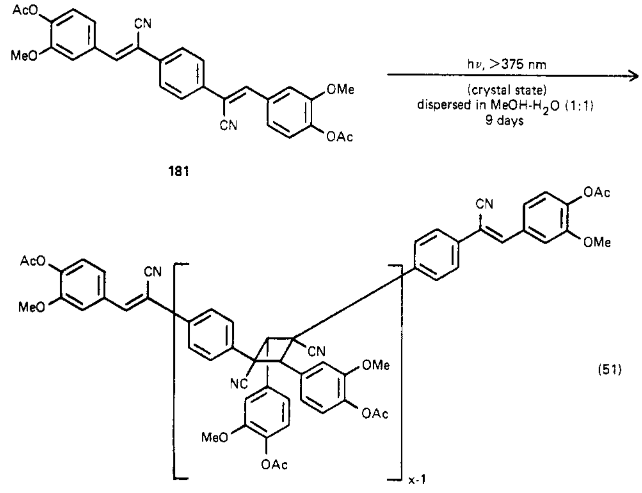
Changes in the polymerization temperature of between −20 °C and ∼+25 °C did not affect the yields or properties of the poly(cyano esters) **170**.[78]

Of all the cyano ester crystals **169**, the densities of the Et, *n*-Pr, and *i*-Pr ester crystals, **173**, **166**, and **175** changed the least on polymerization.[78]

The Et ester **173** did not polymerize on irradiation in benzene or dioxane solutions.[78] Several other compounds, such as the acid, esters, amide, nitrile, and ketone, related to **169** did not polymerize on irradiation in the crystal state.[78]

3. Bis(α-cyano-β-arylvinyl)benzenes

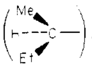
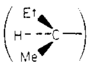
The substituted distyrylbenzene **181** polymerized on irradiation in the crystal state (eq 51).[100] The polymer was tentatively assigned structure **182** having a *cis*-1,3-cyclobutane repeating unit.[100] Dimer **183**, isolated on limited irradiation, was an intermediate in the polymerization.[100] The stereochemistry of both **182** and



182

183, x = 2

TABLE VI. Photopolymerization of α Crystal Form of *sec*-Butyl Ethyl Cyano-*p*-phenylenediacrylate **129** (Eq 46)

R of monomer **129**	dispersion medium for monomer **129**	λ, nm	temp, °C	time, h	products	yield of product, %	ref
(*R*)-*s*-Bu  **133**		>310	5		(*R*)-**130**, $\overline{M}_n \approx 5000$, $\overline{x}_n \approx 15$ (*R*)-**131** (*R*)-**132**		92
133[a,b]		>310			(*R*)-**130**, polymer[c]		93
133		>300	5		(*R*)-**130**, polymer[d] ($CHCl_3$ sol and insol fractions) (*R*)-**132**[d]		87, 93
133		>~280			(*R*)-**130**, polymer (*R*)-**131** (*R*)-**132**[d]		88
(*S*)-*s*-Bu[b,e]  **134**		>350		336	(*S*)-**130**, polymer,[f] low $\overline{M}_n$ (*S*)-**132**[f,g]		93
134[h]		>310	5		(*S*)-**130**,[i] $\overline{M}_n \approx 5000$ (~10, 000 max), $\overline{x}_n \approx 15$ (~30 max) (*S*)-**131**[i] (*S*)-**132**[j]		91, 92
134		>300	−5		(*S*)-**130**, polymer ($CHCl_3$ sol and insol fractions) (*S*)-**131** (*S*)-**132**[k]		90
134	H_2O-MeOH (9:1)	>300	−2	20-60	(*S*)-**130**, polymer ($CHCl_3$ insol) (*S*)-**130**, polymer ($CHCl_3$ sol, MeOH insol) (*S*)-**131**	~5 ~60 ~10	89
134	H_2O-MeOH (9:1)	>300	−2	20	(*S*)-**130**,[l] $\overline{M}_n = 1665$, $\overline{x}_n = 5.1$		89
134	H_2O-MeOH (9:1)	>300	−2	53	(*S*)-**130**,[l] $\overline{M}_n = 3865$, $\overline{x}_n = 11.8$		89
134		>300	5		(*S*)-**130**, polymer[d] ($CHCl_3$ sol and insol fractions) (*S*)-**132**[d]		87, 93
134[m,n]		>300	5	168-336	(*S*)-**130**, $\overline{M}_n = 1117\text{-}2380$, $\overline{x}_n = 3.4\text{-}7.3$[l,o,p] (*S*)-**131**[q] (*S*)-**132**[q]	~40 ~13 ~35	89
134	H_2O-MeOH (9:1)	>300	6	50	(*S*)-**130**,[l] $\overline{M}_n = 2720$, $\overline{x}_n = 8.3$		89
134		>~280			(*S*)-**130**, polymer (*S*)-**131** (*S*)-**132**[d]		88
134[e]	H_2O-EtOH (93:7)				(*S*)-**130**,[r] $\overline{M}_n = 2400$, $\overline{x}_n = 7.3$		93
(*R,S*)-*s*-Bu, **133**, **134**[s,t]		>310	5		(*R,S*)-**130**,[u] oligomer, R = (*R*)- or (*S*)-*s*-Bu (*R,S*)-**132**,[u] R = (*R*)- or (*S*)-*s*-Bu ($\overline{M}_n \approx 4000$, $\overline{x}_n \approx$ 12)[v]		91, 92, 94
133, **134**[s]					(*R,S*)-**130**, polymer[d] (insol) (*R,S*)-**130**, polymer[d] (sol)[w] (*R*)-**132**,[x] $R_\alpha = R_\beta$ = (*R*)-*s*-Bu (*S*)-**132**, $R_\alpha = R_\beta$ = (*S*)-*s*-Bu (*R-S*)-**132**, R_α = (*R*)-*s*-Bu, R_β = (*S*)-*s*-Bu (*S-R*)-**132**, R_α = (*S*)-*s*-Bu, R_β = (*R*)-*s*-Bu		87, 93
133, **134**[s]					(*R,S*)-**130**, polymer, R = (*R*)- or (*S*)-*s*-Bu[y] (*R,S*)-**131**, R = (*R*)- or (*S*)-*s*-Bu[y] (*R*)-**132**,[y] (*S*)-**132**,[y] (*R-S*)-**132**,[y] (*S-R*)-**132**[y]		89
134 + (*R,S*)-($CD_3CD(CD_2CD_3)$), **135** mixtures, (*S*/*R*) = [(61/39) − (99/1)]		>310	5		(*R,S-d*)-**130**, oligomer (*R,S-d*)-**132**,[z] R_α and R_β = (*S*)-*s*-Bu or (*R*)- or (*S*)-(CD_3)CD(CD_2CD_3)		94

[a] $[\alpha]^{25}_{\mathrm{D}} = -21^\circ$. [b] Original assignment of configuration[93] opposite to that reported later.[88-90] [c] $[\alpha]^{25}_{\mathrm{D}} = +54^\circ$. [d] Optically active. [e] $[\alpha]^{25}_{\mathrm{D}} = +21^\circ$. [f] Optically active after chiral *s*-Bu group removed. [g] $[\alpha]^{25}_{\mathrm{D}} = -81^\circ$. [h] $[\alpha]_{\mathrm{D}} = +22.7^\circ$. [i] $[\alpha]_{\mathrm{D}}$ comparable to that of dimer formed, −109°. [j] $[\alpha]_{\mathrm{D}} = -109^\circ$. [k] Some isomerized monomer, CN and CO_2Et interchanged in **134**, was formed. [l] $CHCl_3$ soluble, MeOH insoluble. [m] 99% optically pure. [n] ~10% of monomer **134** recovered after irradiation. [o] Almost no $CHCl_3$ insoluble product formed. [p] Only one enantiomeric form. [q] >97% enantiomeric purity. [r] $[\alpha]^{25}_{\mathrm{D}} = -24^\circ$. [s] Racemic mixutre. [t] Special crystal grown from melt. [u] $[\alpha]_{\mathrm{D}} = -35.0^\circ$ to $+5.8^\circ$ for entire reaction mixture. [v] Entire reaction product. [w] $[\alpha]^{25}_{\mathrm{D}} = -24^\circ$ for soluble (*R,S*)-**130** plus dimers, (*R*)-**132**, (*S*)-**132**, (*R-S*)-**132**, and (*S-R*)-**132**. [x] $[\alpha]^{25}_{\mathrm{D}} = -30^\circ$ for combined dimers. [y] Enantiomer also formed. [z] 60-98% enantiomeric excess of monomer gave ~100% enantiomeric excess of (*R,S-d*)-**132**. 22-40% enantiomeric excess of monomer gave 85-95% enantiomeric excess of (*R,S-d*)-**132**. See also ref 91.

TABLE VII. Photopolymerization of β Crystal Form of *sec*-Butyl Cyano-*p*-phenylenediacrylate 136 (Eq 47)[88]

monomer 136			time,	
R	R′	temp, °C	days	products
(*R*,*S*)-*s*-Bu[a]	Et, 133, 134			(*R*,*S*)-137, polymer (*R*,*S*)-138 (*R*,*S*)-139[b] (*R*,*S*)-140[b]
(*S*)-*s*-Bu + (*R*)-*s*Bu (50:50 mixture)	Et, 134 C_2D_5, 141	−20, 5, and 25	10–35	(*R*,*S*-*d*)-137, R_α and R_β = (*S*)- or (*R*)-*s*-Bu, R_α' and R'_β = Et or C_2D_5, oligomer (*S*)-139, $R_\alpha = R_\beta$ = (*S*)-*s*-Bu, $R'_\alpha = R'_\beta$ = Et[b] (*R*-*d*)-139, $R_\alpha = R_\beta$ = (*R*)-*s*-Bu, $R'_\alpha = R'_\beta = C_2D_5$ (*S*-*R*-*d*)-139, R_α = (*S*)-*s*-Bu, R_β = (*R*)-*s*-Bu, R'_α = Et, $R'_\beta = C_2D_5$ (*R*-*S*-*d*)-139, R_α = (*R*)-*s*-Bu, R_β = (*S*)-*s*-Bu, $R'_\alpha = C_2D_5$, R'_β = Et (*S*)-140, $R_\alpha = R_\beta$ = (*S*)-*s*-Bu, $R'_\alpha = R'_\beta$ = Et[b] (*R*-*d*)-140, $R_\alpha = R_\beta$ = (*R*)-*s*-Bu, $R'_\alpha = R'_\beta = C_2D_5$ (*S*-*R*-*d*)-140, R_α = (*S*)-*s*-Bu, R_β = (*R*)-*s*-Bu, R'_α = Et, $R'_\beta = C_2D_5$ (*R*-*S*-*d*)-140, R_α = (*R*)-*s*-Bu, R_β = (*S*)-*s*-Bu, $R'_\alpha = C_2D_5$, R'_β = Et

[a] Racemic mixture. [b] Yield of 139 type products > yield of 140 type products.

TABLE VIII. Photopolymerization of Cyano-*p*-phenylenediacrylate Esters 142 in the Crystal State (eq 48)

monomer 142			temp,	time,		
R^1	R^2	R^3	°C	weeks	products 143	ref
Me	Me	Et, 144			145,[a] polymer 146,[a] x = 2	96
Me	Et	*n*-Pr, 147[b,c]	5	2	148, oligomer 149, x = 3 150, x = 2	95
Et	Et	Me, 151[d]	5	2	152, oligomer 153, x = 3 154, x = 2	95
		151			152,[a] polymer 154[e]	91
Et	Et	Et, 155[f]	5	2	156, oligomer 157, x = 3 158, x = 2	95
		155			156,[a] polymer 158[a]	96
		144 + 155[d]	5	2	159, oligomer, $R^1 = R^2$ = Me or Et, R^3 = Et 160, x = 3, $R^1 = R^2$ = Me or Et, R^3 = Et 146 161, x = 2, $R^1 = R^2$ = Me or Et, R^3 = Et	95
		144 + 155[g]			159,[a] polymer 161[a]	91
Et	Et	*n*-Pr, 162[d]	5	2	163, oligomer 164, x = 3 165, x = 2	95

[a] Optically active. [b] Racemic mixture. [c] Mixture with 3–15% optically active dimer (*R*)- or (*S*)-132. [d] Mixture with 3–15% optically active dimer (*R*)- or (*S*)-132, or 15% optically active trimer (*R*)- or (*S*)-131, or 8% optically active oligomer (*R*)- or (*S*)-130. [e] Max $[\alpha]_D = +106°$; $[\alpha]_D$ for entire reaction mixture = 0 to +60°. [f] Mixture with 3–15% optically active dimer (*R*)- or (*S*)-132, or 15% optically active trimer (*R*)-131. [g] 1:1 mixture of 144 and 155.

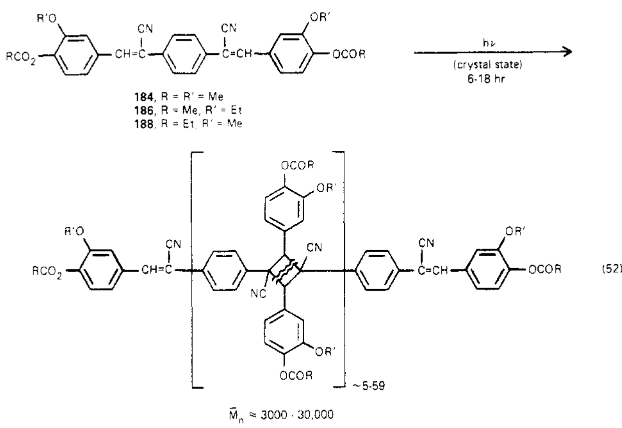
TABLE IX. Photopolymerization of Dipropyl *p*-Phenylenedi(α-cyanoacrylate) (166) in the Crystal State (Eq 49)

dispersion medium for monomer 166	λ, nm	temp, °C	time, h	product 167	yield of 167, %	ref
H_2O-EtOH (19:1)	>~280	~25	0.5	high polymer	100[a]	78, 97
		~25	several	polymer		11
	>360[b]			oligomer, 168	<100	97
168 crystal[c]	~300[d]		1	high polymer		97

[a] Conversion as a function of time given. [b] 383 nm actually used. [c] <1% 166 present. [d] 304 nm actually used.

183 was uncertain. The quantum yield for the formation of cyclobutane rings in both 182 and 183 was 0.7 ± 0.1 at 365.4 nm.[100]

Several compounds, 184, 186, and 188, related to 181 photopolymerized in the crystal state (eq 52).[101] The stereochemistry at the olefinic linkages of the monomers



(52)

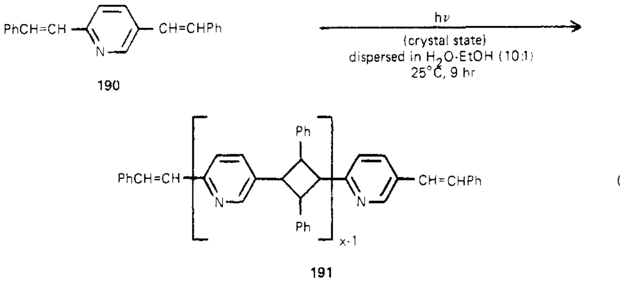
184, R = R' = Me
186, R = Me, R' = Et
188, R = Et, R' = Me

185, R = R' = Me
187, R = Me, R' = Et
189, R = Et, R' = Me

was not specified. Presumably, **184** was identical with **181**. The quantum yield at ~320–400 nm for the disappearance of the olefinic double bonds of **184** as a dry layer of crystals was ~0.7, i.e., one-half that reported above for **181**.[101] The molecular weights of **185**, **187**, and **189** were ~3000–30,000.[101]

F. 2,5-Distyrylpyridine

The crystal state irradiation of pyridine derivative **190** gave a 1,3-cyclobutyl polymer **191** (eq 53).[24]



190

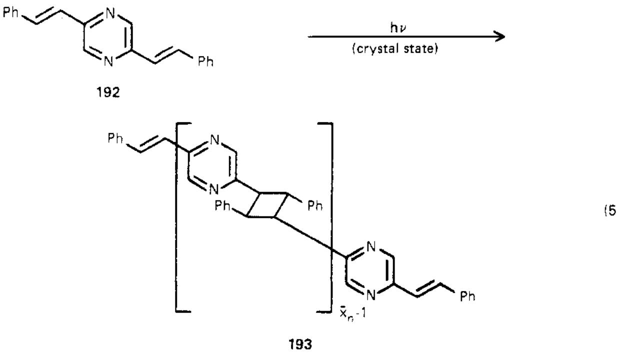
(53)

191
(90%)

G. 2,5-Distyrylpyrazine

1. Crystal State

The photocycloaddition polymerization of *trans*,*trans*-2,5-distyrylpyrazine (**192**) has been studied more extensively than any other polymerization discussed in this review (ref 6, 14, 33, 49, 51, 57, 61, 68, 73, 76, 79, 81–84, 97, 99, 102–122). Nearly all of these studies have dealt with the solid state topochemical polymerization that gave the *trans*-1,3-cyclobutyl polymer **193** (eq 54) (Table XI). Polymer **193** was reported as having a higher molecular weight, >500,000, than any other polymer described in this review.[14,73]



192

(54)

193

TABLE X. Photopolymerization of *p*-Phenylenebis(α-cyanoacrylate) Esters **169** in the Crystal State (Eq 50)[78]

R of monomer **169**	time, h	product **170**	yield of **170**, %
Me, **171**	6–7	**172**, low $\overline{M}_n$ polymer[a]	100
Et, **173**	144	**174**, high polymer	66
	240		≤66
i-Pr, **175**	120	**176**, high polymer	100
n-Bu, **177**	144	**178**	88
n-C_8H_{17}, **179**	240	**180**	100

[a] Low and high $\overline{M}_n$ fractions isolated.

The X-ray crystal structure of the polymerizable[49,73,113] α-crystal form of **192** has been determined[49,76,107] and led to the assignment of the structure of the polymer **193**. The double bonds of the monomer **192** that reacted to form the cyclobutane rings of **193** were separated by 3.939 Å in the crystal.[49,76,107] The γ-crystal form of the monomer **192** did not photopolymerize.[49,76,113]

The quantum yield for the polymerization of **192** was reported to be between 1.2 and ~2 (per double bond).[14,68,81,119] The quantum yields may have depended on the DP and/or the wavelength: ≥1.2 for the initial oligomerization at 436 nm and ≥1.6 for the transformation of the oligomer to polymer at 365 nm.[68]

The di-*p*-methyl and -methoxy derivatives of **192** did not photopolymerize in the crystal state.[83] This lack of reactivity could have been caused by an unfavorable crystal structure or a lower intrinsic reactivity of these monomers compared with that of **192**.

Irradiating monomer **192** with light of wavelengths >400 nm produced solely low molecular weight oligomers because the oligomers absorbed light only at wavelengths shorter than 380 nm.[57,68,104,109] This explanation was analogous to that described above for diester **68** (Scheme II). Irradiating monomer **192** or the *as*-formed oligomer with short wavelength light (<380 nm) produced higher molecular weight polymer.[68,104,109] Recrystallized oligomer did not form higher molecular weight polymer when irradiated further, presumably because it changed to a more stable crystal form.[68,104] This evidence further supports a lattice-controlled reaction.[68]

The rate of conversion of monomer **192** increased with increasing light intensity, but the molecular weight of the polymer **193**, as indicated by reduced viscosity, was nearly constant at a given conversion for different light intensities.[57,84] This behavior was in accord with the stepwise mechanism described in a later paragraph.[84]

The rate of polymerization as measured by consumption of monomer **192** increased slightly as the temperature increased from −20 °C to +50 °C.[57,73,84] At up to 50% conversion, this temperature dependence corresponded to an activation energy of ~3 kcal mol^{-1}.[84] The rate was considerably slower at −42 °C.[57,84] The reduced viscosities at constant conversion were nearly equal for polymerizations carried out at −55 °C to 0 °C.[73,84] At higher temperatures, up to 50 °C, the reduced viscosity and DP decreased markedly with an increase in temperature.[57,73,84] The temperature dependence of the DP indicated that polymerization de-

TABLE XI. Photopolymerization of 2,5-Distyrylpyrazine (**192**) in the Crystal State (Eq 54)

dispersion medium for monomer **192**	λ, nm	temp, °C	time, h	product **193**	yield of **193**, %	$\phi_{\text{-(C=C)}}$	ref
KBr	436			oligomer		1.2–~2	68
	≥435			oligomer			114, 116
	≥431			oligomer			33
	>430			oligomer			109
KBr	430		*a*	oligomer, $\bar{x}_n \approx 5$, **194**	~99		68
H_2O-MeOH (3:1)	>420		~20[b]	oligomer, $\bar{x}_n = 6$			115
MeOH-H_2O (3:2)	>400	~25	~1	oligomer, $\bar{M}_n \approx 900$, $\bar{x}_n \approx 3.2$	~100		104
MeOH-H_2O (3:2)	>400	~25	1	oligomer, $\bar{x}_n \approx 5$, **195**	100		68
oligomer[c], KBr	365			polymer		1.6–~2	68
194, KBr	350		d	polymer			68
195, MeOH-H_2O (3:2)	350	~25		polymer			68
KBr	350			polymer			68
	≥345		0.0003-0.01	polymer			114
	≥345[e]		0.17-0.25	polymer			117
	>345			polymer			116
	≥340			polymer			33
MeOH-H_2O (3:2)	340	~25	~1	polymer, $\bar{M}_n > 100{,}000$, $\bar{x}_n > 350$	100		104
oligomer	340			high polymer			49
	>280[f]		10	polymer	89		83
c-C_6H_{12}[g]	quartz[h]	30	1	polymer	~88[i]		57, 84
c-C_6H_{12}	quartz[j]	30	1	polymer	~81[i]		57, 84
c-C_6H_{12}	quartz[k]	30	1	polymer	~14[i]		57, 84
n-C_6H_{14}	quartz	−42	0.17	polymer	~5[i]		57, 84
n-C_6H_{14}	quartz	−20	0.17	polymer	~44[i]		57, 84
n-C_6H_{14}	quartz	0	0.17	polymer	~62[i]		57, 84
n-C_6H_{14}	quartz	50	0.17	polymer	~91[i]		57, 84
c-C_6H_{12}	quartz	30	1	polymer	60.0[i]		57, 84
c-C_6H_{12}	quartz	30	1[l]	polymer	65.8		57, 84
n-C_6H_{14}	quartz	−25		polymer	~98		84
MeOH-H_2O (3:2)	quartz	30	1	polymer	99.5		84
	no filter	25		polymer			49
			0.83	high polymer[m]			49
		~25	2	polymer	100		57
c-C_6H_{12}		~25	2	polymer[n]	~100		83
c-C_6H_{12}		~25	5	polymer, high $\bar{M}_n$	~100		102
		~25	*o*	polymer, $\bar{M}_n = >500{,}000$, $\bar{x}_n = >1700$			14, 73
	p			polymer, $\bar{M}_n = 60{,}000$, $\bar{x}_n = 210$			103
H_2O-MeOH (3:1)		~25		polymer[q], $\bar{x}_n = 124.8$ and 36.5			115
H_2O		~25		polymer, $\bar{M}_n = 10{,}000$, $\bar{x}_n = 35$			112
none[r]			~24	polymer	100		120
				polymer, $\bar{M}_n = 63{,}000$, $\bar{x}_n = 220$, and $\bar{M}_n = 10{,}000$, $\bar{x}_n = 35$			110
				polymer		1.2–1.6	119

[a] 1.3 μE cm^{-2}. [b] No **192** remaining at end of reaction. [c] Unspecified. [d] 1.2 μE cm^{-2}. [e] Wavelength limit, ≤345 nm, given in ref 117 is probably a misprint. [f] Sunlight. [g] Cyclohexane. [h] Relative light intensity = 100. [i] Conversion as a function of time given. [j] Relative light intensity = 64. [k] Relative light intensity = 14. [l] Further data at various times given. [m] Intermediate oligomer detected. [n] Linear. [o] Several tens of hours. [p] UV lamp or sunlight. [q] 450-W high pressure mercury lamp excited the terminal double bond of the oligomer more selectively than 500-W xenon lamp did. Oligomers hardly accumulated throughout the whole polymerization process. [r] Single crystal.

pended on the crystal state at the growing chain end.[73] The decrease in DP at higher temperature was presumably caused by more random motions of the molecules in the crystal. No polymerization occurred when the molten monomer **192** was irradiated at 250 °C.[84]

Irradiating crystalline **192** in the presence of initiators, presumably of the radical type, did not produce any polymer.[84] The radical inhibitors, hydroquinone and oxygen, did not retard the solid state polymerization of **192**.[84]

Monomer **192** polymerized faster when dispersed in methanol–water (3:2) than in cyclohexane.[84] This behavior was attributed to the greater solubility of **192** in cyclohexane and the resulting greater absorption of light by dissolved **192**.[84] Only the light absorbed by crystalline **192** was effective in causing polymerization in the solid state.

Scheme IV

$$\mathbf{192} \xrightarrow[>380\text{ nm (or }<380\text{ nm)}]{h\nu} \mathbf{192}^{*} \tag{55}$$

$$\mathbf{192}^{*} + \mathbf{192} \xrightarrow{k_{56}} \mathbf{193}\ (\bar{x}_n = 2) \tag{56}$$

$$\mathbf{192}^{*} + \mathbf{193}\ (\bar{x}_n = n) \xrightarrow{k_{57}} \mathbf{193}\ (\bar{x}_n = n + 1) \tag{57}$$

$$\mathbf{193}^{*}\ (\bar{x}_n = n) \xrightarrow[<380\text{ nm}]{h\nu} \mathbf{193}^{*}\ (\bar{x}_n = n) \tag{58}$$

$$\mathbf{193}^{*}\ (\bar{x}_n = n) + \mathbf{192} \longrightarrow \mathbf{193}\ (\bar{x}_n = n + 1) \tag{59}$$

$$\mathbf{193}^{*}\ (\bar{x}_n = n) + \mathbf{193}\ (\bar{x}_n = m) \longrightarrow \mathbf{193}\ (\bar{x}_n = m + n) \tag{60}$$

The mechanism for photopolymerization of the pyrazine **192** was a stepwise process (Scheme IV) analogous to that shown in Scheme II for diester **68**.[49,57,68,84] A relative rate constant ratio [k_{57}/k_{56}, defined by eq 61]

$$-\frac{d[\mathbf{192}]}{dt} = k_{56}[\mathbf{192}^*][\mathbf{192}] + k_{57}[\mathbf{192}^*][\mathbf{193}] \qquad (61)$$

was estimated as ~5 for addition of excited monomer **192*** to oligomer **193** and to ground state monomer **192**.[68] This rate constant ratio accounted for the average pentamer formation when **192** was irradiated with >400 nm light.[68] The change in distance between reacting double bonds during the polymerization may explain the difference in rate constants.[49,68] The distance between the reacting double bond of a monomer molecule **192** and that of an adjacent oligomer **193** was expected to be shorter than the corresponding distance between the double bonds of two adjacent monomer molecules. This shortening occurred because of the twisting motion of the monomer as it became the terminal unit of an oligomer.[49,68]

The DP increased gradually with the initial increase in conversion of the monomer **192**.[57,73,84] Typical of stepwise polymerizations, the DP continued to increase even after all the monomer was consumed, at both −25 °C and +30 °C.[57,84] The reduced viscosity of the polymer **193** increased sharply at ~95–98% conversion of the monomer.[73,84] Polymer **193**, after residual monomer **192** and oligomer **193** had been removed, continued to increase in DP when irradiated further with a broad spectrum light source.[84] On irradiation at 350 nm, the oligomer **193** ($\bar{x}_n \approx 5$) continued to increase in molecular weight.[68] These observations were consistent with step 60 in Scheme IV.

The molecular weight distribution of **193** was broad at low monomer conversion when a broad spectrum radiation source was used.[84] In contrast, irradiation of **192** at 350 nm gave only polymer **193**; no oligomer was detectable during the course of the reaction.[68] This result implied relatively few intermediate oligomers existed at any time under these conditions and was in qualitative agreement with $k_{57}/k_{56} \approx 5$.

Little has been reported about the nature of the excited states involved in the photocycloaddition polymerization of **192**, only that an excited complex (exciplex) may have been involved in the process.[111]

The enthalpy of polymerization of monomer **192** to **193**, when both were in the crystal state, was +3.7 ± 0.9 kcal mol^{-1} of monomer.[112] This endothermic behavior was attributed to the endothermic change in crystal states predominating over the exothermic change in chemical bonding.[112] The calculated enthalpy of reaction, **192** (l) → **193** (amorphous) was −5.4 kcal mol^{-1} of monomer.[112] The probable explanation for the overall positive enthalpy change in the crystal state photopolymerization is that the molecules in the polymer crystal were looser and more disordered than those in the monomer crystal.[112] During the polymerization, the strain energy, caused by molecular movement, accumulated in the reacting crystal step by step and resulted in a thermodynamically unstable polymer crystal.[112] Part of the strain was relieved by cracking of the crystal in the later stages of the polymerization.[112] The conclusion was reached that the strain energy might have competed with the molecular chain growth so as to place an upper limit on the chain length.[112]

Considerable effort has been expended to elucidate the crystallographic features of the solid state photopolymerization of **192**. Polymer **193** as formed in the solid state was highly crystalline[14,82,84,106] and resulted from a reaction in which the stereochemistry was controlled by the crystal lattice of monomer **192**.[57,106] Numerous other aspects of the reaction, such as the rate, were also undoubtedly influenced by the crystal lattice of the reactant.

The original reports on the crystallographic aspects of the polymerization of **192** indicated that the polymer **193** crystal and the monomer crystal belonged to the same space group and had the same three crystal axes.[81,104,106] The oligomer also had the same crystal axes.[49] The degrees of orientation of the polymer were about the same whether or not the oligomer was formed in a separate step.[49] The postulate was made that the reaction proceeded by direct rearrangement of the monomer crystal to the polymer crystal.[49,104] The *c* axis, the direction along which the polymer chain grew,[107] contracted 1.5% during the polymerization,[81] while the *a* axis contracted 11% and the *b* axis expanded 13%.[49] The latter two changes were suggested to result from displacement of the phenyl rings and formation of an sp^3 bond, respectively, during the cycloaddition process.[49] The small movement along the axis in the direction of the chain growth may have been an important factor in producing a linear polymer in good yield.[49,111] The center of gravity of **192** moved very little in the direction of chain growth.[49]

A later report indicated that the space groups of **192** and **193** were different, but that the structure **193** was probably still correct.[117] A more recent publication argued that the original space group assignment for the polymer **193** was correct.[120]

Electron microscopy and X-ray diffraction studies of the crystal state photopolymerization of **192** produced conflicting results concerning the crystallographic aspects of the process.[14,33,51,76,81,106,114,116,117] Several studies indicated that the polymerization occurred homogeneously throughout the bulk of the crystal[14,51,76,81,106,116] in a manner similar to that described in section IID1 on diesters **66**. The relationship of the polymer **193** stereochemistry to the crystal lattice of the monomer **192** is clear for this mechanism.

Other studies indicated polymerization started preferentially at macroscopic defect sites such as cracks and edges.[33,114] As a result of mechanical strain exerted from polymerized sites into unreacted zones, the monomer crystal cracked, thus providing new nucleation sites.[117] The reaction did not occur in the unperturbed state according to these studies.[114] Results indicated that formation of new polymer chains at the surface of a new polymer phase,[117] one to three unit cells thick,[76] was faster than the addition of new monomer units to the chain ends.[117] The polymer thus grew faster in the crystallographic *b* direction than in the *c* direction, the direction of chain growth.[114] Overall, the steps in the polymer growth were suggested as proceeding via: (1) formation of nuclei; (2) chain growth in the *c* direction by addition of monomer **192** to existing chains, **193**; (3) formation of new chains at the surface of the existing polymer phase in the *b*,*c* plane; and (4) nucleation of new layers or growth in the *c* direction.[114] Different quantum yields and temperature dependencies were expected for each of these processes.[114] The measured quantum yield[68,119] (Table XI) would thus have been only an average of those for the various processes.[117]

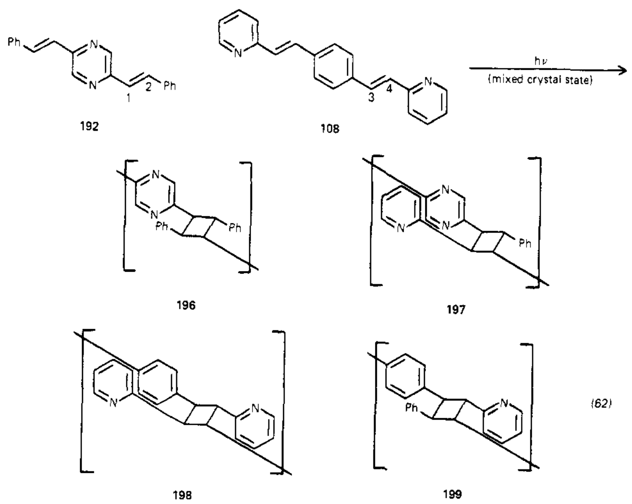
Small crystals of **192** polymerized slightly faster than larger ones; both types had the same crystal structure as shown by X-ray analysis.[84] At the same conversion of monomer **192**, the larger crystals produced the higher molecular weight polymer **193**.[84] Both the faster rate and the lower molecular weight could be attributed to the smaller crystals' having more defect sites per unit weight and thus more initiation sites.

If the cycloaddition reactions of **192** did only occur at defect sites, the question arises as to how the stereospecificity was related to the monomer lattice arrangement.[117]

The most recent results of X-ray diffraction and low temperature transmission electron microscopy studies of the crystal state photopolymerization ($\lambda > 365$ nm) of α-**192** indicated that nucleation began and propagation proceeded within the defect-free structure.[51] Crystal faults were frequently introduced during the irradiation.[51] No evidence was found for discrete nuclei of products.[51] Compared with other monomers that underwent crystal state photopolymerization, the pyrazine **192** had a high reactivity.[51]

The morphological changes that occurred during polymerization of **192** were similar to those noted in section IID2 for the structurally related dipyridyl compound **108**. The crystal exhibited a large shape change and underwent significant cracking.[61] The monomer **192** unit cell and symmetry were analogous to those of **108**.[82]

A solid–solution mixed crystal of the pyrazine **192** and pyridine **108** derivatives was prepared in which the monomer ratio was 0.60:0.40 (**108**:**192**).[121] An X-ray crystal structure determination showed the molecular packing modes were nearly identical with those of the pure crystals of **108** or **192**.[121] In the mixed crystal the nearest intermolecular double bond separations were 3.846 Å (C_1–$C_{2'}$ and C_2–$C_{1'}$), 3.941 Å (C_3–$C_{4'}$ and C_4–$C_{3'}$), 3.752 Å (C_1–C_4), and 4.033 Å (C_2–C_3).[121] The double bonds of adjacent mixed pairs **108** and **192** were not parallel.[121] Irradiation of this mixed crystal gave a polymer that presumably consisted of repeating units **196**–**199** in appropriate combinations (eq 62).[121]



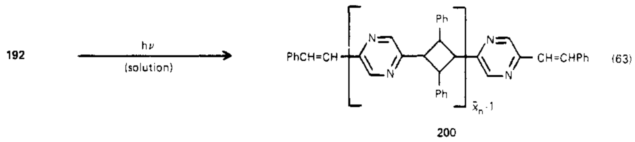
2. Solution Phase

In contrast to the crystal state photopolymerization of distyrylpyrazine **192** where high molecular weights were achievable, irradiating the monomer **192** in solution gave only low molecular weight oligomers **200** (eq 63) (Table XII).[14,57,79,81,84,97,104] Oligomer **200** contained cyclobutanes having mixed stereochemistry[79] in contrast to the stereoregular cyclobutanes formed in the crystal state polymerization. The oligomer was amorphous[14,79,104] rather than crystalline as was the product of the solid state reaction.

TABLE XII. Photopolymerization of 2,5-Distyrylpyrazine (**192**) in Solution (Eq 63)

solvent	λ, nm	time, h	product **200**	yield of **200**, %	ref
$CHCl_3$	>380	a	oligomer		104
$CHCl_3$			oligomer		97
THF[b]	395	1	oligomer	81	79
THF[c]	>380	48[d]	oligomer, $\overline{M}_n$ = 770–900, $\overline{x}_n$ = 2.7–3.2	60	14, 79
THF			oligomer		97

[a] Prolonged, under N_2. [b] 0.00609 M **192**. [c] 0.0141 M **192**. [d] At ~25 °C.



200

The mechanism proposed for the solution-phase photopolymerization of **192** at >380 nm was the same as part of that proposed for the solid state reaction (Scheme IV, eq 55–57).[79] The values of k_{56} and k_{57} were such that more oligomer **200** ($\bar{x}_n$ >2) than dimer **200** ($\bar{x}_n$ = 2) was formed.[79] Because only the monomer **192** absorbed light under these conditions, the molecular weight of the oligomer **200** did not increase after all the monomer had reacted.[79] In contrast, the DP of poly(bismaleimide) **220** continued to increase after the monomer had reacted because the monomer and polymer chromophores absorbed at essentially the same wavelengths (section IIK). Attempts to increase the DP of the oligomer **200** produced in solution by irradiating it in $CHCl_3$ solution at >340 nm led instead to reformation of monomer **192** and a decrease in molecular weight.[79]

As in the crystal state reaction (eq 54), initiators did not promote polymerization of **192**.[84]

The pyrazine **192** and pyridine **108** derivatives had about equal reactivities in solution.[81] Thus some factor in the isolated molecules did not cause the much higher quantum yield for polymerization of **192** than of **108** in the crystal state.[81] Slightly dissimilar molecular packings or overlaps of the nitrogen atoms with the phenyl rings in the crystals could have caused the difference.[81]

Molecular orbital treatment of the α-crystal form of **192** and of **108** reportedly explained the difference in quantum yields for the two polymerizations.[81] Calculating the π stabilization energies of the excimers in the crystals quantitatively explained the difference in reactivities of crystalline **192** and **108**.[99,108] However, this type of calculation also predicted that the photostable γ-crystal form of **192** would be more photoreactive than **108**.[99] Therefore some other factors need to be taken into account. The layer type of packing of γ-**192** probably suppressed molecular deformation that would have been required for a cycloaddition.[99] This calculation method did not quantitatively include a barrier

TABLE XIII. Photopolymerization of Distyryl-*s*-triazine Derivatives 201 (Eq 64)[123]

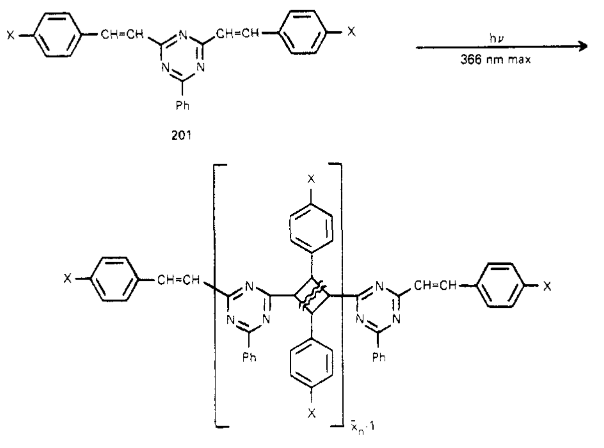
X of monomer 201	solvent	time, h	product 202	conversion of double bonds 202, %
H, 203	PhMe[a]	30	204, $\overline{M}_n$ = 1083, $\overline{x}_n$ = 3.00	39[b]
203	$CHCl_3$	48	204	30[b]
203	none	25	204	19[b]
203	dispersed in H_2O-EtOH (1:1)	2	204	11[b]
203	PhH	72	204	
NMe_2, 205			206	
NO_2, 207	$HCONMe_2$	24	208	c
207	PhMe[a]		208	

[a] Boiling. [b] Conversion as a function of time given. [c] Some monomer remained after irradiation.

to this molecular deformation.[99]

H. Distyryl-*s*-triazines

The difunctional triazine derivatives **201** polymerized rather inefficiently when irradiated in solution or the solid state (eq 64) (Table XIII).[123] Cis-trans isomerization about the double bonds of the monomers **201** occurred during the irradiation.[123]



201

202

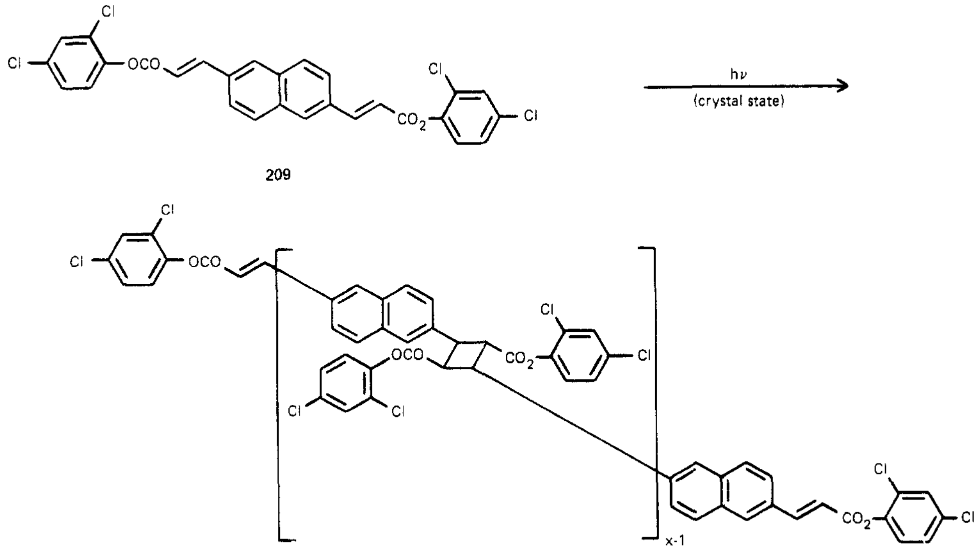
(64)

The initial rates of reaction of the unsubstituted styryl derivative **203** in various solvents decreased in the following order: PhMe > no solvent > dispersion in H_2O-EtOH (1:1) > $CHCl_3$.[123] The maximum conversion of double bonds in **203** occurred at intermediate irradiation times, shown in Table XIII, for the H_2O–EtOH dispersion and probably for the PhMe solution.[123] Further irradiation caused the re-formation of double bonds, probably because of a reversal of the forward reaction (eq 64).[123]

The molecular weight, as indicated by the reduced viscosity of polymer solutions, of polymer **204**, formed in PhH solution, increased sharply during the first 4 h of irradiation of **203**.[123] The molecular weight then increased linearly at a slower rate for the next 68 h of irradiation.[123] Over this same time span, the molecular weight of **204** prepared in PhMe solution first increased to a maximum at ~50 hours and then decreased, again presumably because of decomposition of the polymer.[123]

I. 2,6-Naphthalenediacrylate Ester

Irradiating crystals of the naphthalenediacrylate ester **209** gave a cyclobutyl polymer **210** (eq 65) in a process similar to that exhibited by the pyrazine derivative **192**.[117] The crystal structure of **209** was analogous to that of **192** about the carbon–carbon double bond.[117,124] The double bonds of **209** that reacted to form the cyclobutane rings of **210** were separated by 3.76 Å in the crystal state.[124] A polymer phase, which separated during the irradiation, grew perpendicularly to the boundry of the monomer crystal.[117] Analogous to the polymerization of **192**, the nucleation and growth of polymer **210** in different crystallographic directions probably exhibited different quantum yields and rates.[117]



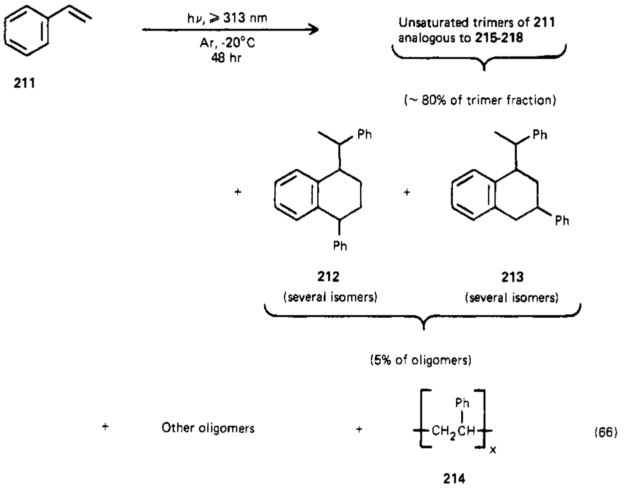
209

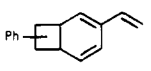
210

(65)

J. Styrene

Among the products of the photopolymerization of styrene (**211**) were several trimers that probably were formed by two successive cycloaddition reactions (eq 66).[125–127] The structures of the unsaturated trimers were not reported, but were described as analogous to several unsaturated dimers, the structures of which were postulated as **215**–**218**.[125] These dimers and several others were isolated from the irradiation of **211** under conditions slightly different from those shown in eq 66.[125] Dimers **215**–**217** and two isomers of **218** constituted 13–15% and 6–7%, respectively, of the dimer fraction.[125]

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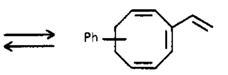
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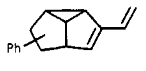
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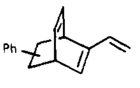
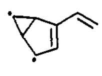

218
(2 isomers)

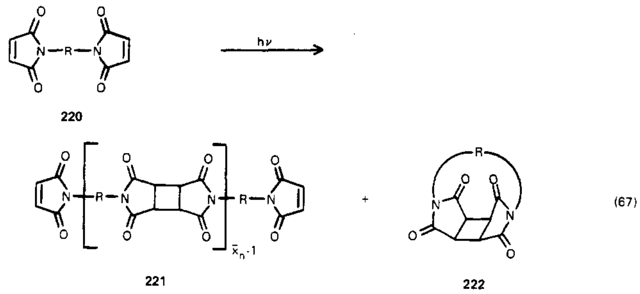

219

Dimer **215** could have resulted from a 2 + 2 cycloaddition of two monomer **211** molecules, **217** from a 2 + 3 cycloaddition via intermediate **219**, and **218** from a 2 + 4 cycloaddition.[125] Presumably the vinyl groups, or other olefinic linkages, of dimers **215**–**218** could have reacted with a molecule of styrene (**211**) to give the trimers in processes similar to those in which **215**–**218** were formed. Higher molecular weight oligomers may have also formed in analogous processes.

K. Bis(maleimides)

1. Unsubstituted

The photochemical intermolecular polymerization and intramolecular cyclization of *N,N′*-bis(maleimides) **220** have been studied extensively (eq 67) (Table XIV).[10,12,128–133] The competition between these two processes was examined for several derivatives.[10,128,129,132]



Scheme V

$$\underset{\textbf{220}}{\text{M·M}} \xrightarrow{h\nu} \text{M·M}^{*1}\ \text{(vibrationally excited)} \quad (68)$$

$$\text{M·M}^{*1} \xrightarrow{k_v} \text{M·M}^{1}\ \text{(localized excitation)} \quad (69)$$

$$\text{M·M}^{1} \xrightarrow{k_d} \text{M·M} \quad (70)$$

$$\text{M·M}^{1} \xrightarrow{k_f} \text{M·M} + h\nu' \quad (71)$$

$$\text{M·M}^{1} \xrightarrow{k_{isc}} \text{M·M}^{3} \quad (72)$$

$$\text{M·M}^{3} \xrightarrow{k'_d} \text{M·M} \quad (73)$$

$$\text{M·M}^{3} + \text{M·M (or } \textbf{221}, \bar{x}_n = n) \xrightarrow{k_p} \textbf{221}\ (\bar{x}_n = 2 \text{ or } n + 1) \quad (74)$$

$$\text{M·M}^{1} \xrightarrow{k_c} (\text{M·M})^{1}\ \text{(intramolecular complex)} \quad (75)$$

$$(\text{M·M})^{1} \xrightarrow{k_{-c}} \text{M·M}^{1} \quad (76)$$

$$(\text{M·M})^{1} \xrightarrow{k''_d} \text{M·M} \quad (77)$$

$$(\text{M·M})^{1} \xrightarrow{k'_f} \text{M·M} + h\nu'' \quad (78)$$

$$(\text{M·M})^{1} \xrightarrow{k_r} \textbf{222} \quad (79)$$

Intermolecular oligomerization to **224** was the only unsensitized reaction exhibited by the dimethylene derivative **223**. Molecular models indicated that the intramolecular product **225** would be very strained.[132] However, **225** apparently was a product from the benzophenone-sensitized photoaddition.[129] The hypothetical *m*-phenylene product **258**, from **256**, would be even more strained than **225**. The trimethylene bis(imide) **226** and the hetero analog **220** (R = CH_2OCH_2) in solution gave only the corresponding cyclized products **222**.[132] The next four higher homologues **229**, **232**, **235**, and **238** also gave primarily the intramolecular products **231**, **234**, **237**, and **240**, respectively,[132] except at high concentrations.[10]

The sudden increase in yield of the oligomers **242**, **245**, **248**, **251**, and **254**, which contain segments of eight, nine, ten, eleven, and twelve methylene groups, respectively, was attributed to the availability of more conformations than were possible for the lower homologues.[132] The probability that the molecule will reach a conformation suitable for cyclization within the lifetime of the reactive excited singlet state decreased rapidly with increasing chain length.[132]

The quantum yield for intramolecular addition, Φ_{222}, varied considerably more than the chemical yield of **222** did.[132]

The yield of oligomer increased from 5% to 100% when the initial concentration of the hexamethylene bis(imide) **235** was increased from 0.005 or 0.01 to 1 M (Table XIV). At 10^{-3} M **235** no oligomer was formed.[132]

The presence of oxygen in solutions of **220** did not affect the reaction.[10,128,132] At long irradiation times, the oligomers underwent crosslinking.[132]

Φ_{222} was not dependent on the radiation wavelength (300–350 nm) or on the temperature (15–55 °C).[132] The quantum yields for cyclization of **235**, Φ_{237}, decreased with increasing solvent polarity, whereas the chemical yields remained constant, implying that the rates of deactivation processes leading back to **235** increased as the solvent polarity increased.[132] Adding benzophenone as a sensitizer increased the yield of oligomer **236**.[132] No ultraviolet spectroscopic evidence was observed for the

TABLE XIV. Photopolymerization and Photocyclization of Bis(Unsubstituted Maleimides) 220 (Eq 67)

R of monomer 220	phase	concn of 220, M	sensitizer, concn, M	λ, nm	temp, °C	time, h	atm over soln	product[a] 221	yield of 221, %	product 222	yield of 222, %	Φ_{222}[b]	$\tau_{220^{*1}}$, s[c]	$\Phi_{220^{*3}}$	ref
$(CH_2)_2$, **223**	CH_2Cl_2 or MeCN soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**224**	100	**225**	0				132
223	MeCN soln	0.01	Ph_2CO, 0.005	~350		3.5		**224**		**225**					129
$(CH_2)_3$, **226**	crystal		none					**227**[d]		**228**	0				131
$(CH_2)_4$, **229**	CH_2Cl_2 soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**230**	15	**231**	85				132
229	CH_2Cl_2 soln	0.01	none	300 ± 5	20,30			**230**		**231**		0.42 ± 0.02	7.35×10^{-10}	0.045 ± 0.01	132
$(CH_2)_5$, **232**	CH_2Cl_2 soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**233**	2	**234**	98				132
232	CH_2Cl_2 soln	0.01	none	300 ± 5	20,30			**233**		**234**		0.54 ± 0.02	7.7×10^{-10}	0.045 ± 0.01	132
$(CH_2)_6$, **235**	CH_2Cl_2 soln	0.005	none					**236**	5	**237**	95				10
235	CH_2Cl_2 or MeCN soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**236**	5	**237**	95				132
235	CH_2Cl_2 or MeCN soln	0.05	none	300, 310, or 350	30-40	~4	N_2	**236**	10	**237**	90				132
235	CH_2Cl_2 soln	0.05	none					**236**	15	**237**	85				10
235	CH_2Cl_2 or MeCN soln	0.05	none					**236**[d]		**237**	85				128
235	CH_2Cl_2 or MeCN soln	0.1	none	300, 310, or 350	30-40	~4	N_2	**236**	20	**237**	80				132
235	CH_2Cl_2 soln	1	none					**236**	100	**237**	0				10
235	C_6H_{14}-CH_2Cl_2 (3:2) soln	0.01	none	300 ± 5	20,30			**236**		**237**		0.50			132
235	CH_2Cl_2 soln	0.01	none	300 ± 5	20,30			**236**		**237**		0.42 ± 0.02	8.8×10^{-10}	0.12 ± 0.02	132
235	MeCN soln	0.01	none	300 ± 5	20,30			**236**		**237**		0.34 ± 0.02	5.66×10^{-10}	0.04 ± 0.01	132
235	MeCN soln	0.05	Ph_2CO, 0.005	~350				**236**[d,e]	15-20	**237**	0				129
235	crystal		none	~350	~25-30			**236**[d]		**237**	0				133
$(CH_2)_7$, **238**	CH_2Cl_2 soln	0.01	none	300, 310, 350	30-40	~4	N_2	**239**	20	**240**	80				132
238	CH_2Cl_2 soln	0.01	none	300 ± 5	20,30			**239**		**240**		0.15 ± 0.02		0.15 ± 0.02	132
$(CH_2)_8$, **241**	CH_2Cl_2 or MeCN soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**242**	90	**243**	10				132
$(CH_2)_9$, **244**	CH_2Cl_2 or MeCN soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**245**	100	**246**	0				132
$(CH_2)_{10}$, **247**	CH_2Cl_2 or MeCN soln	10^{-4}	none	300 310, or 350	30-40	~4	N_2	**248**	100	**249**	0				132
247	CH_2Cl_2 or MeCN soln	0.01	none	300 310, or 350	30-40	~4	N_2	**248**	100	**249**	0				132
247	*f*		Ph_2CO					**248**[d]		**249**	0				130
$(CH_2)_{11}$, **250**	*f*		none					**251**[d]		**252**	0				132
$(CH_2)_{12}$, **253**	CH_2Cl_2 or MeCN soln	10^{-4}	none	300, 310, or 350	30-40	~4	N_2	**254**	100	**255**	0				132
253	CH_2Cl_2 or MeCN soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**254**	100	**255**	0				132
m-C_6H_4, **256**	CH_2Cl_2 or MeCN soln	0.01	none	300, 310, or 350	30-40	~4	N_2	**257**[d]	100	**258**	0				128,132
256	MeCN soln	0.01	Ph_2CO, 0.005	~350		3.5		**257**[g]		**258**	0				129
p-C_6H_4, **259**	*f*		Ph_2CO					**260**[d]		**261**	0				130

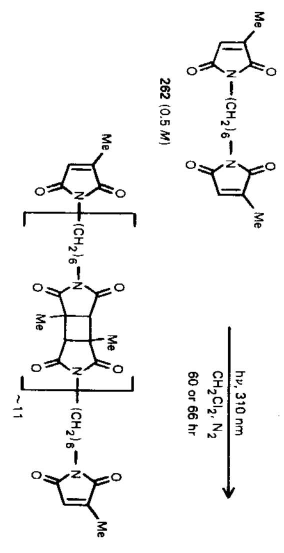
[a] Oligomer except as noted. [b] <10% conversion of **220**. [c] Lifetime of excited singlet state. [d] Polymer. [e] Probable structure. [f] Presumably in soln. [g] Insol and sol fractions. Fraction sol in DMSO: $\overline{M}_n \approx 10{,}000$, $\overline{x}_n \approx 37$.

formation of a strong ground state interaction between the two maleimide moieties of **220**.[132]

The mechanism proposed for polymerization and cyclization of **220** is shown in Scheme V.[132] Polymers **221** were the only products reported from the photosensitized reactions of **235** and **247** in solution and the crystal state reactions of **226** and **235**.[129-131,133] Monomers **247**, **256**, and **259** exhibited partial cross-linking by vinyl polymerization under the sensitized conditions shown in Table XIV.[130]

2. Disubstituted

The cyclobutyl polymer from bis(methylmaleimide) **262** apparently had the head-to-tail structure **263** (eq 80),[129] although no structural evidence was presented.

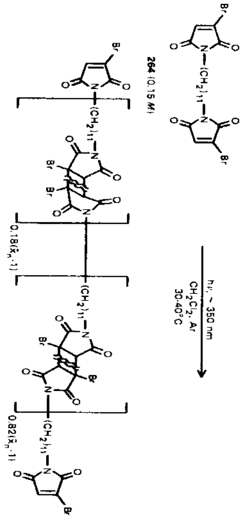


262 (0.5 *M*)

263, $\overline{M}_n \approx 3650$

(80)

When irradiated, the bis(bromomaleimide) **264** polymerized to **265** possessing mainly anti stereochemistry about the cyclobutane ring (eq 81).[134] Structure **265**



264 (0.15 *M*)

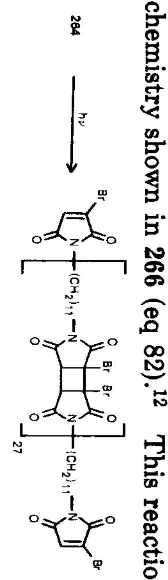
265

(78%), $\bar{x}_n = 17$, $\overline{M}_n = 8{,}600$ (in 41 hr)
(80%), $\bar{x}_n = 29$, $\overline{M}_n = 14{,}500$ (in 96 hr)

(81)

describes the overall composition of the polymer and does not represent a block structure of anti units and syn units. The regiochemistry of the photocycloaddition was not reported.

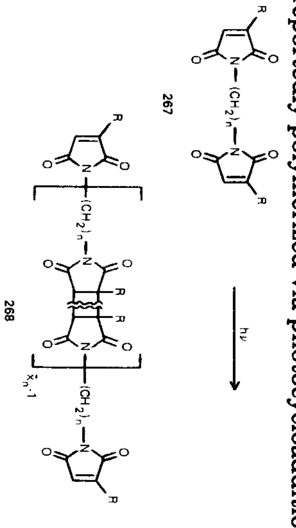
Another publication described the cycloaddition polymer from **264** as having the head-to-head regiochemistry shown in **266** (eq 82).[12] This reaction occurred on direct irradiation via the triplet state, under unspecified conditions.[12] No structural evidence for **266** was given.



266, $\overline{M}_n = 14{,}300$

(82)

Several other bis(monosubstituted maleimides) **267** reportedly polymerized via photocycloaddition (eq 83)



267

268

(83)

TABLE XV. Photopolymerization of Bis(Monosubstituted Maleimides) 267 (Eq 83)

monomer 267													
R	*n*	phase	concn of 267, M	sensitizer	λ, nm	temp, °C	time, h	atm over soln	product 268	yield of 268, %	$\Phi_{-(C=C)}$	$\tau_{267^{*3}}$, s	ref
Me	6, 262	*a*		Ph_2CO					269[b]				10,130
	262	crystal			~350	~25-30	0.5		269				29,133
Me	9, 270	*a*		Ph_2CO					271[b]				10,130
Me	11, 272	CH_2Cl_2 soln	0.15		~350	30-40	17	Ar	273, $\overline{M}_n = 10{,}000$, $\bar{x}_n = 27$	84			134
	272	CH_2Cl_2 soln	0.15		~350	30-40	65	Ar	273[b]	100			134
Cl	6, 274	CH_2Cl_2 soln	0.1	Ph_2CO[c]					275, $\bar{x}_n = 11$-12	70			10,130
Br	3, 276	crystal			~350	~25-30	0.5		277				29,133
Br	6, 278	crystal			~350	~25-30			279				29,133
Br	10, 280	CH_2Cl_2 soln	0.1		~350	30-40	93	Ar	281, $\overline{M}_n = 9500$, $\bar{x}_n = 19$	74			134
	280	CH_2Cl_2 soln	0.1		~350	30-40	165	Ar	281, $\overline{M}_n = 9700$, $\bar{x}_n = 20$	80			134
Br	11, 264	CH_2Cl_2 soln	10^{-3}		350	20		*d*	282			1.36 × 10^{-7}	135
	264	CH_2Cl_2 soln	5 × 10^{-3}		350	20		*d*	282			1.13 × 10^{-7}	135
	264	CH_2Cl_2 soln	0.01		350	20		*d*	282			0.849 × 10^{-7}	135
	264	CH_2Cl_2 soln	0.15		350	25	6	*d*	282, $\overline{M}_n = 2570$, $\bar{x}_n = 5.11$[e]	76[f]			135
	264	CH_2Cl_2 soln	0.1		350	35	10		282, $\bar{x}_n = 11$[g]	88[h]			131
	264	CH_2Cl_2 soln	7.5 × 10^{-3}		338 ± 5	20		*d*	282	≤8	0.0949 ± 0.0016		135
	264	CH_2Cl_2 soln	0.02		338 ± 5	20		*d*	282	≤8	0.151 ± 0.004		135
	264	CH_2Cl_2 soln	0.05		338 ± 5	20		*d*	282	≤8	0.195 ± 0.022		135

[a] Presumably in CH_2Cl_2 solution. [b] Cross-linked. [c] 0.01 M. [d] Degassed. [e] Data at shorter reaction times also given. [f] Conversion of double bonds. [g] $\bar{x}_n$ as a function of time given. [h] Conversion of double bonds given as a function of time.

Scheme VI

$$\underset{\mathbf{264}}{\text{M-M}} \xrightarrow{h\nu} \text{M-M}^1 \qquad (84)$$

$$\text{M-M}^1 \xrightarrow{k_d^S} \text{M-M} \qquad (85)$$

$$\text{M-M}^1 \xrightarrow{k_{isc}} \text{M-M}^3 \qquad (86)$$

$$\text{M-M}^3 \xrightarrow{k_d^T} \text{M-M} \qquad (87)$$

$$\text{M-M}^3 + \mathbf{283} \xrightarrow{k_q^T} \text{M-M} \qquad (88)$$

$$\text{M-M}^3 + \text{M-M (or } \mathbf{282}, \bar{x}_n = n) \xrightarrow{k_r^T} \mathbf{282}\ (\bar{x}_n = 2 \text{ or } n + 1) \qquad (89)$$

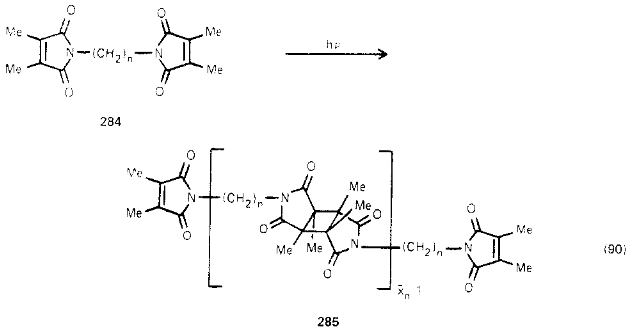
(Table XV).[29,130,131,133-135]

Benzophenone sensitization produced cross-linked methylmaleimide polymers **269** and **271**,[10,130] and the lattice-controlled crystal state reactions of **262**, **276**, and **278** may have produced cross-linked polymers.[133] Polymer **275** from chloromaleimide **274** was not cross-linked, presumably because the chlorine atom changed the multiplicity of the intermediate formed in the polymerization from the multiplicity that occurred with the methyl derivatives **262** and **270**.[10] This proposal[10] is rather surprising because all three polymerizations were sensitized by benzophenone.

A mechanistic and kinetic study of the polymerization of the bromo derivative **264** showed the reactive species was the triplet bromomaleimide moiety (M^3).[135] The polymerization was sensitized with benzophenone and quenched by oxygen or 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide (**283**).[135] The proposed mechanism is outlined in Scheme VI.[135] The rate constants determined for the addition reaction, k_r^T, and the sum of all unimolecular deactivation processes, k_d^T, were 2.4×10^8 M^{-1} s^{-1} and 6.8×10^6 s^{-1}, respectively.[135] The quantum yield for intersystem crossing, Φ_{ics}, was 0.355 ± 0.008, and the lifetime of the reactive excited state τ_{267*3} (Table XV) was longer than expected for an excited singlet state.[135]

3. *Tetrasubstituted*

The bis(dimethylmaleimides) **284** with nine and eleven methylene groups in the connecting link, **286** and **288**, gave polymers **285** having anti stereochemistry about the cyclobutane ring (eq 90) (Table XVI).[12,131,134,136]

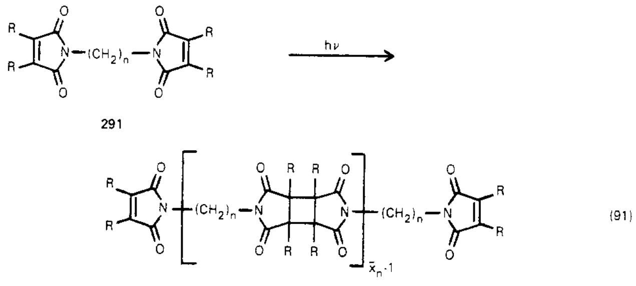


The quantum yields for polymerization [$\Phi_{-(C=C)}$] of **286** and **288** were rather insensitive to wavelength or the length of the methylene chain connecting the maleimide moieties.[136] The polymerization was sensitized with acetophenone or benzophenone and quenched with ferrocene (**290**) or the diazetine dioxide **283**.[136]

Kinetic studies were in agreement when based on the rate of conversion of monomer **288** and on molecular weight determinations for the polymer **289** as a function of conversion.[134,136]

The low quantum yields, less than one, for the disappearance of monomers **286** and **288** [$\Phi_{-(C=C)}$] were cited as evidence that the polymerizations were not chain processes.[136] The condition that k_d^T must not be much larger than k_r^T[monomer], as was shown for **286** and **288**,[136] must also be established for one to confirm the nonchain character of the polymerizations.

Several other bis(disubstituted maleimides) **291** were photopolymerized in either the crystal state or in solution giving cyclobutane moieties of unspecified stereochemistries (eq 91) (Table XVII).[12,29,129-131,133-135,137]



All crystal state polymerizations described in Table XVII were lattice-controlled processes in which some cross-linking may have occurred.[131,133] Crystals of higher homologues of dichloromaleimide **302**, i.e., **291**, R = Cl, *n* = 4, 5, 6, 7, 8, and 11, failed to polymerize when irradiated, presumably because of unfavorably aligned molecules in the crystal lattice.[133]

The molecular weights obtained for polymers **309** and **313**, 30,000 and 60,000, respectively (Table XVII), were higher than those for other homologues, **305**, **307**, and **311**, on benzophenone-sensitized photopolymerization.[130,137] This behavior was attributed to **309** and **313** remaining in solution whereas the other polymers precipitated during formation.[130]

Polymerization of tetrahydrophthalimide **300** was sensitized by acetophenone and quenched by oxygen, the diazetine dioxide **284**, or ferrocene (**290**).[135] The long lifetimes for the excited state of **300** implied a triplet-state reaction.[135] The same conclusion was reached regarding photopolymerization of the chloro monomer **308**, which was sensitized by benzophenone and quenched by oxygen or **284**.[135]

Kinetic data for monomers **286**, **288**, **300**, and **308** were consistent with a triplet-state mechanism analogous to that shown for the bromomaleimide **264** in Scheme VI.[135,136] Rate constants for the cycloaddition (k_r^T) and deactivation (k_d^T) processes were determined (Table XVIII).[135,136]

In acetonitrile the ratio of the rate constants for deactivation to that for cycloaddition (k_d^T/k_r^T) was higher in the presence of ferrocene (0.057 M for **286**, 0.0628 M for **288**, 0.165 M for **300**) than in the absence of a quencher (0.0184 M for **286**) or in the presence of the diazetine dioxide **283** (0.0205 M for **288**, 0.12 M for **300**).[135,136] These higher ratios were attributed to occurrence of a higher deactivation rate constant (triplet to singlet) in the presence of ferrocene.[135,136] This explanation may hold for the dimethylnonamethylene derivative **286** where the ratio in the absence of a quencher was determined from the dependence of the

TABLE XVI. Photopolymerization of Bis(dimethylmaleimides) 284 in Solution (Eq 90)

n of monomer 284	solvent	concn of 284, M	λ, nm	temp, °C	time, h	atm over soln	product 285	yield of 285, %	$\Phi_{-(C=C)}$	$\Phi_{284^{*3}}$[a]	$\tau_{284^{*3}}$, s[b]	ref
9, 286	CH_2Cl_2	0.004	352 ± 20			*c*	287	$\leq 10^d$			$1.70 \times 10^{-6\,e}$	136
286	CH_2Cl_2	0.011	352 ± 20			*c*	287	$\leq 10^d$			$1.13 \times 10^{-6\,e}$	136
286	CH_2Cl_2	0.02	352 ± 20			*c*	287	$\leq 10^d$			$0.76 \times 10^{-6\,e}$	136
286	CH_2Cl_2	0.1	~350	25	2.5		287, $\overline{M}_n = 2860, \overline{x}_n = 7.64^{f,g}$	88.9^d				136
286	CH_2Cl_2	0.02	334	20		*c*	287	$\leq 8^d$	0.23			136
286	CH_2Cl_2	0.01	313	20		*c*	287	$\leq 8^d$	0.17	0.182		136
286	CH_2Cl_2	0.02	313	20		*c*	287	$\leq 8^d$	0.24	0.182		136
286	CH_2Cl_2	0.1	313	20		*c*	287	$\leq 8^d$	0.33	0.182		136
286	MeCN	0.002	352 ± 20			*c*	287	$\leq 10^d$		0.29	$8.45 \times 10^{-7\,h,i}$	136
286	MeCN	0.01	352 ± 20			*c*	287	$\leq 10^d$		0.29	$6.72 \times 10^{-7\,h,i}$	136
286	MeCN	0.025	352 ± 20			*c*	287	$\leq 10^d$		0.29	$4.82 \times 10^{-7\,h,i}$	136
286	MeCN	0.02	334	20		*c*	287	$\leq 8^d$	0.23			136
286	MeCN	0.01	313	20		*c*	287	$\leq 8^d$	0.19	0.180		136
286	MeCN	0.02	313	20		*c*	287	$\leq 8^d$	0.24	0.180		136
286	MeCN	0.05	313	20		*c*	287	$\leq 8^d$	0.30	0.180		136
286	MeCN	0.02	297	20		*c*	287	$\leq 8^d$	0.22			136
11, 288	CH_2Cl_2	0.004	352 ± 20			*c*	289	$\leq 10^d$			$1.90 \times 10^{-6\,e}$	136
288	CH_2Cl_2	0.008	352 ± 20			*c*	289	$\leq 10^d$			$1.40 \times 10^{-6\,e}$	136
288	CH_2Cl_2	0.012	352 ± 20			*c*	289	$\leq 10^d$			$1.07 \times 10^{-6\,e}$	136
288	CH_2Cl_2	0.10	350		23	*c*	289, $\overline{M}_n = 32{,}550, \overline{x}_n = 81^{f,j}$	98.8^d				131,134
288	CH_2Cl_2	0.15	~350	30-40	48	Ar	289, $\overline{M}_n = 17{,}900, \overline{x}_n = 45$	90				134
288	CH_2Cl_2	0.15	~350	30-40	72	Ar	289, $\overline{M}_n = 20{,}800, \overline{x}_n = 52$	90				12,134
288	CH_2Cl_2	0.1	~300	25	4.66		289, $\overline{M}_n = 3{,}700, \overline{x}_n = 9.22^f$	89.0^d				136
288	MeCN	0.004	352 ± 20			*c*	289	$\leq 10^d$			$7.36 \times 10^{-7\,e}$	136
288	MeCN	0.011	352 ± 20			*c*	289	$\leq 10^d$			$4.98 \times 10^{-7\,e}$	136
288	MeCN	0.022	352 ± 20			*c*	289	$\leq 10^d$			$3.25 \times 10^{-7\,e}$	136
288	MeCN	0.002	352 ± 20			*c*	289	$\leq 10^d$			$6.64 \times 10^{-7\,h}$	136
288	MeCN	0.011	352 ± 20			*c*	289	$\leq 10^d$			$5.27 \times 10^{-7\,h}$	136
288	MeCN	0.025	352 ± 20			*c*	289	$\leq 10^d$			$3.91 \times 10^{-7\,h}$	136
288	MeCN	0.02	334	20		*c*	289	$\leq 8^d$	0.21			136
288	MeCN	0.02	313	20		*c*	289	$\leq 8^d$	0.21			136
288	MeCN	0.02	297	20		*c*	289	$\leq 8^d$	0.23			136

[a] Quantum yield for intersystem crossing of 284^{*1}. [b] Lifetime of triplet state. [c] Degassed. [d] Conversion of double bonds. [e] In presence of 283. [f] Further data at shorter reaction times given. [g] Reduced viscosity of polymer solution much higher at higher conversion. [h] In presence of ferrocene (290). [i] Similar data at 25 °C given in ref 131. [j] Similar data given in ref 131. The scale in Figure 6 of this reference apparently is in error by a factor of 10.

TABLE XVII. Photopolymerization of Bis(Disubstituted Maleimides) 291 (Eq 91)

monomer 291		phase	concn of 291, M	sensitizer, concn, M	λ, nm	temp, °C	time, h	atm over soln	product 292	yield of 292, %	$\Phi_{-(C=C)}$	$\tau_{291^{*3}}$, s	ref
R	n												
Me	3, **293**	crystal			~350	~25-30	0.5		**294**				131,133
Me	6, **295**	CH_2Cl_2 soln			310		60	N_2	**296**, $\overline{M}_n \approx 3300$, $\overline{x}_n \approx 10$				129
	295	crystal			~350	~25-30			**296**				133
Me	11, **288**								**297**, $\overline{M}_n = 20{,}800$, $\overline{x}_n = 52$				12
$(CH_2)_2$[a]	3, **298**	crystal			~350	~25-30	1		**299**				29,131,133
$(CH_2)_2$[a]	9, **300**	CH_2Cl_2 soln	0.002		350	20		*b*	**301**			2.47×10^{-6}[c]	135
	300	CH_2Cl_2 soln	0.010		350	20		*b*	**301**			2.17×10^{-6}[c]	135
	300	CH_2Cl_2 soln	0.020		350	20		*b*	**301**			1.75×10^{-6}[c]	135
	300	CH_2Cl_2 soln	0.15		~350	30-40	72	Ar	**301**, $\overline{M}_n = 2500$, $\overline{x}_n = 5.9$	28			134
	300	CH_2Cl_2 soln	0.15		~350	30-40	166	Ar	**301**, $\overline{M}_n = 5100$, $\overline{x}_n = 12$	50			134
	300	CH_2Cl_2 soln	0.02		313	20		*b*	**301**		0.03		135
	300	CH_2Cl_2 soln	0.1		310	25	72		**301**, $\overline{x}_n = 4.41$[d]	76.1[e]			135
	300	MeCN soln	0.002		350	20		*b*	**301**			1.35×10^{-6}[c]	135
	300	MeCN soln	0.011		350	20		*b*	**301**			1.23×10^{-6}[c]	135
	300	MeCN soln	0.025		350	20		*b*	**301**			0.98×10^{-6}[c]	135
	300	MeCN soln	0.002		350	20		*b*	**301**			4.30×10^{-6}[f]	135
	300	MeCN soln	0.011		350	20		*b*	**301**			4.05×10^{-6}[f]	135
	300	MeCN soln	0.022		350	20		*b*	**301**			3.50×10^{-6}[f]	135
	300	MeCN soln	0.02		334	20		*b*	**301**		0.074		135
	300	MeCN soln	0.02		313	20		*b*	**301**		0.08		135
Cl	3, **302**	crystal			~350	~25-30			**303**				29,131,133
Cl	7, **304**	CH_2Cl_2 soln	0.049	Ph_2CO, 0.026	~350	30-40	114	N_2	**305**, $\overline{M}_n = 4130$, $\overline{x}_n = 10$	73			137
	304	CH_2Cl_2 soln	0.052	Ph_2CO, 0.033	~350	30-40	112	N_2	**305**, $\overline{M}_n = 1600$, $\overline{x}_n = 4$	51			137
	304	CH_2Cl_2 soln	0.195	Ph_2CO, 0.137	~350	30-40	121	N_2	**305**, $\overline{M}_n = 4160$, $\overline{x}_n = 9.7$	100			130,137
Cl	8, **306**	CH_2Cl_2 soln	0.068	Ph_2CO, 0.055	~350	30-40	112	N_2	**307**, $\overline{M}_n = 2000$, $\overline{x}_n = 5$	86			130, 137
Cl	9, **308**	CH_2Cl_2 soln	0.0015		350	20		*b*	**309**			2.25×10^{-5}[c]	135
	308	CH_2Cl_2 soln	0.005		350	20		*b*	**309**			1.81×10^{-5}[c]	135
	308	CH_2Cl_2 soln	0.008		350	20		*b*	**309**			1.57×10^{-5}[c]	135
	308	CH_2Cl_2 soln	0.15		350	25	80	*b*	**309**, $\overline{M}_n = 1510$, $\overline{x}_n = 3.31$[d]	71.2[e]			135
	308	CH_2Cl_2 soln	0.005		334				**309**		0.04		135
	308	CH_2Cl_2 soln	0.01	Ph_2CO, 0.027	350		100	N_2	**309**, $\overline{M}_n \approx 6000$, $\overline{x}_n \approx 14$				129
	308	CH_2Cl_2 soln	0.039	Ph_2CO, 0.027	~350	30-40	113	N_2	**309**, $\overline{M}_n = 3800$, $\overline{x}_n = 8$	75			137
	308	CH_2Cl_2 soln	0.044	Ph_2CO, 0.027	~350	30-40	117	N_2	**309**, $\overline{M}_n = 6300$, $\overline{x}_n = 14$	100			130,137
	308	CH_2Cl_2 soln	0.20[g]	Ph_2CO, 0.12	~350	30-40	120	N_2	**309**, $\overline{M}_n = 30{,}000$, $\overline{x}_n = 66$	98			130,137
Cl	10, **310**	CH_2Cl_2 soln	0.043	Ph_2CO, 0.007	~350	30-40	111	N_2	**311**, $\overline{M}_n = 2700$, $\overline{x}_n = 6$	48			130,137
	310	CH_2Cl_2 soln	0.051	Ph_2CO, 0.036	~350	30-40	118	N_2	**311**	82			130,137
	310	CH_2Cl_2 soln	0.127	Ph_2CO, 0.165	~350	30-40	115	N_2	**311**	90			137
Cl	11, **312**	CH_2Cl_2 soln	0.15		~350	30-40	72	Ar	**313**, $\overline{M}_n = 1960$, $\overline{x}_n = 4.1$	69			134
	312	CH_2Cl_2 soln	0.15		~350	30-40	200	Ar	**313**, $\overline{M}_n = 3880$, $\overline{x}_n = 8.0$	69			134
	312	CH_2Cl_2 soln			350		~123		**313**	~91[d,e]			131
	312	CH_2Cl_2 soln	0.12	Ph_2CO, 0.10	~350	30-40	74	N_2	**313**, $\overline{M}_n = 7000$, $\overline{x}_n = 15$	76[e]			12,137
	312	CH_2Cl_2 soln	0.16	Ph_2CO, 0.11	~350	30-40	118	N_2	**313**, $\overline{M}_n = 60{,}000$, $\overline{x}_n = 120$	98[e]			12,130,137
Cl	12, **314**	CH_2Cl_2 soln	0.183	Ph_2CO, 0.183	~350	30-40	115	N_2	**315**	63			137

[a] Cyclohexenedicarboximide. [b] Degassed. [c] In presence of **284**. [d] Further data at shorter reaction times given. [e] Conversion of double bonds. [f] In presence of **291**. [g] Reference 130 reported this concn as 0.020 M.

TABLE XVIII. Rate Constants for Cycloaddition (k_r^T) and Deactivation (k_d^T) of Bis(dimethylmaleimide) 286, 288, 300, and 308 Triplets

		CH$_2$Cl$_2$ soln		MeCN soln		
compound	quencher	k_r^T, M^{-1} s^{-1}	k_d^T, s^{-1}	k_r^T, M^{-1} s^{-1}	k_d^T, s^{-1}	ref
286	283	2.2×10^7	4.1×10^5			136
286	290			1.93×10^7	1.10×10^6	136
288	283	2.55×10^7	3.2×10^5	4.75×10^7	9.75×10^5	136
288	290			2.26×10^7	1.42×10^6	136
300	283	4.5×10^6	3.8×10^5	6.1×10^6	7×10^5	135
300	290			1.35×10^6	2.23×10^5	135
308	283	1.4×10^6	4×10^4			135

TABLE XIX. Photosensitized Polymerization of Bis(coumarin) Ethers 318 (Eq 93)[140]

n of monomer 318	concn of 318, M	concn of Ph$_2$CO, M	time, h	product 319	yield of 319, %
10, 320	0.05	2.98[a]	65	**321**[b]	80
11, 322				**323**[c]	

[a] Absorbed 50% of light. [b] Intrinsic viscosity = 0.25. [c] Intrinsic viscosity = 0.38.

reaction quantum yield on the monomer concentration. However, only the ratio was determined, not the individual rate constants. For the dimethylundecamethylene derivative **288** the 2.10-fold decrease in k_r^T is larger than the 1.46-fold increase in k_d^T. The reported value of k_d^T for tetrahydrophthalimide derivative **300** was smaller in the presence of ferrocene than in its absence although the latter value may have been in error because the quenching rate constant (k_q^T) with **283** may not have been diffusion controlled.[135]

The quantum yield for the singlet to triplet conversion for monomer **286**, Φ_{isc}, was higher in the presence of ferrocene than in its absence (Table XVI).

The rate constant for singlet state deactivation (k_d^S in Scheme VI) was nearly zero for the undecamethylene monomer **288**.[134]

Polymerization of monomers **300** and **312** did not occur by either simple zero- or first-order kinetics, but the data could be fit to an equation containing both zero and first order terms.[135] The rate constants k_r^T and k_d^T were the same order of magnitude for **312**.[131]

L. Bis(thymine)

Photocycloadditions of pyrimidine derivatives have been studied extensively. Polymerization of a difunctional pyrimidine derivative has also been observed. Crystal state irradiation of the trimethylenebis(thymine) **316** gave an uncharacterized insoluble polymer **317** (eq 92),[138] the structure of which was inferred from an X-ray crystal structure determination of the monomer **316**.[139]

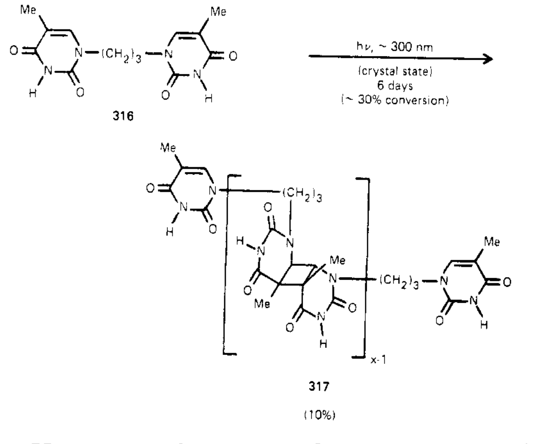


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TABLE XX. Photosensitized Polymerization of Bis(coumarin) Ethers 318 (Eq 94)[141]

n of monomer 318	concn of Ph$_2$CO, M	time, h	product, 324
10, 320	1.75	67.5	**325**, $\overline{M}_n = 5900$, $\overline{x}_n = 12$
11, 322	0.030	64.75	**326**[a]
322	0.322	51	**326**, $\overline{M}_n = 7900$, $\overline{x}_n = 17$[b]
322	0.322	64.75	**326**[c]
322	2.988	64.75	**326**[d]

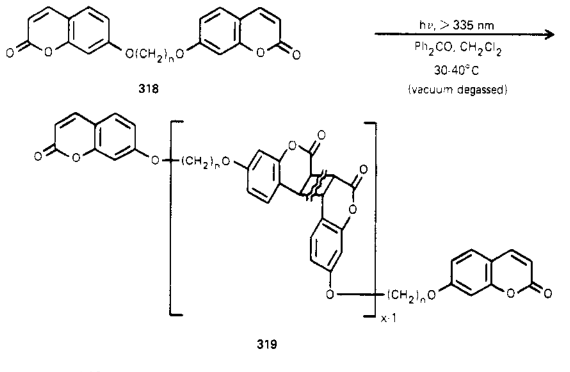
[a] Intrinsic viscosity = 0.14. [b] Intrinsic viscosity = 0.38. [c] Intrinsic viscosity = 0.24. [d] Intrinsic viscosity = 0.28.

In water or aqueous acetone solution, the manner **316** gave an intramolecularly cyclized cis head-to-head cyclobutane derivative.[138]

The crystal structure of **316** was such that either intramolecular cyclization to a trans head-to-head cyclobutane derivative or intermolecular cycloaddition to **317** could have occurred.[139] The intramolecular separation, 3.501 Å, of the double bonds was shorter than the intermolecular separation, 3.688 Å.[139] However, the thymine moieties were aligned so their π orbitals probably interacted more intermolecularly than intramolecularly.[139] Orientation of the orbitals participating in the cycloaddition may, thus, have had more influence than the distance between the reacting atoms.[139]

M. Bis(coumarins)

The benzophenone-sensitized photopolymerization of the bis(coumarin) ethers **318** gave products **319** that contained *anti*-cyclobutane moieties (eq 93) (Table XIX).[140] The regiochemistry was not reported.[140]



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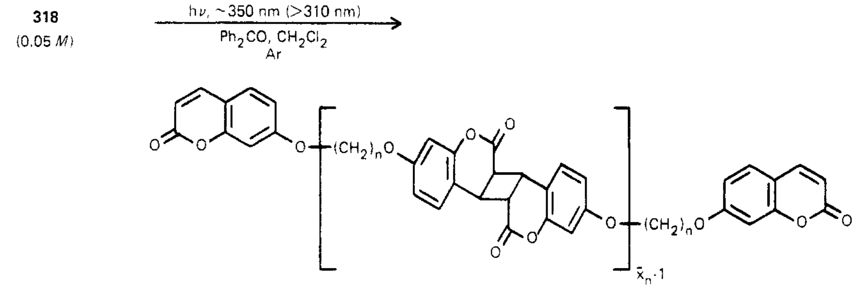

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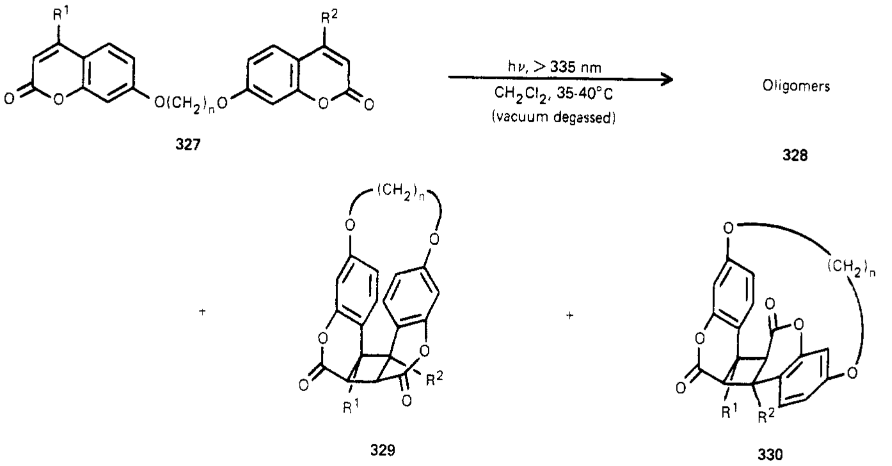

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TABLE XXI. Photopolymerization and Photocyclization of Bis(coumarin) Ethers **327** (Eq 95)[140]

monomer **327**					oligomeric	yield of	
R^1	R^2	*n*	concn of **327**, M	time, h	product **328**	**328**, %	ratio **329**:**330**
H	H	2, **331**	>0.002		**332**[a]		85 (**333**):15 (**334**)[b]
H	H	3, **335**	0.01	72	**336**	3	41 (**337**):59 (**338**)
H	H	4, **339**	0.01	39	**340**	3-15[c,d]	42 (**341**):58 (**342**)[e]
H	H	5, **343**	0.01	15.5	**344**	3-15[c]	40 (**345**):60 (**346**)
H	H	6, **347**	0.01	29.75	**348**	3-15[c]	30 (**349**):70 (**350**)
H	H	7, **351**	0.01	52.75	**352**	3-15[c]	40 (**353**):60 (**354**)
H	H	8, **355**	0.01	91	**356**	3-15[c]	28 (**357**):72 (**358**)
H	H	9, **359**	0.01	115.5	**360**	11[f]	33 (**361**):67 (**362**)[g]
H	H	10, **320**	0.01	160	**363**	3-15[c]	32 (**364**):68 (**365**)
H	H	11, **322**	0.01	142	**366**	15	33 (**367**):67 (**368**)
H	H	2-11	0.05		*h*	30	
H	H	2-11	0.1		*h*	35	
Me	H	4, **369**	0.01	44	**370**	3-15[c]	30 (**371**):70 (**372**)
		369	0.05		**370**	30	
		369	0.1		**370**	35	
Me	Me	5, **373**	0.01[i]	65	**374**	3-15[c]	3 (**375**):97 (**376**)
		373	0.05		**374**	30	
		373	0.1		**374**	35	

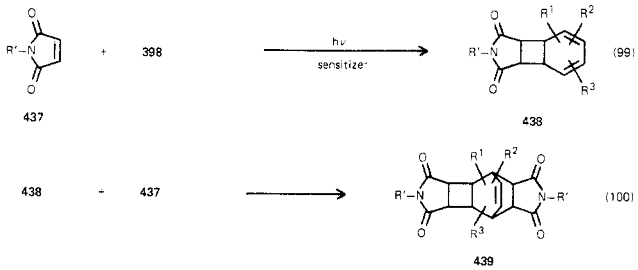
[a] Insoluble polymeric material. [b] At 0.002 M **331**. [c] Yield was within stated range. [d] 100% conversion of **339**. [e] **341** (34.6% yield) and crude **342** (36% yield) isolated. [f] 89% conversion of **359**. [g] **361** (19% yield) isolated. [h] As in above entries. [i] This reaction also performed under N_2 or Ar atmosphere instead of solution being vacuum degassed.

Several patents reported that under slightly different conditions (eq 94) the same reactions gave the anti head-to-tail cyclobutane polymers **324** (Table XX).[141]

Direct irradiation of these same bis(coumarins) **318** and several other homologues **327** gave mainly the intramolecularly cyclized products **329** and **330** and the intermolecular oligomeric photoproducts **328** (eq 95) (Table XXI).[140] Although oligomers **328** presumably were formed by 2 + 2 cycloadditions, no data were reported concerning the structures.

As expected, increased concentrations of the monomers **327** led to a larger fraction of oligomers **328**.[140] Although no systematic study was reported, the amount of intermolecular products **336**, **360**, and **366** increased with increasing length of the methylene chain. At 0.002

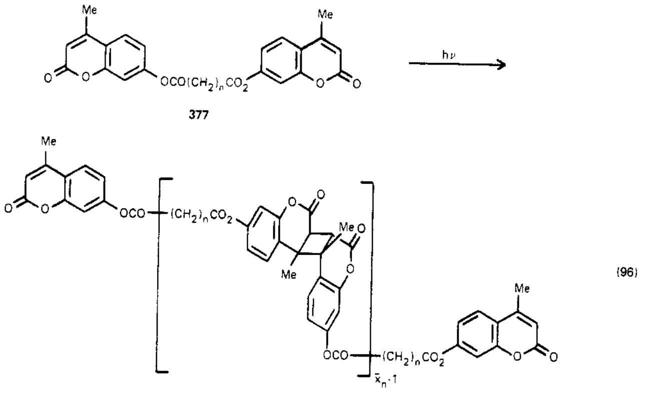
Scheme VII



In general, as the length of methylene chain of **327** increased, the ratio of head-to-tail cyclomer **330** to M the ethylene glycol ether **331** gave only intramolecular products **333** and **334**.

head-to-head cyclomer **329** increased, presumably because the two attachment points of **330** became easier to span. The high proportion of head-to-tail dimethylcyclomer **376** was attributed to the steric effect of the vicinal cis methyl groups.[140]

Anti head-to-head stereochemistry was suggested for polyesters **378** obtained by irradiating bis(coumarin) esters **377** with a sensitizer (eq 96) (Table XXII).[29,131]



377

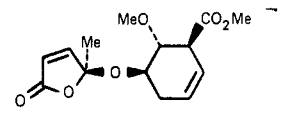
378

(96)

Two of these monomers, **379** and **381**, and their demethyl homologues reportedly gave anti head-to-tail cyclobutane polymers **390** under similar conditions (eq 97) (Table XXIII).[141]

N. Other Cyclic Olefins

Irradiating the diene ether **397** gave an uncharacterized polymer, whereas a diastereomer of **397** gave an intramolecular 2 + 2 photocycloaddition product.[142] This difference is easily explained on examination of molecular models. Although the diastereomer of **397** could have readily assumed a conformation allowing the intramolecular cycloaddition, **397** could not. The polymer from **397** presumably contained cyclobutane linkages, although no supporting evidence was presented.

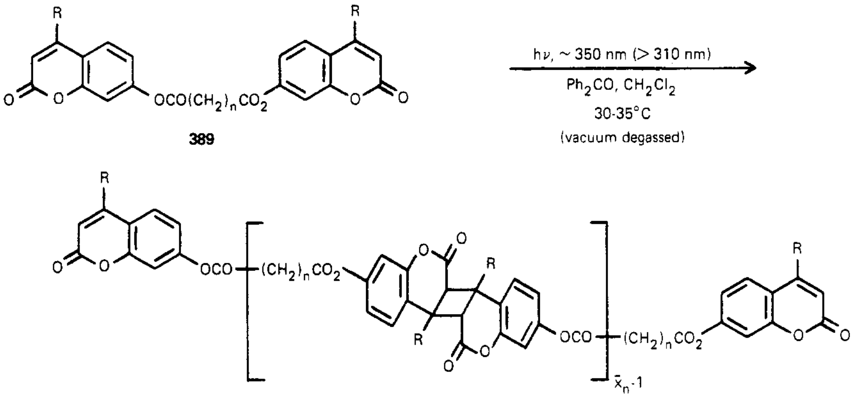


397

O. Bis(maleimides) with Aromatic Hydrocarbons (Copolymerizations)

Irradiating bis(maleimides) **220** in aromatic hydrocarbon solvents **398** in the presence of acetophenone gave copolymers **399** (eq 98) (Table XXIV).[143-147] These results were in distinct contrast to those from homopolymerizing some of the same monomers **220** described in section IIK1. Structure **399** illustrates the three types of bonding possible for each bis(succinimide) unit rather than representing a regular sequence of monomer units.

Scheme VII shows the mechanism thought to occur in this copolymerization.[143,144] Initially, a photosensitized cycloaddition of **437** with **398** gave the diene **438** (eq 99), which underwent a nonphotochemical Diels–Alder reaction with the dienophile **437** to give the bicyclooctene **439** (eq 100). Each maleimide moiety **437** of the bis(maleimide) **220** presumably reacted independently. Each thus could have participated in the



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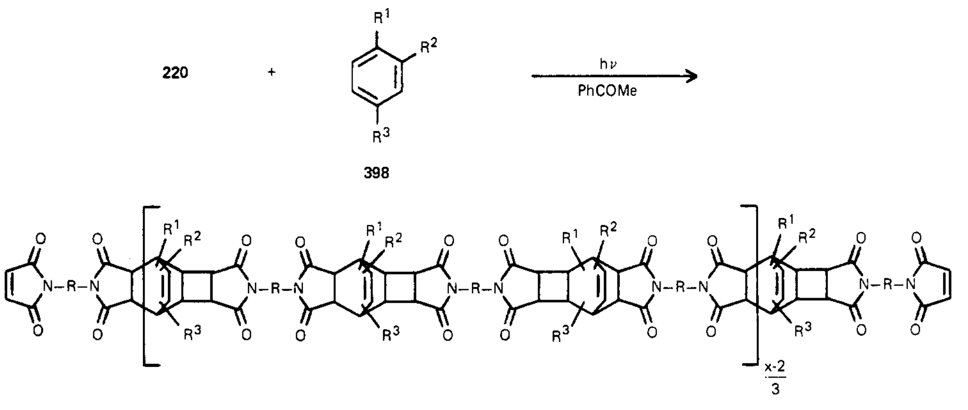
(97)



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(98)

TABLE XXII. Photosensitized Polymerization of Bis(methylcoumarin) Esters 377 (Eq 96)

n of monomer **377**	solvent	sensitizer	λ, nm	product **378**	ref
7, **379**		Ph_2CO		**380**	131
8, **381**		Ph_2CO		**382**	131
10, **383**	CH_2Cl_2	*a*	>335	**384**, $\overline{M}_n = 6000$, $\bar{x}_n = 11$	29
383		Ph_2CO		**384**	131
11, **385**	CH_2Cl_2	*a*	>335	**386**, $\overline{M}_n = 9400$, $\bar{x}_n = 16.8$	29
385		Ph_2CO		**386**	131
12, **387**	CH_2Cl_2	*a*	>335	**388**, $\overline{M}_n = 22{,}300$, $\bar{x}_n = 38.8$	29
387		Ph_2CO		**388**, $\overline{M}_n = 22{,}000$, $\bar{x}_n = 38$	131

[a] Not reported.

TABLE XXIII. Photosensitized Polymerization Bis(coumarin) Esters 389 (Eq 97)[141]

monomer **389**		concn of **389**, M	concn of Ph_2CO, M	time, h	product **390**
n	R				
7	H, **391**	0.1	0.015	96	**392**, $\overline{M}_n = 2420$, $\bar{x}_n = 5.08$
7	Me, **379**	0.096	0.06	67	**393**, $\overline{M}_n = 7700$, $\bar{x}_n = 15$
8	H, **394**	0.055	0.008	36	**395**[a]
	394	0.062	0.032	53	**395**[b]
	394	0.067	0.061	48	**395**
8	Me, **381**	0.095	0.060	63	**396**, $\overline{M}_n = 10{,}000$, $\bar{x}_n = 19$[c]

[a] Intrinsic viscosity = 0.18. [b] Intrinsic viscosity = 0.12. [c] Intrinsic viscosity = 0.42.

photochemical reaction (eq 99), or each in the thermal reaction (eq 100), or one in the photoreaction and the other in the thermal reaction.[144,145] The three bis(succinimide) portions of structure **399** illustrate the kind of linkages that result from these three sets of reactions.

The copolymers **399** were largely insoluble and possibly cross-linked via vinyl polymerization through the maleimide double bonds of monomer **220** and the bicyclooctene double bonds of polymer **399**.[143-146] The soluble portions of polymers **399** had low reduced solution viscosities, presumably because the higher molecular weight fractions precipitated during irradiation.[146]

The trimethylene **409** and hexamethylene **410** copolymers were formed in slightly lower yields than the dimethylene analogue **400**, probably because bis(maleimides) **226** and **235** underwent intramolecular cyclization (eq 67).[143,144]

The higher yields from copolymerization of benzene with monomers **235** and **421**, compared with those from the analogous alkylbenzene, **401**, **403**, **405**, and **414**, copolymers,[144,145] were attributed to benzene having lesser steric effects. However, other[146] results for copolymerization of bis(imide) **235** with benzene and its derivatives, **401**, **403**, and **405**, showed a slight opposite trend. The bis(imide) **421** gave no polyimide when irradiated with ethyl- (**403**) or isopropylbenzene (**405**) under conditions where toluene (**401**) and *tert*-butylbenzene (**414**) did form a polyimide.[145]

Copolymerizations of alkylbenzenes with bis(imides) **235**, **421**, and **431** produced the highest yields from toluene (**401**) and *tert*-butylbenzene (**414**), and the lowest yields from ethylbenzene (**403**) and cumene (**405**).[145] This behavior was attributed to a balance between inductive and steric effects of the alkyl groups.[145] Because the maleimide moiety **437** was electrophilic in both the 2 + 2 and 2 + 4 cycloaddition reactions (eq 99 and 100), alkyl groups on benzene should have enhanced the reactivity in the order *t*-Bu > *i*-Pr > Et > Me.[145] The steric effects of these alkyl groups should have retarded the rates in the same order.[145] This explanation required that the copolymer yields were a reliable measure of the relative rates for the various alkylbenzenes.

The complete lack of reactivity exhibited by the bis(*o*-methyl) monomer **421** with ethyl- (**403**) and isopropylbenzene (**405**) was attributed to steric retardation caused by the methyl groups of **421**.[145]

The inductive and steric arguments noted above require that the inductive effect of the *t*-Bu group outweigh the steric effect.[145] This situation seems unlikely because the inductive effect of the *t*-Bu group is only slightly greater than that of an isopropyl group, whereas the steric effect is considerably greater. Abstraction of a hydrogen atom from the alkyl group by an extraneously generated radical or an excited-state species may have contributed to the observed relative yields of copolymers from the four alkylbenzenes. The relative ease of this reaction is *i*-Pr > Et > Me > *t*-Bu. Occurrence of this side reaction would have reduced the yield of copolymer **399**.

The low yields of copolymers **426** and **430** were attributed to the lack of a substituent ortho to the maleimide ring in monomers **425** and **429**, similar to results observed in nonpolymerizing systems.[143,144] A related monomer **427** that contained ortho substituents gave a higher yield of copolymer **428**. Diene **438** was isolated from the polymerization of bis(imide) **427** with benzene.[144]

Unexpectedly high yields of copolymers of sulfone **431** were obtained, possibly because the sulfone linkage has an electron-withdrawing effect.[144,145] A charge-transfer interaction between the bis(maleimide) **431** and the alkylbenzenes was suggested as possibly occurring.[145]

III. Cycloadditions Involving Carbon 2 + 3 Addition

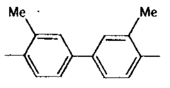
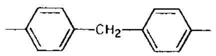
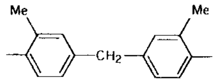
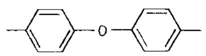
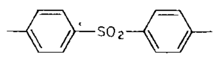
A. Benzene

One of the earliest reported polymerizations achieved by photocycloaddition reactions was polymerization of benzene in the presence of a small amount of an olefin.[148] Irradiating benzene (**13**) that contained minor quantities of cyclooctene (**440**) or the 1:1 adduct **441** gave oligomer and polymer (**442**) in low conversion (eq 101).[148] Several fractions (**443**–**446**) of various molecular weights were isolated; the major one had a molecular weight of ~1500, **444**.[148]

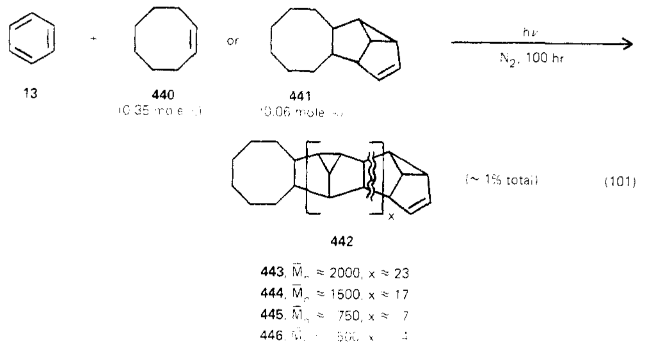
The polymer structure as originally reported consisted entirely of head-to-head units, as in the 2:1 adduct **448**. However, the polymer probably contained both head-to-head and head-to-tail structures, as in **447**. Polymer **442** also may have contained some bicyclo[2.2.0]hexane units.[148]

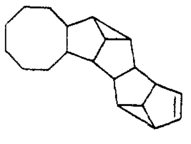
Conditions similar to those in which polymer **442** was formed, e.g., reaction of **13** with **440**, gave the 2:1 adducts **447** and **448**, two other unidentified 2:1 (**13**:**440**)

TABLE XXIV. Photosensitized Copolymerization of Bis(maleimides) 220 and Aromatic Hydrocarbons 398 (Eq 98)

R of monomer 220	monomer 398			solvents-sensitizers	concn of 220, M	concn of PhCOMe, M	λ, nm	temp, °C	time, h	product 399	yield of 399, %	ref
	R^1	R^2	R^3									
$(CH_2)_2$, **223**	H	H	H, **13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**400**	~95	143, 144, 147
223			**13**	**13**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	20	**400**	73	146
223	Me	H	H, **401**	**401**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	20	**402**	55	146
223	Et	H	H, **403**	**403**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	20	**404**	60	146
223	*i*-Pr	H	H, **405**	**405**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	20	**406**	45	146
223	Me	Me	H, **407**	**407**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	20	**408**	51	146
$(CH_2)_3$, **226**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**409**	~80	143, 144, 147
$(CH_2)_6$, **235**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**410**	~70	143, 144, 147
235			**13**	**13**	*c*	0.3		20	20	**410**	56	146
235			**401**	**401**, Me_2CO^a	0.2	0.2	>280		24	**411**	40	145, 147
235			**401**	**401**	*c*	0.3		20	27	**411**	73	146
235			**403**	**403**, Me_2CO^a	0.2	0.2	>280		24	**412**	23	145, 147
235			**403**	**403**	*c*	0.3		20	18	**412**	80	146
235			**405**	**405**, Me_2CO^a	0.2	0.2	>280		24	**413**	28	145, 147
235			**405**	**405**	*c*	0.3		20	18	**413**	62	146
235	*t*-Bu	H	H, **414**	**414**, Me_2CO^a	0.2	0.2	>280		24	**415**	34	145, 147
235			**407**	**407**	*c*	0.3		20	20	**416**	71	146
235	Me	H	Me, **417**	**417**	*c*	0.3		20	26	**418**	61	146
$(CH_2)_{10}$, **247**			**13**	**13**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	30	**419**	30	146
247			**405**	**405**, $CHCl_3$ or $EtOH^b$	*c*	0.3		20	60	**420**	5	146
 **421**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**422**	~65	143, 144, 147
421			**401**	**401**, Me_2CO^a	0.2	0.2	>280		40	**423**	45	145, 147
421			**414**	**414**, Me_2CO^a	0.2	0.2	>280		40	**424**	44	145, 147
 **425**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**426**	~15	143, 144, 147
 **427**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**428**	~80	143, 144, 147
 **429**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**430**	~30	144, 147
 **431**			**13**	**13**, Me_2CO^a	0.2	0.2	>280		18	**432**	~85	144, 147
431			**401**	**401**, Me_2CO^a	0.2	0.2	>280		5	**433**	89	145, 147
431			**403**	**403**, Me_2CO^a	0.2	0.2	>280		5	**434**	50	145, 147
431			**405**	**405**, Me_2CO^a	0.2	0.2	>280		5	**435**	60	145, 147
431			**414**	**414**, Me_2CO^a	0.2	0.2	>280		5	**436**	85	145, 147

[a] Minimum amount required to dissolve monomer 220. [b] 1 part to 2 parts 398 by weight. [c] 2.5-5% solution.





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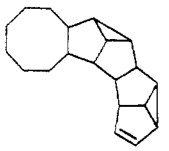
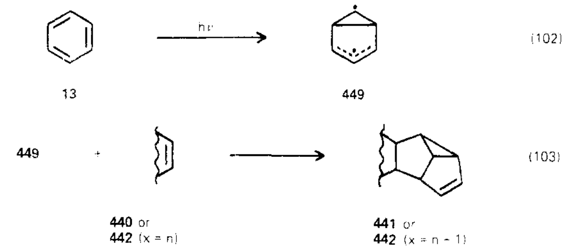


448

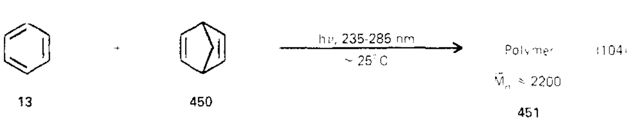
Scheme VIII



adducts, and trace amounts of a 1:2 (**13**:**440**) adduct.[149] Photoaddition of benzene to the 1:1 adduct **441** gave the 2:1 adducts **447** and **448**.[149]

The mechanism suggested for the benzene polymerization involved its excitation to a diradical state **449** (eq 102) and subsequent addition of the latter to the olefinic linkage of **440** in an initiation step or to the polymer **442** in a propagation step (eq 103) (Scheme VIII).[149] 1,3 Cycloadditions to benzene are allowed concerted processes.[150] Woodward–Hoffmann rules cannot be applied to photoreactions involving benzene rings because the molecular orbitals Ψ_2 and Ψ_3 are degenerated as are Ψ_4 and Ψ_5.[150]

Irradiating a mixture of benzene and norbornadiene (**450**) gave a polymer **451** of unspecified structure (eq 104).[149] Whether this polymer **451** consisted mainly of benzene (**13**) units or diene **450** units, or both was not clear. Because both monomers **13** and **450** were difunctional, any of the three possibilities could have occurred. Molecular weight determinations indicated the polymer **451** had a DP of 24–28.

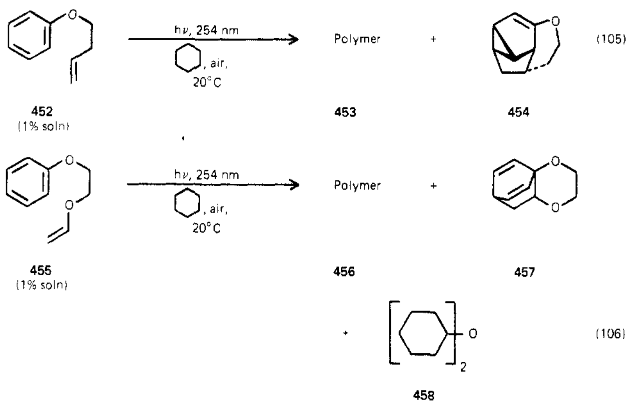


B. Substituted Benzenes

The styrene trimer(s) analogous to the 2 + 3 dimer **217**, formed via diradical **219**,[125] was discussed in section IIH.

Several intramolecular 2 + 3 photocycloadditions have been reported for substituted benzenes containing olefinic linkages in the side chain.[151]

Two of these reactions gave excessive polymer deposits (eq 105 and 106).[151] The structures of these polymers, **453** and **456**, were not reported, although they may have been intermolecular analogues of the intramolecular products **454** and **457**. Quantum yields for disappearance of starting compounds **452** and **455** were greater, the latter ~20 times, than those for the formation of the corresponding cyclization products **454** and **457**.[151] The latter two quantum yields were very low.



IV. Cycloadditions Involving Carbon 2 + 4 Addition

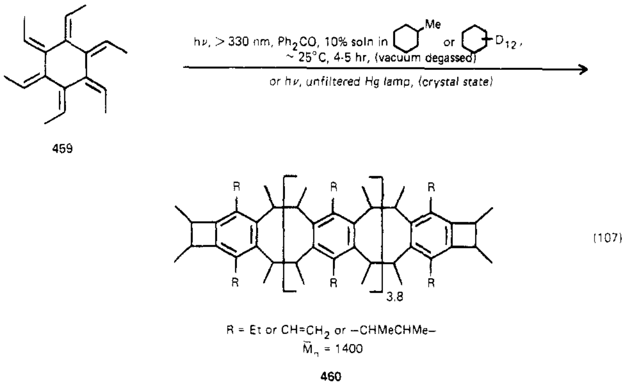
The only unrefuted polymerization or oligomerization reported as occurring via a photochemical 2 + 4 cycloaddition involved formation of the styrene trimer(s) analogous to the 2 + 4 dimers **218**[125] discussed in section IIJ.

The original reports indicated the crystal-state photopolymerization of certain conjugated diacetylenes via 2 + 4 cycloadditions gave polyacenes. Later work showed these polymers were not polyacenes and the polymerizations were not cycloaddition reactions.[152]

V. Cycloadditions Involving Carbon 4 + 4 Addition

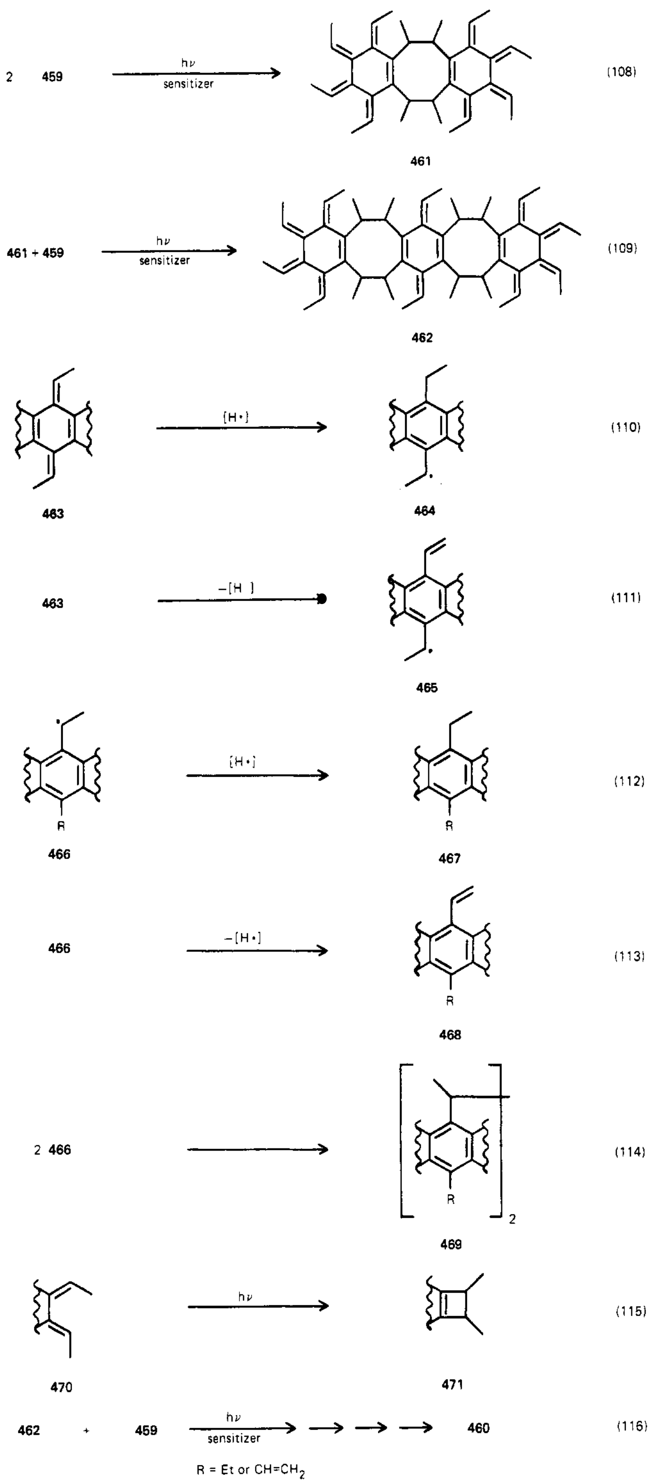
A. Hexaethylidenecyclohexane

The radialene **459** reportedly underwent photochemical oligomerization to approximately a hexamer, the structure of which was postulated as **460** (eq 107).[153]



The same product was reported for both the benzophenone-sensitized reaction in solution and the direct irradiation in the crystal state. The crystal structure of the monomer was reported.[153] The rate of the crystal state reaction was independent of temperature in the range –75 °C to 20 °C.[153]

Scheme IX

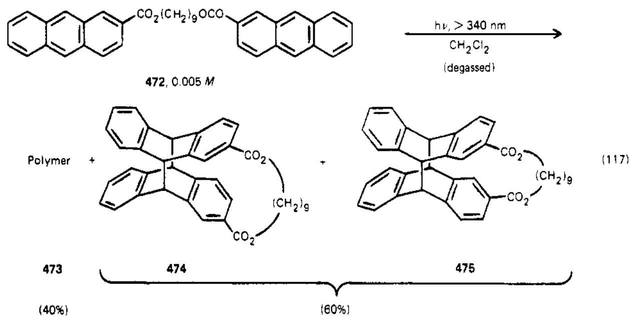


The suggested reaction path leading from monomer **459** to oligomer **460** (Scheme IX) involved 4 + 4 cycloadditions (eq 108, 109, and 116), various hydrogen atom additions (eq 110 and 112) and abstractions (eq 111 and 113), a radical coupling (eq 114), and cyclization of butadienes to cyclobutenes (eq 115).[153] Numerous other structural features could be envisaged for the oligomer in addition to those shown in **460** because of the high degree of functionality of the monomer **459**. The DP of 5.8 shown in structure **460** is valid only for R = Et and CH=CH$_2$. The number of repeating units in **460** requires modification if bridging groups (R = —CHMeCHMe—) occur.

B. Bis(anthracenes)

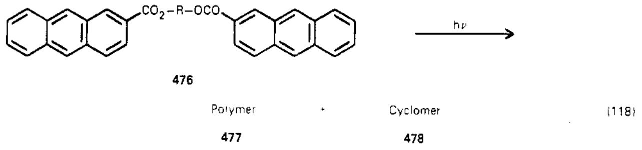
1. 2-Substituted

Irradiating the nonamethylene bis(anthracene) **472** in dilute solution gave two intramolecular cyclic products **474** and **475** and an intermolecular reaction product that presumably was polymeric, **473** (eq 117).[154]

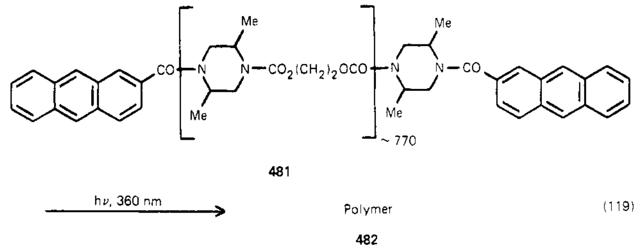


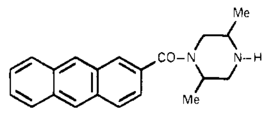
The pentamethylene and heptamethylene homologues of **472** gave only intramolecular products analogous to **474** and **475**.[154] The intermolecular reaction presumably occurred via 4 + 4 photocycloaddition reactions similar to the intramolecular reactions.

Rate constants have been reported for inter- and intramolecular processes for bis(anthracenes) **476** in their excited singlet states under unspecified conditions (eq 118) (Table XXV).[155] Both polymerization and cyclization presumably occurred via 4 + 4 cycloadditions. Neither product structure was reported. The rate of the intermolecular process was nearly independent of the nature of R in monomer **476**.[155] The rate of the intramolecular process decreased slightly with increasing length of connecting link R.



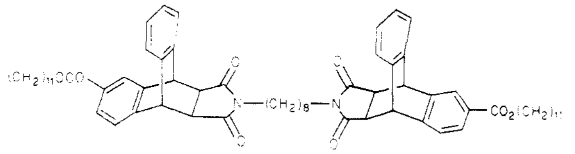
Polyurethane **481**, which contained anthracenecarboxamide end groups, polymerized by "photodimerization" of the end groups, presumably via 4 + 4 cycloaddition at the 9,10-positions of the anthracene moieties (eq 119).[156] Polyurethane **481** was prepared by copolymerizing 0.13 mol percent of the photodimer of the anthracene **483** and 99.87 mol percent of 2,5-dimethylpiperazine with ethylene glycol bis(chloroformate), to give presumably the same polymer **482** formed in reaction 119, followed by short-wavelength photolysis to cleave the dianthracenes to the free an-





483

TABLE XXV. Rate Constants for Inter- and Intramolecular Processes of Di-2-anthracenecarboxylic Esters **476** (Eq 118)[115]

	rate constant for **476**^{*1} [a]	
R of monomer **476**	polymerization (→**477**) + other intermolecular deactivation processes, $M^{-1}\ s^{-1}$	cyclomerization (→**478**) + other intramolecular deactivation processes, s^{-1}
$(CH_2)_9$, **472**	7.7×10^9	2×10^8
$(CH_2)_{16}$, **479**	8×10^9	1×10^8
, **480**	7×10^9	4×10^7

[a] Excited singlet state of **476**.

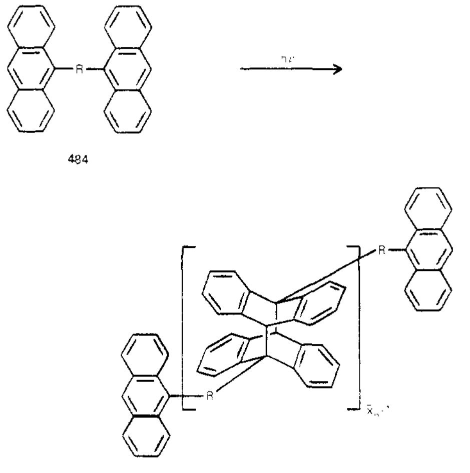
thracene end groups of **481**.[156] Because the original polymer was a rigid matrix, after the short-wavelength photolysis the freed anthracene moieties were oriented favorably for readdition (eq 119).[156] The molecular weight of the polyurethane **481** was not reported; its structure was deduced from the relative amounts of its constituents as noted above and by assuming that short-wavelength photolysis completely dissociated the dianthracene links.

The rate of reaction 119 was faster than a similar photocycloaddition reaction of the model compound, **483**, that was oriented in a polyurethane matrix similar to the polyurethane portion of **481**.[156] The same kind of orientation process employed in preparing **481** was used.[156] The rate of reaction 119, however, was much slower than that of photocycloaddition of anthracene **483** oriented in a poly(methyl methacrylate) matrix having a low glass transition temperature.[156]

Irradiating mixtures of bis(anthracenes) **472** and **480** gave copolymers of unspecified structure,[155] presumably of the 4 + 4 type. The ratios of monomers in the starting reaction mixtures controlled the ratios of monomers in the polymers.[155]

2. 9-Substituted

The bis(9-substituted anthracenes) **484** shown in Table XXVI reportedly polymerized by head-to-tail 4 + 4 photocycloaddition (eq 120).[131,157-162] This regiochemical assignment, at least for the anthracenecarboxylic esters, apparently was based on the analogous photodimerization of the model compound, methyl anthracene-9-carboxylate, which formed only the head-to-tail adduct.[157] The other anthracene polymers **511** and **513** were also tentatively assigned head-to-tail regiochemistries.[159]



484

(120)

485

Polyether **484** [R = $CO_2(CH_2CH_2O)_3CO$], irradiated under the same conditions as was monomer **500** (Table XXVI), gave an insoluble, cross-linked but otherwise uncharacterized polymer.[161] Part of the polymerization may have occurred via photocycloaddition.

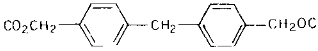
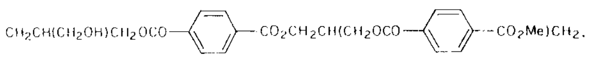
Although monomers **490**[160] and **510**[159] underwent inter- and intramolecular cycloaddition, **512**[159] exhibited primarily an intermolecular reaction. A plot of $1/\Phi_{\text{dimerization}}$ vs. 1/concn for the diester **490** in CH_2Cl_2 solution showed a sharp break at 0.012 M **490** ($\Phi_{\text{dim}} = 0.045$).[160] At higher concentrations Φ_{dim} increased significantly, e.g., 0.10 at 0.03 M **490**, indicating the occurrence of an intermolecular reaction.[160] In contrast, at much lower concentrations Φ_{dim} decreased only slightly, e.g., 0.041 at 5.0×10^{-4} M **490**, indicating an intramolecular or concentration independent reaction.[160]

Because of the rigid connecting chain between the anthryl groups of monomer **512**, it exhibited more intermolecular reaction than did monomer **510** in which the flexible connecting chain allowed more intramolecular cycloaddition.[159] The intramolecular process was ~5 times faster in **510** than in **512**.[159] The extent of intramolecular reaction was determined by measuring the initial rates of photocycloaddition at low monomer concentrations and extrapolating these rates to zero initial concentration.[159]

At high conversion, *p*-phenylene monomer **512** was slightly more reactive than monomer **510** (Table XXVI), but at up to ~25% conversion, the reverse was true.[159] Pseudo-first-order kinetics were expected at low anthryl group concentrations, ~10^{-4} M.[159] A first-order kinetic plot for monomer **512** was generally linear to ~90% conversion whereas a similar plot for **510** showed that the reaction was retarded in the later stages compared to the rate expected if first-order kinetics had prevailed throughout the reaction.[159] Existence of the trianthryl analogue in dianthryl monomer **510** may have accounted for the observed kinetic behavior. Negative deviations from first-order kinetics were expected because photodimerized anthryl groups in the polymer would restrict movement and thus reactivity of the remaining anthryl groups.[159]

Several polyanthryl derivatives related to **510** and **512** were studied similarly to those described above.[159] However, these polymer cross-linking reactions are

TABLE XXVI. Photopolymerization of Bis(9-Substituted anthracenes) 484 (Eq 120)

R of monomer 484	phase	concn of 484, M	λ, nm	temp, °C	time, h	atm over sample	product 485	conversion of 484, %	ref
$CO_2(CH_2)_6OCO$, **486**	CH_2Cl_2 soln	0.2	366		48	Ar	**487**		158
$CO_2(CH_2)_8OCO$, **488**	CH_2Cl_2 soln	0.1	>320	50-60	36	*a*	**489**	80	161
$CO_2(CH_2)_9OCO$, **490**	CH_2Cl_2 soln	0.05			~12		**491**, $\bar{x}_n$ = 7[b]	97	160
490	CH_2Cl_2 soln	0.2			~63		**491**, $\bar{x}_n$ = 12[b]	93	160
490	CH_2Cl_2 soln	0.2	~350		24		**491**		131, 157
$CO_2(CH_2)_{10}OCO$, **492**	CH_2Cl_2 soln	0.2	366		48	Ar	**493**, $\overline{M}_n$ = 21,000, $\bar{x}_n$ = 36		158
492	CH_2Cl_2 soln	0.2	~350		24		**493**		131, 157
$CO_2(CH_2)_{11}OCO$, **494**	CH_2Cl_2 soln	0.2	~350		41		**495**, $\overline{M}_n$ = 52,000, $\bar{x}_n$ = 87		131, 157, 160
$CO_2(CH_2)_{12}OCO$, **496**	CH_2Cl_2 soln	0.2	~350		24		**497**, $\overline{M}_n$ = 28,000, $\bar{x}_n$ = 46		131, 157
496	CH_2Cl_2 soln	0.2	>320	50-60	36	*a*	**497**	82	161
496[c]	film[d]		365	20	2.0	N_2	**497**	37[b]	162
496[c]	film[d]		365	60	2.0	N_2	**497**	52[b]	162
 **498**	CH_2ClCH_2Cl soln	0.1	>320	50-60	9	*a*	**499**	86	161
$CO_2(CH_2)_4OCO(CH_2)_4CO_2(CH_2)_4OCO$, **500**	CH_2Cl_2 soln	0.2	>320	50-60	48	*a*	**501**	81	161
$CO_2(CH_2)_4OCO(CH_2)_8CO_2(CH_2)_4OCO$, **502**	CH_2Cl_2 soln	0.2	>320	50-60	48	*a*	**503**	59	161
502[c]	film[d]		365	20	1.5	N_2	**503**	25[b]	162
502[c]	film[d]		365	40	1.5	N_2	**503**	27[b]	162
502[c]	film		365	60	1.5	N_2	**503**	50[b]	162
$CO_2(CH_2)_4OCO(CH_2)_{12}CO_2(CH_2)_4OCO$, **504**	CH_2Cl_2 soln	0.2	>320	50-60	48	*a*	**505**	51	161
504[c]	film[d]		365	20	1.5	N_2	**505**	30[b]	162
504[c]	film[d]		365	40	1.5	N_2	**505**	15[b]	162
504[c]	film[d]		365	60	1.5	N_2	**505**	30[b]	162
$CO_2(CH_2)_4OCONH(CH_2)_6NHCO_2(CH_2)_4OCO$, **506**[c]	film[e]		365	~25	1.0	N_2	**507**	22[b]	162
506[c]	film[d]		365	~25	1.0	N_2	**507**	53[b]	162
506[c]	film[d]		365	20	1.0	N_2	**507**	52[b]	162
506[c]	film[d]		365	40	1.5	N_2	**507**	29[b]	162
506[c]	film[d]		365	60	1.2	N_2	**507**	12[b]	162
$CO_2(CH_2)_4OCO(CH_2)_{10}NHCO_2(CH_2)_4OCO$, **508**[c]	film[d]		365	20	1.5	N_2	**509**	54[b]	162
508[c]	film[d]		365	40	1.5	N_2	**509**	24[b]	162
508[c]	film[d]		365	60	1.5	N_2	**509**	10[b]	162
$CH_2CH(CH_2OH)CH_2OCO(CH_2)_2CO_2CH_2CH(CH_2OCOCH_2CH_2COCl)CH_2$, **510**[f]	PhMe soln	~2 × 10^{-4}	370	30 ± 2	(3.2)[g]	N_2	**511**	88[b]	159
 **512**	PhMe soln	~2.6 × 10^{-4}	370	30 ± 2	(3.0)[g]	N_2	**513**	91[b]	159

[a] Degassed. [b] Data at shorter reaction times also reported. [c] Prepared by photolysis of corresponding polymer **485** at 300 nm, <5% conversion. [d] Preformed polymer **485** annealed at 80 °C for 2 h and slowly cooled; irradiated at 300 nm at 20 °C to prepare **484**. [e] Preformed polymer **507** annealed at 80 °C for 2 h and cooled quickly; irradiated at 300 nm at 20 °C to prepare **506**. [f] Mixture with trianthryl analog; acid chloride moiety may have hydrolyzed to acid.

outside the scope of this review.

The monomers in Table XXVI that were irradiated as films were actually several of the indicated monomer units joined together by dianthracene links. These monomers were formed by 300 nm irradiation of the preformed polymers **485**, prepared by a nonphotochemical polymerization.[162] This short wavelength radiation restored <5% of the anthracene moieties from the dianthracene links, thus accounting for the oligomeric nature of the monomers. Preformed polymer **497** had a lower molecular weight than did preformed **503** or **505**.[162]

Residual casting solvent reduced the rates of redimerization of anthroate groups in the films (Table XXVI). It acted as a plasticizer so that reactive groups in the monomer were mobile and not aligned for ready cycloaddition.[162]

The thermal history of the preformed polymers significantly affected the rate and extent of redimerization of anthroate moieties in the films.[162] The two different reaction rates of bis(carbamate) **506** at ~25 °C (Table XXVI) was attributed to the different rates at which the preformed polymers **507** cooled after being annealed at 80 °C.[162] The slower rate at which the quickly cooled sample dimerized presumably was a consequence of the strain in the polymer caused by this cooling. Relaxation of the strain when the polymer was photolyzed to monomer positioned the anthroate groups so that they could not easily dimerize. The slowly cooled polymer was largely relaxed before the monomerization process. Heating monomer **506** at 80 °C in a film and then cooling it to 20 °C completely destroyed its ability to undergo photocycloaddition.[162]

The effect of temperature on the rates at which the monomers repolymerized in films (Table XXVI) was studied extensively.[162] In principle, increasing temperature could increase the rate because of the usual activation energy requirement or because of increased polymer chain segment mobility for those reactions in which preformed ground state complexes (sandwich dimers) did not control the rate of polymerization. Alternately, increasing temperature could also decrease the rate for those reactions in which preformed ground state complexes were intermediates in the cycloaddition by destroying these complexes.

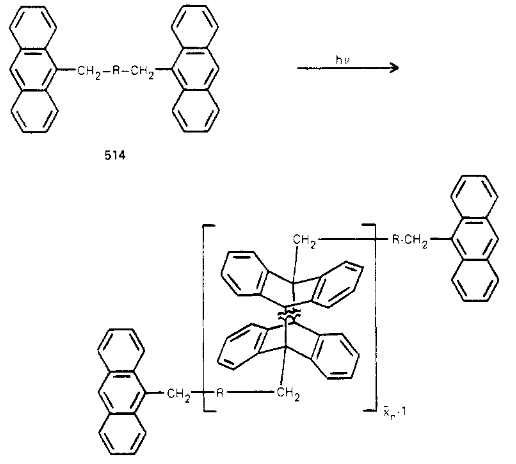
Monomers **506** and **508**, at 20 °C and 40 °C and **504**, at 20 °C, initially photorepolymerized rapidly because of preformed ground state complexes.[162] Monomer **508** exhibited a higher rate at 40 °C than at 20 °C. These reactions decreased in rate after only unpaired anthroate groups were available for reaction and the polymer lacked segment mobility. At 60 °C, both **506** and **508** photopolymerized slowly because the ground state complexes had been destroyed.

Esters **496** and **502** did not form stable ground state complexes.[162] Later stages of the photopolymerizations of **496** at 20 °C and 60 °C were faster than the corresponding reactions for the bis(carbamates) **506** and **508** because the polyester possessed greater segment mobility than the polycarbamate did.

Although tetraester **504** reacted to the same extent at 20 °C and 60 °C after 1.5 h (Table XXVI), it initially reacted much faster at 20 °C.[162]

The nonamethylene dianthroate **490** underwent a singlet state, photocycloaddition polymerization as shown by a 10.5 ns lifetime for its excited state at infinite dilution.[160] This lifetime was determined by extrapolating a plot of $1/\tau$, obtained by quenching the polymerization with $t\text{-}Bu_2NO\cdot$, vs. concentration of **490**. The fluorescence lifetime of **490** at 10^{-5} M was 10 ns.[160] Photopolymerizations of the other α,ω-polymethylenedi-9-anthroates, **492**, **494**, and **496**, also presumably occurred via singlet states.[132]

Irradiating a series of bis(9-anthrylmethyl) derivatives **514** gave polymers **515** that formed by 4 + 4 cycloaddition (eq 121) (Table XXVII).[157,158,163,164] These 4 + 4 cycloadditions may have occurred via both head-to-tail and head-to-head reactions.[157] The model compound, 9-(acetoxymethyl)anthracene, gave a 4:1 mixture of head-to-tail and head-to-head cycloadducts, respectively.[157]



514

515

(121)

A head-to-tail encounter of the anthryl groups in the ionene **526** was implied as a necessary condition for photodimerization of this monomer.[164] However, no structural evidence was presented to corroborate this implication.

A 1,5-sigmatropic shift of a methylene hydrogen atom to the 10-position of the anthracene nucleus was suggested as a side reaction that limited the molecular weights of diesters **516**, **518**, **520**, **522**, and **524**.[157] Steric hindrance to formation of head-to-head adducts from the diesters in Table XXVII was also cited as a possible reason for the lower molecular weights.[157] The higher molecular weights of the related polyesters **495** and **497** (Table XXVI) were attributed to the unfeasibility of a 1,5 shift.[157]

The lower molecular weight of the heptamethylene diester polymer **523**, formed in the argon-purged solution, compared with that formed in the vacuum degassed solution (6000 vs. 12,000) was attributed to formation of more endo peroxides in the former.[157] Endo peroxide formation across the 9,10-positions of an anthracene ring would terminate chain growth on that end of a polymer chain. Removing oxygen from solutions by vacuum degassing is usually more effective than purging argon through the solution.

Photocycloaddition of the ionene **526** may have occurred inter- or intramolecularly.[164] The photoreaction of **526** below the critical micelle concentration (CMC) may have been an intermolecular reaction by analogy with a more thoroughly studied polyanthrylionene.[164] The initial conversion rates of the **526** anthryl groups in both water and KCl solution were independent of the

TABLE XXVII. Photopolymerization of Bis(9-anthracenes) 514 (Eq 121)

R of monomer 514	solvent	concn of 514, M	λ, nm	temp, °C	time, h	atm over solution	product 515	yield of 515, %	ref
$OCO(CH_2)_4CO_2$, **516**	CH_2Cl_2	0.1	~350	30-40	69	Ar	**517**, $\overline{M}_n = 6800$, $\overline{x}_n = 13$		157, 158[a]
$OCO(CH_2)_5CO_2$, **518**	CH_2Cl_2	0.2	~350	30-40	48	Ar	**519**, $\overline{M}_n = 5435$ or 6400, $\overline{x}_n = 10$ or 12		157, 158[a]
$OCO(CH_2)_6CO_2$, **520**	CH_2Cl_2	0.2	~350	30-40	48	Ar	**521**, $\overline{M}_n = 4500$ or 4560, $\overline{x}_n = 8.1$ or 8.2		157, 158[a]
$OCO(CH_2)_7CO_2$, **522**	CH_2Cl_2	0.2	~350		48	Ar	**523**, $\overline{M}_n = 6000$,[b] $\overline{x}_n = 11$		157
522	CH_2Cl_2	0.2	~350		48	*c*	**523**, $\overline{M}_n = 12{,}000$, $\overline{x}_n = 21$		157
$OCO(CH_2)_8CO_2$, **524**	CH_2Cl_2	0.2	350	30-40	48	Ar	**525**, $\overline{M}_n = 11{,}600$, $\overline{x}_n = 19.9$		158[a]
524	CH_2Cl_2	0.2	~350		48	*c*	**525**, $\overline{M}_n = 11{,}600$, $\overline{x}_n = 19.9$		157
$(CH_2)_2OCOCH_2N^+Me_2(CH_2)_6N^+Me_2CH_2CO_2(CH_2)_2$, 2 Cl^-, **526**	H_2O	2.50×10^{-4}	366		(58.4)[d]	Ar	**527**	35.1[e]	163, 164
526	0.25 M KCl in H_2O	2.50×10^{-4}	366		(48.5)[d]	Ar	**527**	36.7[e]	163, 164

[a] Data given in this table from cited references is probably correct; data in U.S. patents were confusing. [b] $\overline{M}_n$ given as 12 000 for this polymer prepared at 30–40 °C.[158] [c] Degassed. [d] Relative light energy input. [e] Data at lower conversions also given.

TABLE XXVIII. Rate Constants for Inter- and Intramolecular Processes of Di-9-anthracenecarboxylic Esters 528 (Eq 122)[155]

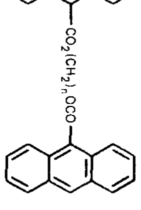
n of monomer 528[a]	rate constants for 528*¹ [a]: polymerization (→529) + other intermolecular deactivation processes, $M^{-1}\ s^{-1}$	rate constants for 528*¹ [a]: cyclomerization (→530) + other intramolecular deactivation processes, s^{-1}
9, 490	6.5×10^9	1.3×10^8
16, 531	6.9×10^9	8.5×10^7

[a] Structure of **528** in ref 155 showed nine methyl groups on one of the anthracene rings; the actual monomer probably does not contain methyl groups.

526 concentration (zero-order reaction) above the CMC. Thus these reactions either occurred in the micellar state or intramolecularly.[164]

The rate of photocycloaddition of **526** was slightly faster in 0.25 M aqueous KCl solution than in water.[163,164] This behavior was attributed to a higher local anthryl group concentration resulting from volume shrinkage of the monomer and polymer aggregates in KCl solution. This shrinkage was caused by reduced Coulombic repulsion and enhanced hydrophobic interactions.[164]

Rate constants were reported for inter- and intramolecular processes for bis(anthracenes) **528** in their excited singlet states under unspecified conditions (eq 122) (Table XXVIII).[155] Both polymerization and



528

Polymer + Cyclomer (122)

529 530

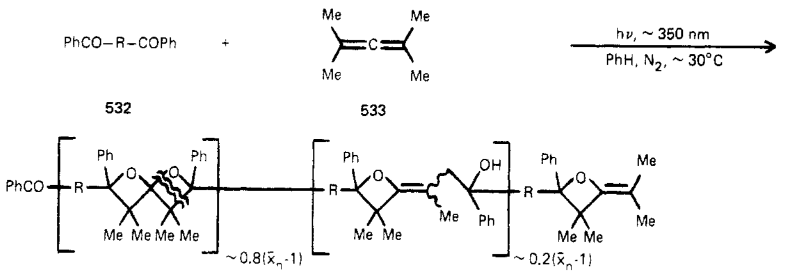
cyclization presumably occurred via 4 + 4 cycloadditions although neither structure was reported. The rate of the intermolecular process(es) was nearly independent of the number of methylene groups or the position of attachment on the anthracene nucleus (Table XXV).[155] The rate of the intramolecular process(es) decreased slightly with increasing length of the connecting link as was also observed for the 2-anthryl derivatives (Table XXV).

Irradiating mixtures of bis(anthracenes) **490** and **531** gave copolymers of unspecified structure,[155] but presumably of the 4 + 4 type. The ratios of monomers in the polymers were controlled by the ratios of monomers in the starting reaction mixtures.[155]

VI. Cycloadditions Involving Carbon and Oxygen 2 + 2 Addition (Copolymerizations)

A. Bis(benzophenones) with Tetramethylallene and Other Diolefins

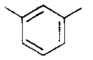
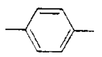
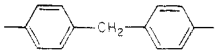
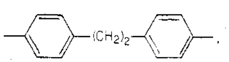
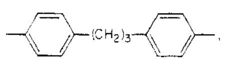
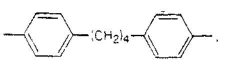
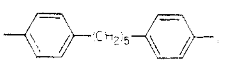
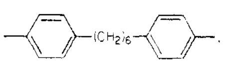
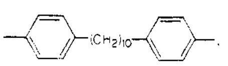
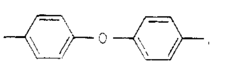
Several series of polymers were prepared in which the chain-growth step was formation of an oxetane by photocycloaddition of a carbon–carbon double bond to a carbonyl group. These are copolymerizations because the two addends are in different kinds of molecules. In all examples reported, bis(benzophenones) **532** served



534
(100%)

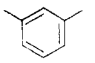
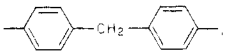
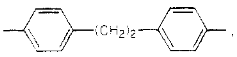
(123)

TABLE XXIX. Photocopolymerization of Bisbenzophenones 532 with Tetramethylallene 533 (Eq 123)[166]

R of comonomer 532	concn of 532 and 533, M	time, h	product 534	crude product		precipitated product	
				$\overline{M}_n$	$\bar{x}_n$	$\overline{M}_n$	$\bar{x}_n$
 535	0.419	550	536	6610	17.3		
 537	0.112	790	538[a]	2200	5.8	3900	10.2
 539	0.02	160[b]	540	4400[c,d]	9.3		
539	0.111[e]	22[b]	540	10 600	22.5		
539	0.129	360	540	13 000	27.5		
 541	0.00922	500	542	2800	5.8	4200	8.6
542	f		543	6400	13.2	7300	15.0
 544	0.0301	440	545	5300	10.6	8100	16.2
 546	0.0318	520	547	4100	8.0	6100	11.9
 548	0.0225	510	549	2800	5.3	6300	11.9
 550	0.0190	370	551	3100	5.7	6200	11.4
 552	0.0363	430	553	3700	6.2	7400	12.4
 554	0.033	670	555	6200	13.1		

[a] May contain cyclobutanone units. [b] Light intensity was twice that of other reactions in this table. [c] Data at shorter reaction times also given. [d] $\overline{M}_n$ near the maximum attained was achieved in ~2-3 h. [e] Data at lower concn also given. [f] Concn unspecified, >0.00922 M (based on monomer).

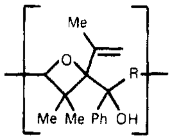
TABLE XXX. Photocopolymerization of Bis(benzophenones) 532 with Furan 572 (Eq 140)[167]

R of comonomer 532	concn of 532, M	concn of 572, M	time, h	product 573	crude product		yield of 573, %
					$\overline{M}_n$	$\bar{x}_n$	
 535	0.199	0.199	670	574	1250	3.5	
 539	0.133[a]	~13[b]	530	575[c]	617	1.39	
 541	0.0187	~13	170	576[d]	567	1.24	100

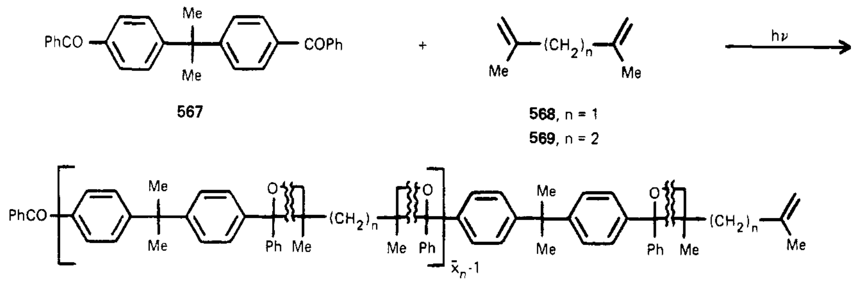
[a] At 0.0282 M 539, the 2:1 adduct 589 formed in 100% yield. [b] Furan used as solvent. [c] Some 2:1 adduct 589 formed. [d] Assumed to be ~85% 2:1 adduct 578 by weight and ~15% 3:2 adduct 580.

as the carbonyl component. Tetramethylallene (**533**) was one of the diolefins (eq 123) (Table XXIX).[165,166]

The polymer structures, **534** or closely related isomers, were assigned on the basis of the product structures from model compound reactions and spectroscopic data.[166] In addition to regioisomeric oxetanes and olefinic cis–trans isomers, the polymer apparently contained the alternate isomeric unsaturated minor unit **556**.[166] The sequence of dioxetane or methyleneoxetane repeating units in the copolymer was not necessarily only as shown in structure **534**. The sequences may have been reversed in parts of the polymer. They presumably depended on which type of moieties (unreacted or singly reacted **533**) reacted in the chain-extending steps (see Scheme X).



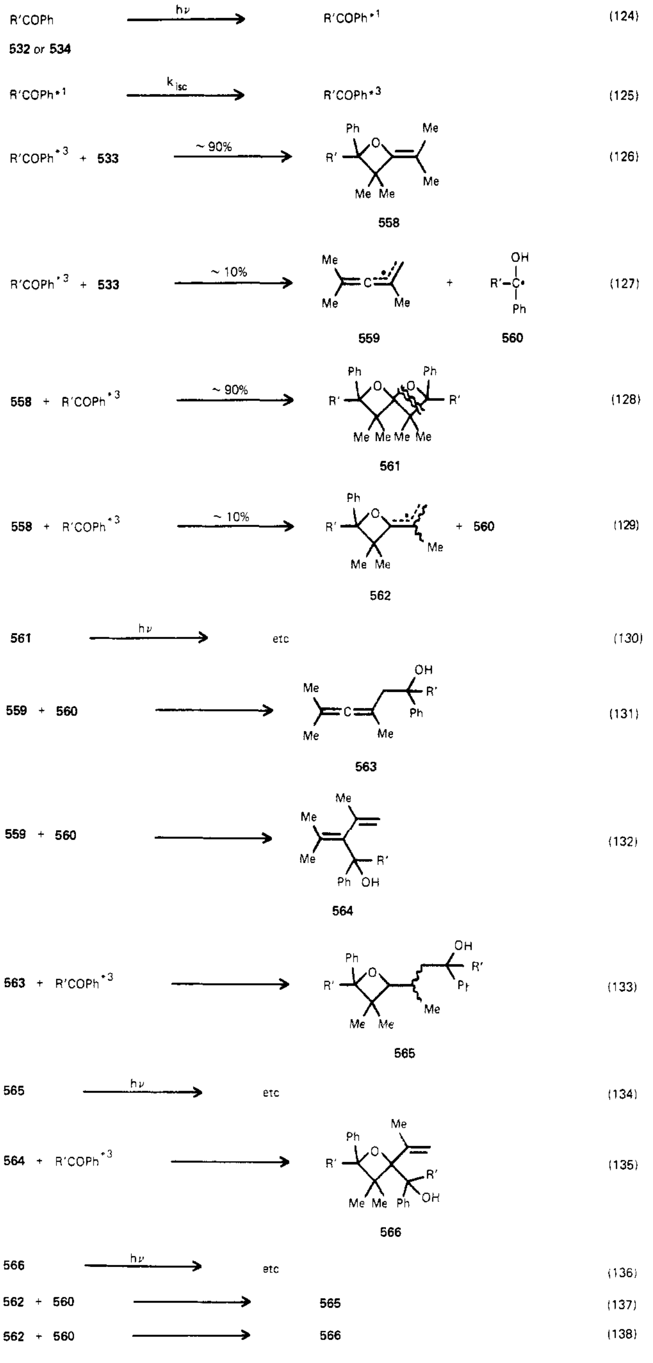
556



(139)

570, n = 1, $\bar{x}_n$ = 15.6, $\bar{M}_n$ = 7800
571, n = 2, $\bar{x}_n$ = 41.4, $\bar{M}_n$ = 21,300

Scheme X



The biphenyl derivative, **532** (R = $-p\text{-}C_6H_4\text{-}p\text{-}C_6H_4-$, **557**) did not polymerize when irradiated with allene **533**, both 0.0110 M, for 1730 h under the conditions shown in eq 123.[166] This lack of reactivity was attributed to the π,π* character of the lowest triplet state of this diketone **557**.[166] The other derivatives of **532** in Table XXIX presumably had n,π* lowest triplet states.

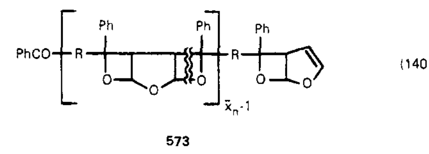
Copolymerizing the methylenebis(benzophenone) **539** with allene **533** gave polymer **540**, which achieved its maximum molecular weight in only a few hours (Table XXIX, line 3).[166] Continued irradiation had little effect on the DP.[166] The maximum molecular weight increased with increasing concentration of the monomers (Table XXIX, lines 3–5).[166] Cessation of polymer growth could have been caused by destruction of chain-end functionality by side reactions, by cyclization, by formation of quenching species, or by dilution of the reactive chain-end functional groups so that the excited states did not live long enough to find a reaction partner.[166] In one set of experiments (Table XXIX, lines 6 and 7), the DP increased with increasing concentration of oligomer **542** formed from the dimethylene monomer **541**, an observation consistent with the dilution effect.[166]

The mechanism proposed for copolymerization of monomers **532** and **533** involved the triplet excited ketone **532***^{3} (Scheme X).[166] Approximately 10% of the excited ketones abstracted allylic hydrogen atoms rather than cycloadding to a carbon–carbon double bond. The first cycloaddition of a carbonyl group to allene **533** was apparently regiospecific, but the second was not. Cycloadditions of **532***^{3} to radical coupling products **563** and **564** could have produced the products shown, **565** and **566**, respectively, or their regioisomers. Hydrogen atom abstraction presumably also occurred to a small extent in these reactions.

Bisphenol A derivative **567** copolymerized with α,ω-dienes **568** and **569** to give the polyoxetanes **570** and **571** (eq 139).[29] No further details, such as side reactions, were reported.[29]

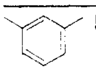
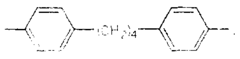
B. Bis(benzophenones) with Furans and Derivatives

Several furans and derivatives have been copolymerized with bis(benzophenones) **532**. Furan (**572**) gave low molecular weight oligomers when irradiated (eq 140) with the diketones shown in Table XXX.[167]



(140)

TABLE XXXI. Photocopolymerization of Bis(benzophenones) 532 with 2,5-Dimethylfuran 581 (Eq 145)[167]

R of comonomer 532	concn of 532 and 581, M	product 582	crude product $\overline{M}_n$	crude product $\bar{x}_n$	precipitated product $\overline{M}_n$	precipitated product $\bar{x}_n$
 535	0.072	583	2400	6.3	3000	7.8
 546	0.047	584	4000	7.8	6700	13.0

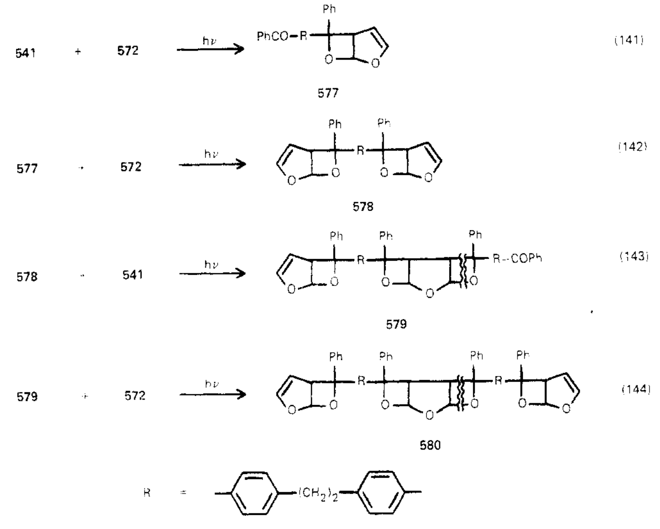
The first photocycloaddition of a carbonyl group to the furan ring probably gave only a dioxabicycloheptene acetal, e.g., eq 141, 142, and 144 (Scheme XI), by analogy with the regiochemistry of model reactions.[167] The addition of the second carbonyl group to the furan ring was nonregiospecific, e.g., eq 143.

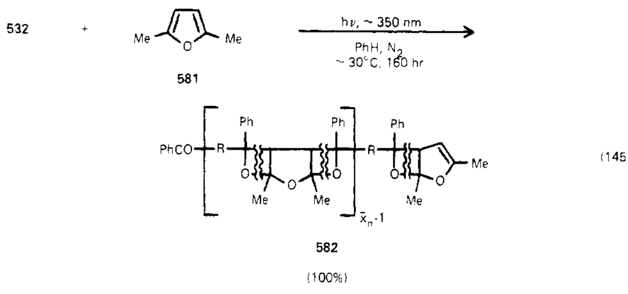
The sequence of acetal and non-acetal type oxetane rings in oligomer **573** could have been reversed in parts of the polymer depending on which type of molecule—unreacted or singly reacted **572**—reacted in the chain-extending steps. This situation is analogous to that shown in Scheme X for the allene reactions.

The low molecular weight of the polymer **574** was attributed to the presence of unequal amounts of the comonomers **532** and **572** in the reaction mixture.[167] The unequal amounts arose because of the difficulty of measuring an amount of furan (**572**) exactly equivalent to that of the diketone **535**.[167] Reactions of diketones **539** and **541** with excess furan solvent gave 2:1 adducts, e.g., **578**, which were used for further polymerizations as described in a later section.[167] Small quantities of higher cooligomers formed in both reactions.

Two copolymerizations of unspecified regiochemistry were performed using 2,5-dimethylfuran (**581**) instead of furan (eq 145) (Table XXXI).[167]

Scheme XI





Copolymerizations of dimethylfuran **581** with the diketones **535** and **546** produced almost no cross-linking in contrast to some of the copolymerizations involving the furan derivatives described in the following paragraphs.[167] The lower degree of cross-linking in **581** copolymers was attributed to the absence of hydrogen atoms on carbon atoms alpha to two oxygen atoms.[167]

Because of the poor results obtained in copolymerizations of furan (**572**) with diketones **532**, the 2:1 adducts **585** were synthesized and photocopolymerized with the diketones **532** (eq 146) (Table XXXII).[167] Improving the control with which the amounts of comonomers **532** and **585** were charged to the reactor gave higher DP's than attained from the direct reaction.[167] The 2:1 adducts **585** were synthesized in quantitative yield by irradiating the diketones **532** in a large excess of furan as the solvent under conditions comparable to those shown in eq 146 and Table XXXII.[167]

Table XXXI shows the DP of copolymers **586** on the basis of diketone **532** and furan (**572**), not the 2:1 adduct **585**, as the comonomers. The DP based on the monomers **532** and **585** is one-half the value given in Table XXXII, thus the $\bar{x}_n/2$ subscript in structure **586**. Interestingly, the purified, precipitated copolymers **592** and **599** had lower DP's than the crude products.

The sequence of regioisomeric oxetanes in copolymer **586** formed from the 2:1 adducts **585** was theoretically different from that formed directly from furan. In the

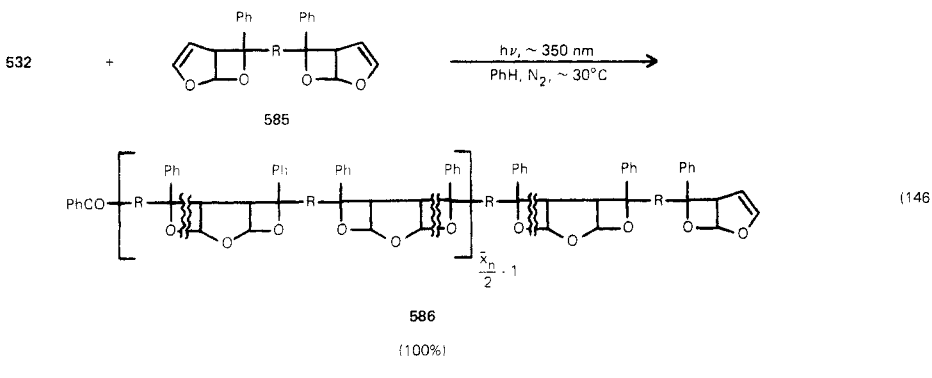
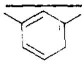
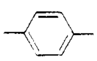
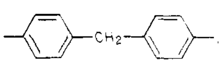
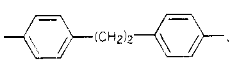
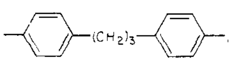
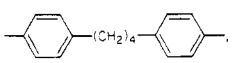
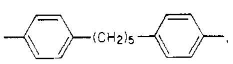
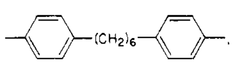
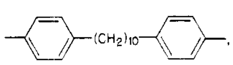
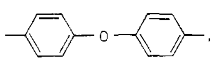


TABLE XXXII. Photocopolymerization of Bis(benzophenones) 532 with Furan-Bis(benzophenone) 2:1 Cycloadducts 585 (Eq 146)

R of comonomers 532 and 585[a]		concn of 532 and 585, M	time, h	product 586	crude product		precipitated product		ref
					$\overline{M}_n$	$\overline{x}_n$[b]	$\overline{M}_n$	$\overline{x}_n$[b]	
	**535, 587**	0.0175		**588**	*c*				167
	535, 587	0.0846	410	**588**[d]	4800	13.5	8000	22.6	167
	**537, 589**	0.0293	640	**590**	1800	5.1	2200	6.2	167
	**539, 591**	0.00975	90	**592**	5400	12.1	4300	9.7	167
	539, 591	0.0176	200	**592**					167
	**541, 578**	0.00843[e]	110	**593**	3400	7.4	6100	13.3	167
	**544, 594**	0.0142	210	**595**	6000	12.7	6500	13.8	167
	**546, 596**	0.0216	120	**597**	7600	15.6	9000	18.5	167
	**548, 598**	0.00864	140	**599**	3700	7.4	3500	7.0	167
	**550, 600**	0.0172	270	**601**	4100	8.0	7300	14.2	167
	**552, 602**	0.00812	340	**603**	2500	4.4			167
603		0.0134[f]		**604**	2900	5.1	8600	15.1	167
	**554, 605**[g]			**606**					27

[a] First compound number is for derivative of **532**, and second compound number is for derivative of **585**. [b] Based on diketone **532** and furan **572** as the monomer units. [c] $\overline{M}_n$ increased linearly with irradiation time and reached plateau in 160–180 h. [d] Hydroxyl functionality increased with extent of polymerization. [e] **578** contained ~15% by weight of 3:2 adduct **580**; amount calcd to give 1:1 (**541**:**572**) ratio used. [f] Concn of **603** calcd as concn of monomers. [g] Reference 167 reported no polymer formed in the irradiation of **554** with furan (**572**).

former, every second diketone in the chain had both carbonyl groups incorporated into acetal type oxetanes whereas the latter copolymer **573** contained a more random distribution of isomeric oxetanes. In both copolymers, each trioxatricyclononane unit contained one regiospecific oxetane and one regiorandom oxetane.

As in the reaction of biphenyl derivative **557** with the allene **533**, irradiating furan (**572**) with **557** also gave no polymer,[167] presumably for the reason cited previously.

Formation of hydroxyl groups occurred in all copolymerizations of diketones **532** and furans or derivatives.[167] Some cross-linking took place in all except those diketones lacking benzylic hydrogen atoms. Both processes presumably occurred because of photoreduction of the triplet carbonyl group by readily abstractable hydrogen atoms.[167] Some hydrogen abstraction occurred even from the solvent benzene.

Thus formation of polyoxetanes via reactions 140, 145, and 146 was limited by the slowness of reactions at attainable monomer concentrations and intervention of at least three types of hydrogen abstraction reactions.[167]

VII. Summary

Polymerization reactions occurring by photocycloaddition of bi- and polyfunctional unsaturated monomers are reviewed. Solution and solid state 2 + 2, 2 + 3, 2 + 4, and 4 + 4 cycloaddition reactions of bis(olefins), aromatic, and carbonyl monomers gave cyclobutane, bicyclo[3.1.0]hexane, cyclohexene, cyclooctadiene, and oxetane linkages when the monomers were irradiated with ultraviolet or visible radiation. The reactive monomer moieties included cinnamic acids, cinnamate esters, cinnamides, cinnamonitriles, styrenes, stilbenes, vinylnaphthalenes, vinylpyridines, vinylpyrazines, vinyltriazines, maleimides, thymines, coumarins, furans, benzenes, anthracenes, benzophenones, allenes, and ethylenes. Both direct irradiation and photosensitization have been employed for these polymerizations, which included both singlet and triplet state processes. Most processes were homopolymerizations although a few were copolymerizations.

VIII. Addendum

Since the original portion of this review was written, several additional pertinent publications have appeared or come to the author's attention. This addendum should complete coverage of this subject through 1981 and part of 1982. The same subject headings as used in the original portion of the review are maintained here for continuity.

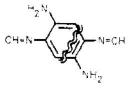
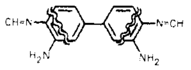
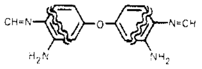
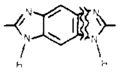
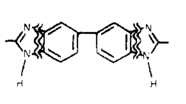
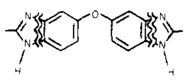
Three additional reviews covering some aspects of photocycloaddition polymerization have appeared.[168–170]

II. Cycloadditions Involving Carbon 2 + 2 Addition

A. Acyclic Bis- and Poly(cinnamic acid) Derivatives

High conversions of the tetracinnamate ester **32** in the crystal state to an amorphous polymer, presumably **33** or **34**, were reported.[170] The crystal structure of the monomer **32** apparently did not change during the po-

TABLE XXXIII. Photopolymerization of Bis(9-substituted anthracenes) 484 (Eq 120)[a] [180]

R of monomer 484		solvent	concn of 484, M	temp, °C	time, h	product 485	inherent viscosity of 485, dL g^{-1}	yield of 485, %
	**637**	Me_2SO or NMP[b]	0.03	60	120	**638**[c]	0.51[d]	100, 91[d]
	**639**	Me_2SO or NMP	0.05	60	110	**640**[c]	0.67[f]	100, 93[f]
	639	Me_2SO	0.05	60	120	**640**[e]	0.67[f]	100, 94[f]
	**641**	Me_2SO or NMP	0.05	60	110	**642**[g]	0.75[h]	100, 95[h]
	**643**	Me_2SO	0.05	60	120	**644**, $\overline{M}_n = 1380$, $\bar{x}_n = 2.70$	0.09	11
	**645**	Me_2SO	0.025	60	24	**646**	0.11	12
	645	Me_2SO	0.050	~25	120	**646**, $\overline{M}_n = 1820$, $\bar{x}_n = 3.10$	0.12	23
	645	Me_2SO	0.050	60	120	**646**	0.12	22
	645	HOAc	0.050	~25	120	**646**	0.12	22
	645	NMP[i]	0.050	60	120	**646**	0.13	25
	**647**	Me_2SO	0.050	60	120	**648**, $\overline{M}_n = 3190$, $\bar{x}_n = 5.29$	0.15	37

[a] Irradiated at >~280 nm and under high vacuum (10^{-5}–10^{-4} torr). [b] *N*-Methyl-2-pyrrolidone. [c] Isolated as **644** by air oxidation. [d] Of **644**. [e] Isolated as **646** by air oxidation. [f] Of **646**. [g] Isolated as **648** by air oxidation. [h] Of **648**. [i] 5% LiCl added.

lymerization, and no morphological change in crystal shape occurred.[170]

C. *m*-Phenylenediacrylic Acid and Esters

Irradiating a 1:1 mixture, by weight, of the diacid **55** and picramide (**57**) (Table I) as an aggregate of microcrystals in a KBr matrix (>430 nm, few min–2 h) gave **56** ($\overline{M}_n \approx 1000$, $\bar{x}_n \approx 4.6$).[171] An 80% conversion of the double bonds of **55** occurred in 1.5 h.[171] When the amount of **57** was decreased to 0.1 or 0.01 that of **55**, very low conversions of **55** were observed.[171] Thus, relatively large amounts of **57** were required for covering the **55** crystals so that significant sensitization could be achieved.[171] 1,2-Benzanthraquinone and 2-nitrofluorene also sensitized this reaction, but were less effective than **57**, which sensitized the phosphorescence of **55** on excitation at 440 nm.[171]

D. *p*-Bis(monosubstituted vinyl)benzenes

1. *p*-Phenylenediacrylic Acid, Esters, and Amides

The diacid **63** had a low reactivity, compared to similar compounds, on photopolymerization to **65** in the crystal state.[170]

In contrast to the medium photoreactivity reported earlier for the diethyl ester **70** in the crystal state, a more recent publication cited its reactivity as high at -25 °C and low at ~25 °C compared to similar compounds.[170]

A reaction model was proposed for topochemical photoreactions such as polymerization of the diethyl ester **70** (eq 25) to explain the kinetics as a function of temperature.[172] The assumption was made that the extent of deviation of the two olefinic bonds from their optimal positions for reaction controlled the reaction rate under constant irradiation conditions.[172] The temperature dependence of the primary photochemical process was assumed to be negligible.[172] The reaction rate depended only on thermal motion of molecules in the crystal.[172] Both unidimensional and two-dimensional models were developed.[172] The equation for the rate constant in the latter was, $k = \alpha(T_{opt}/T)\exp(-T_{opt}/T)$, where α is a non-temperature-dependent constant that includes light intensity, quantum yield, etc., and T_{opt} is the optimal temperature at which the maximum rate occurs.[172] T_{opt} for **70** was ~-20 °C.[172]

Excimer emission from the diethyl ester **70** was observed in concentrated solutions (≥0.1 M, MeCN, PhH, or $CHCl_3$) but not in the crystal state.[173] Activation parameters were reported.[173] The structure of the mirror symmetric dimer, analogous to that of the oligomer **78**, formed on irradiating ($\lambda > 350$ nm) concentrated solutions of **70**, was cited as evidence for a stack-type excimer of **70**.[173] The same dimer was formed by irradiating ($\lambda > 340$ nm) **70** at high concentration; only ground state complexes of **70** were excited.[170] At unspecified temperature, the dimer yield increased on increasing the concentration (12% and 34% yields at 5% and 13% concentrations, respectively) whereas it decreased on increasing the temperature (17% and 9% yields at 5 and 45 °C, respectively) at unspecified concentration.[170] The excimer fluorescence intensity and dimer yields changed as functions of concentration of **70** and temperature in similar manners.[170]

Both the *n*-propyl **80**, at 0–5 °C, and isopropyl **82**, at ~25 °C, diesters had low reactivities on photopolymerization in the crystal state compared with related compounds.[170] The bisamide **94** had a medium reactivity at ~25 °C.[170]

The effect of temperature on the reaction and the continuous changes in the X-ray diffraction diagrams of monomers **68**, **70**, and **76** demonstrated that the polymerization proceeded by a diffusionless crystal-lattice-controlled mechanism.[170]

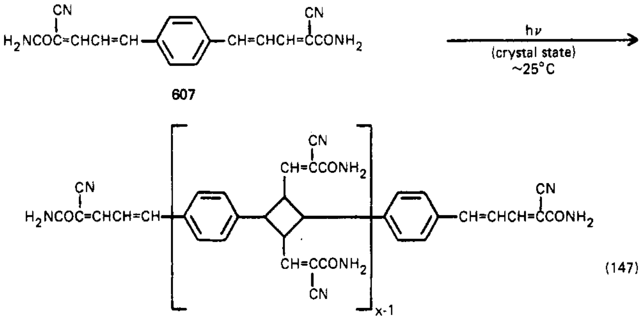
2. *p*-Bis(β-nitro- and β-arylvinyl)benzenes

The yield of polymer **109** was 100% from crystal-state irradiation of dipyridyl monomer **108** at ~25 °C.[170] The effect of temperature on the reaction and the continuous changes in the X-ray diffraction diagrams of **108** demonstrated that the polymerization proceeded by a diffusionless crystal-lattice-controlled mechanism.[170]

3. *p-Di-1,3-butadienylbenzenes*

The tetraene diester **119** had a high reactivity compared to related compounds on photopolymerization to **120** in the crystal state.[170]

The tetraene diamide **607** had a low photoreactivity compared to related compounds on photopolymerization in the crystal state (eq 147).[170] The polymer **608** had a structure analogous to that of **120**.[170]

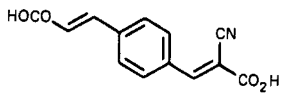


607

608

E. *p*-Bis(polysubstituted vinyl)benzenes

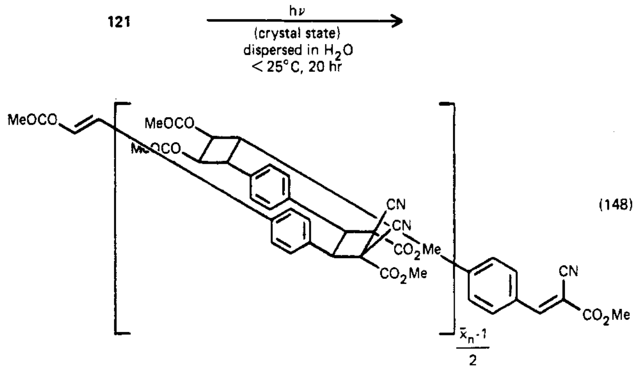
In contrast to the dimethyl ester **121**, the corresponding crystalline diacid **609** in KBr was extremely stable to light,[174] presumably because its crystal structure did not allow cyclobutane formation or other reactions.



609

1. *Cyano-p-phenylenediacrylate Esters*

Irradiation of crystalline dimethyl ester **121** with a Xe lamp through quartz gave a polymer or oligomer in high conversion (eq 148).[174] The structure of the polymer may be **610**, at least in part. The two types of cyclobutane rings of **610** were formed at approximately the same rate.[174]



610

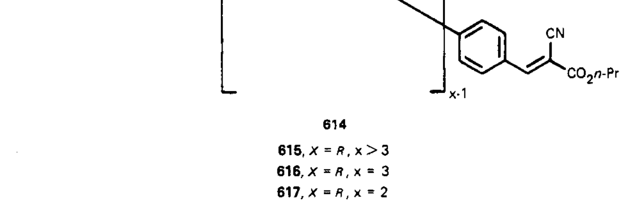
The molecular weight of the polymer **610** formed from crystalline monomer **121** in KBr was determined as a function of time.[174] The DP increased rapidly in the first few hours; loss of monomer was detected after irradiation for 1 min.[174] The DP increased more slowly after the first few hours, and after 20 h, $\bar{M}_n$ had reached 1200 ($\bar{x}_n$ = 4.4).[174]

Excimer emission was observed from monomer **121** in both the crystal state and in $CHCl_3$ solution.[173] In the crystal state the molecules are aligned in the overlapping sandwich form that is often implicated for excimers. The same is probably true in solution. However, the involvement of the excimer as an intermediate in the photocycloaddition process was not established.

Irradiating crystalline monomer **121**, as a film, through a negative, in the 300-nm range formed an image.[174] The polymerization of **121** was also sensitized, thus allowing the use of longer wavelength light.[174] Irradiating equimolar mixed crystals of **121** and 1,2-benzanthraquinone (**611**) suspended in water at ≥430 nm for 200 h gave oligomer, presumably **610**, $\bar{M}_n$ = 580, $\bar{x}_n$ = 2.1.[174] After 50 h, ~82% of **121** was converted to oligomer.[174] *p*-Nitroaniline and 2-nitrofluorene had weaker sensitizing effects; **121** conversions of ~49% and ~44%, respectively, in 60 h were observed under comparable conditions.[174] On a synthetic scale the sensitized reactions were much slower than the unsensitized reaction.[174] Image formation occurred on irradiating (≥430 nm, 5–60 min) mixtures of monomer **121** and sensitizer **611** in a poly(methyl methacrylate) film.[174] Monomer **121** was more sensitive and produced a clearer image than did the *m*-phenylene diester **58**.[174]

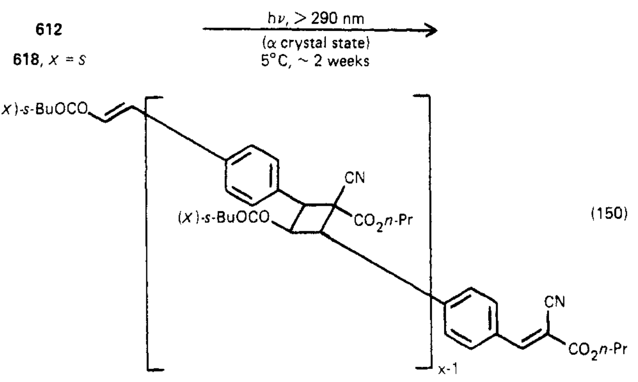
The details of the crystal structure of the (*S*)-*sec*-butyl ethyl diester **134** (α form) have been published,[175] with the same conclusions noted previously. Irradiation times for photochemical polymerization, trimerization, and dimerization of **133** and **134** (Table VI) were 4–6 weeks (>300 nm, ≤5 °C).[106,107]

Irradiating the α crystal form of the (*R*)-*sec*-butyl *n*-propyl diester **613** (90% optically pure) gave cycloadducts **615–617** in which the cyclobutane configuration was (*RRRR*) (eq 149).[176,178] See **147** in Table VIII for previous work on this compound. The α crystal form of the enantiomer **618** (also 90% optically pure) under the same conditions gave the enantiomeric products **620–622** [(*SSSS*) cyclobutane configuration] (eq 150).[178]



612
613, *X* = *R*

614
615, *X* = *R*, x > 3
616, *X* = *R*, x = 3
617, *X* = *R*, x = 2



619
620, X = S, x > 3
621, X = S, x = 3
622, X = S, x = 2

The cyclobutane configurations were reversed in the products that resulted from irradiating the β crystal forms of **613** and **618** (eq 151 and 152).[178] Nearly quantitative optical yields were obtained in the dimers **617**, **622**, **625**, and **628**.[178] The optical yields of the higher molecular weight products were not reported. The crystal structure of the β form of (*R*)-ester **613** was consistent with that expected to give the products **623**–**625**.[178]

$$\mathbf{613} \xrightarrow[(\beta\text{ crystal state})\ 5\,^\circ\text{C},\ \sim 2\text{ weeks}]{h\nu,\ >290\text{ nm}} \mathbf{619} \qquad (151)$$

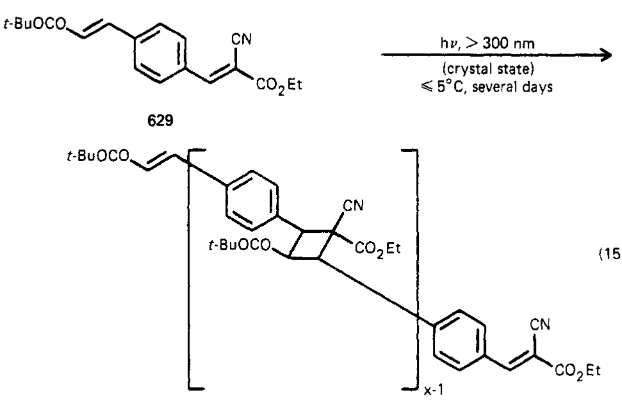
623, X = R, x > 3
624, X = R, x = 3
625, X = R, x = 2

$$\mathbf{618} \xrightarrow[(\beta\text{ crystal state})\ 5\,^\circ\text{C},\ \sim 2\text{ weeks}]{h\nu,\ >290\text{ nm}} \mathbf{614} \qquad (152)$$

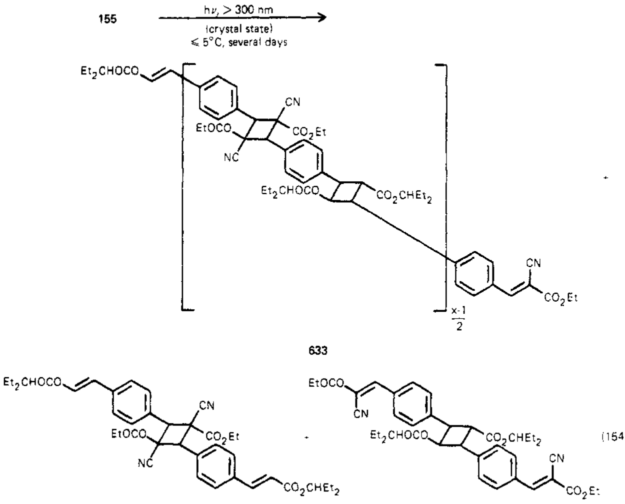
626, X = S, x > 3
627, X = S, x = 3
628, X = S, x = 2

More details were reported on the photocycloaddition (>300 nm, ≤5 °C, several days) of the 3-pentyl methyl diester **151** (Table VIII) to give **152**–**154**.[176,179] The structure of the dimer **154** agreed with that predicted from the crystal structure of the monomer **151** determined by X-ray analysis.[179] In the absence of any additives, specially grown crystals of the symmetric monomer **151** gave asymmetric cycloadducts. The enantiomeric yields depended on the perfection of the crystals and ranged from 0 to ~100% for the dimers **154**.[179] The high enantiomeric yields were interpreted in terms of autoseeding, i.e., the asymmetric influence exercised on crystallization by the first chiral seed, which drives all of the supersaturated solution to crystallize in the same chirality.[179]

Irradiating metastable crystals of the *tert*-butyl ethyl ester **629** that had been crystallized rapidly from the melt gave oligomer **630**, trimer **631**, and dimer **632** (eq 153).[176,179] Slow crystallization of **629** from the melt or from solution gave a different crystal form, which, on irradiation under the same conditions as in eq 153, gave a dimer with structure **140** ($R_\alpha = R_\beta = t$-Bu, $R_\alpha' = R_\beta' =$ Et).[179]



630
631, x = 3
632, x = 2



633

634 80 : **635** 20

In contrast to results reported earlier (Table VIII),[95,96] irradiating the 3-pentyl ethyl diester **155** in the crystal state gave the centrosymmetric dimers **634** and **635** and corresponding higher oligomers **633** (eq 154).[176,179] These products resulted from irradiating the stable centrosymmetric polymorph formed by slow crystallization.[177] The optically active products **156**–**158** were derived from a chiral metastable polymorph, which was obtained on fast crystallization.[177]

Additional details on the crystal-state photooligomerization (>300 nm, ≤5 °C, several days) of the 1:1 mixture of the isopropyl ethyl **144** and 3-pentyl ethyl **155** diesters (Table VIII) were reported.[176,179] Irradiating the solid solution formed from 40:60 to 60:40 mixtures of **144** and **155** gave a nearly random distribution of the dimers **146** and **158** and the two heterocycloadducts **161**.[179] The structure of the mixed crystal was isomorphous to that of the *sec*-butyl ethyl diesters **133** and **134** and was different from that of **144** or **155** alone.[179] Specially melt grown crystals of a 1:1 mixture of **144** and **145** gave the above products, the homooligomers **145**, **156**, and the heterooligomer **159**, all of which were slightly enriched enantiomerically.[179] The low enantiomeric excesses (≤7%), of random chirality, were probably caused by micro- and macrotwinning involving enantiomeric domains and to technical difficulties associated with growth of such crystals from melts containing two components.[179]

Additional experiments were reported on the asymmetric induction of crystallization by chiral additives, and the subsequent oligomerization of the monomers in these crystals by photocycloaddition (>300 nm, 5 °C, ~2 weeks).[177] The monomers **133** and **134** (1:1 mixture), **144** and **155** (1:1 mixture), **147**, **151**, **155**, and **162** in the presence of 3–15% dimer (*R*)-**132** or its enantiomer gave the same optically active oligomers, trimers, and dimers reported previously (Tables VI and VIII).[176,177] In all instances the configuration of the product dimers present in excess was opposite to that of additive (*R*)-**132** or its enantiomer.[177] Similar results were obtained on adding 15% trimer (*R*)-**131** or 8% oligomer (*R*)-**130** or their enantiomers.[177]

For the monomers **151** and **162**, a measurable asymmetric induction occurred when as little as ∼0.05% (*R*)-**132** was added.[177] The minimum amount of (*R*)-**132** required to give maximum induction was ∼1%.[177] Similar results were obtained on adding resolved dimer **158**. Asymmetric induction in the crystallization was also achieved by adding 10% *sec*-butyl *n*-propyl diester dimers **617** or **628**.[177]

Several other derivatives of **142** and mixtures of these derivatives gave cyclobutyl dimers and 1:1 cross adducts when irradiated in the crystal state (>300 nm, ≤5 °C, several days).[177,179] Although not reported, the higher oligomers analogous to these dimers and cross adducts also may have been formed. *n*-Propyl ethyl diester **142** ($R^1 = R^3 = \mathrm{Et}$, $R^2 = \mathrm{H}$) (**636**) gave a dimer analogous to **128**.[177] In the presence of ∼10% of this latter dimer, **636** gave dimer **143** ($R^1 = R^3 = \mathrm{Et}$, $R^2 = \mathrm{H}$, $x = 2$).[177] The full paper reported that the isopropyl ethyl diester **144** alone gave dimers analogous to **127** and **128**[179] (see Table VIII[96]). A 70:30 mixture of (*S*)-*sec*-butyl ethyl diester **134** and **144** gave homodimers **146** and (*S*)-**132** and mixed 1:1 cross adducts analogous to **143** ($x = 2$).[179] A 75:25 mixture of **134** and 3-pentyl methyl diester **151** gave homodimers (*S*)-**132** and **154** and mixed 1:1 cross adducts analogous to **143** ($x = 2$).[179] A (60 or 70):(30 or 40) mixture of 3-pentyl ethyl diester **155** and **134** gave homodimers (*S*)-**132** and **158** in addition to mixed 1:1 cross adducts analogous to **143** ($x = 2$).[179]

2. *Dicyano-p-phenylenediacrylate Esters*

The dicyano diesters had the following relative reactivities toward crystal-state photocycloaddition polymerization: very high, **166**; high, **171**; low, **173**, **175**, **177**, **179**.[170] The dimethyl ester polymer **172** contained a small number of cyclobutane rings, presumably from the cis form of the olefin **171**.[170] Otherwise the polymer was stereoregular.[170] The effect of temperature on the reaction and the continuous changes in the X-ray diffraction diagrams of monomer **166** demonstrated that the polymerization proceeded by a diffusionless crystal-lattice-controlled mechanism.[170]

3. *Bis(α-cyano-β-arylvinyl)benzenes*

Compared to the reactivities of similar compounds, that of monomer **181** toward crystal-state photopolymerization was high.[170]

G. 2,5-Distyrylpyrazine

1. *Crystal State*

Relative to similar monomers, pyrazine **192** was very reactive toward crystal-state photocycloaddition polymerization.[170] Explanations offered for its reactivity and that of dipyridyl monomer **108** crystals were based on stabilization energies of the transient complex.[170] These energies depended on both the electronic structures of the monomers and the intermolecular arrangements in the monomer crystals.[170] A quantitative correlation between photoreactivities and intermolecular plane-to-plane distances in the crystals was proposed.[170]

Excimer fluorescence has been reported for **192** crystals.[170]

The effect of temperature on the reaction and the continuous changes in the X-ray diagrams of **192** demonstrated that the polymerization proceeded by a diffusionless crystal-lattice-controlled mechanism.[170]

V. Cycloadditions Involving Carbon 4 + 4 Addition

B. Bisanthracenes

2. *9-Substituted*

Several bis(anthrylimines) and bis(anthrylbenzimidazoles) **484** polymerized when irradiated (eq 120) (Table XXXIII).[180] The polyimines **638**, **640**, and **642** were converted to the polybenzimidazoles **644**, **646**, and **648**, respectively, by air oxidation.[180] The presumed head-to-tail regiochemistry of the 4 + 4 photocycloaddition was not rigorously established.

Polymers of higher molecular weight were formed from the bis(imines) than from the bis(benzimidazoles) because the former remained in solution whereas the latter precipitated from solution when the DP reached ∼3–5.[180]

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IX. References

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