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Tetramethylene Diradicals in the Photoinduced Cycloaddition and Copolymerization of the Styrene/Acrylonitrile System

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ABSTRACT: The photoinduced cycloaddition and copolymerization reactions of styrene (St) and acrylonitrile (AN) are studied. St is excited with 313-nm light; St* then reacts with either AN or St to form •StAN• or •StSt• diradicals, respectively, which either form the respective dimers or initiate the copolymerization. The •StAN• diradical prefers to initiate, while •StSt• prefers to cyclize. Evidence for these diradicals includes structure of dimers, lack of solvent polarity effect, increased molecular weight of the polymer with time, trapping of the diradical with TEMPO, competitive formation of dimers vs copolymers with changes in feed ratio, and competitive formation of the two dimers with changing feed ratio. Triplet sensitization leads to higher molecular weight polymer.

Introduction

Recently, thermal spontaneous reactions and copolymerizations of donor olefins with acceptor olefins have received increasing interest.[1–6] To correlate these reactions, Hall and Padias[4,5] proposed a unifying mechanism that involves bond formation between the β-carbons of the two olefins, possibly from the collapse of the charge-transfer complex (CT complex):

(1)

where the asterisk represents "+", "–", or "•". The tetramethylene (T) 1,4-diradicals (DR) or zwitterions (ZI) are the key intermediates for both the small-molecule products (e.g., cyclobutanes, butenes) and the polymer products (copolymer and/or homopolymers).

The question arose if such tetramethylene intermediates could also be formed by collapse of exciplexes and excimers and initiate photopolymerization and photocyclization. We have recently reviewed this general topic.[7] Experimentally in previous work, we[8,9] and Raetzsch[10,11] have investigated several photoinduced copolymerization systems, in which charge-transfer interaction occurs in the ground state. Care was taken to excite the CT complex only by selecting incident light at 365 nm:

$$\mathrm{D} + \mathrm{A} \rightarrow \underset{\substack{\text{CT}\\ \text{complex}}}{(\mathrm{D,A})} \xrightarrow{h\nu} \underset{\substack{\text{excited}\\ \text{complex}}}{(\mathrm{D,A})^*} \rightarrow \text{initiating diradicals} \qquad (2)$$

The resulting copolymers were of high molecular weight, possibly because of DR propagation, so the solutions quickly became too viscous to stir even at low conversion. Our evidence was consistent with, but not proof for, tetramethylene diradical intermediates. The systems that gave the best results were generally styrene donors (to get light-absorbing complexes) with 1,2-disubstituted electron-poor olefins that interacted strongly enough to form CT complexes. Although such excitation might lead directly to a T, the process was not very efficient. The CT absorption is low and the 365-nm light is not very energetic; thus very concentrated solutions had to be used.

It is known that the excited complex can be formed alternatively, i.e., through the exitation of the D or A molecule, followed by interaction with the partner. It is usually called "exciplex". Some studies have shown that exciplexes and excited CT complexes are identical chemical species. They have the same spectral character and undergo the same follow-up reaction. In the present work, we describe the styrene (St)/acrylonitrile (AN) system in which no ground-state CT complex exists. We report photoinitiation by irradiating D (St) directly at 313 nm. Its large absorption coefficient results in efficient generation of the excited St. Reaction of St* with AN and St gives an exciplex and an excimer, respectively; the former is comparable to the excited complexes studied earlier.

Results

Spectroscopy. The UV spectra of styrene did not change when the solvent CH_2Cl_2 was replaced by AN, indicating that no charge-transfer interaction occurs in the ground state for the St/AN system.

Figure 1 shows the fluorescence spectra of St and the fluorescence quenching by addition of AN. Although no new fluorescence emission appeared at longer wavelengths, the fluorescence quenching confirmed the formation of the exciplex between the excited St and the ground-state AN. Similar nonfluorescent exciplexes were also reported in the naphthalene/AN[12] and *N*-ethylcarbazole/AN[13] systems.

Copolymerization and Cycloadditions. The St/AN system does not undergo copolymerization at room temperature in the absence of initiator. Under irradiation, however, St can absorb 313-nm light, leading to the photopolymerization. The polymerization also occurs with St alone but is much faster in the presence of AN, indicating the important role of St/AN interaction in the initiation. During the polymerization, cycloadducts are also formed.

Free Radical Character of the Reactions. A trace of 2,2,6,6-tetramethylpiperidinyloxy radical (TEMPO) (2×10^{-3} M), a well-known radical scavenger, completely inhibits the polymerization. In our experimental conditions, the absorbances of St (5 M, in 1,2-dichloroethane) and TEMPO (2×10^{-3} M) at 313 nm were 0.15 and 0.04, respectively. So strong competitive absorption by TEMPO could be ruled out as a reason for the lack of products. Oxygen in the system prolongs the induction period and reduces the rate of copolymerization, while methanol does not affect the polymerization very much.

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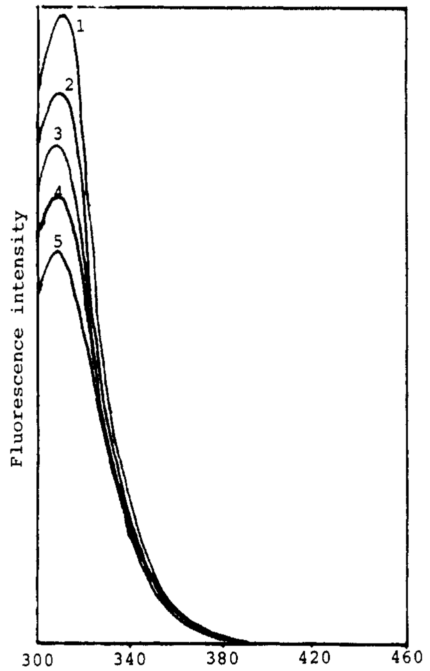


Figure 1. Fluorescence of St and fluorescence quenching by addition of AN in benzene [St] = 10^{-3} M, λ_{ex} = 298 nm). [AN] (M): (1) 0; (2) 2.67 × 10^{-3}; (3) 5.34 × 10^{-3}; (4) 8.01 × 10^{-3}; (5) 1.25 × 10^{-1}.

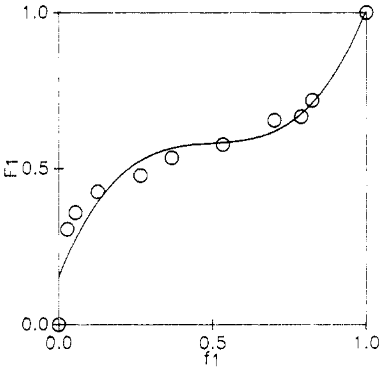


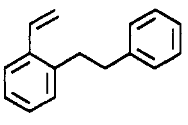
Figure 2. Dependence of the instantaneous copolymer composition on the comonomer feed composition of the St (M_1)/AN (M_2) system.

Accordingly, we can conclude that the polymerization follows a radical mechanism.

Propagation Reactivity Ratios. Figure 2 shows the dependence of the initial copolymer composition on the composition of the feed for the St (M_1)/AN (M_2) system. The copolymerization yields were kept below 10% conversion, and the copolymer compositions were determined by elemental analysis. The reactivity ratios were calculated to be r_1 = 0.44 and r_2 = 0.05, which are in good agreement with the literature values (r_1 = 0.4, r_2 = 0.04).[14] This means that irradiation does not change the propagation process. Hill[15] has studied the copolymer/comonomer composition relationship and the monomer sequence distributions of St/AN system in detail.

Small-Molecule Products. The copolymerization is accompanied by small-molecule formation, which provided information about the initiation mechanism. We analyzed the small-molecule products of the St/AN photoreaction system by gas chromatography, mass spectroscopy, and NMR and compared our results with Kirchner and Riederle's thermal results for St/St,[16] Kauffmann's photo results for St/St,[17] and Schlapkohl's thermal results for St/AN.[18] Two classes of dimers were obtained: St/St adducts (1–5), which are formed from the St/St excimer, and St/AN adducts (6–8), which come from the exciplex of St/AN. A very small amount of trimers was also detected.

The structures of the St/St adducts are in good agreement with Kauffmann's results, so St/St reactions also occur when AN is present.



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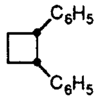

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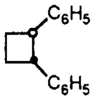

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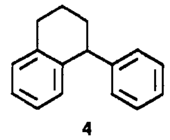

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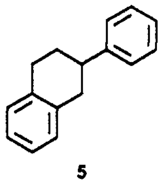

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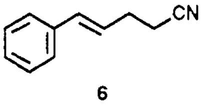
The St/AN adducts have the following structures:



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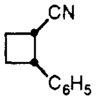

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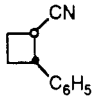

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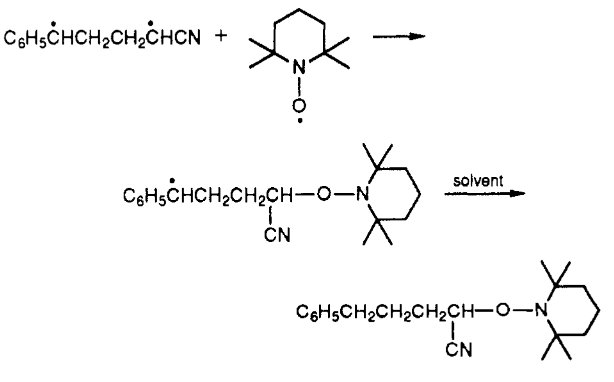
Addition of the cyclobutane adducts to the St/AN photopolymerization system did not increase the rate of copolymerization. Therefore, these cyclobutanes are stable products in the photopolymerization rather than the initiating intermediates.

Trapping the Tetramethylene Intermediates. When TEMPO was added to the St/AN photoreaction system, none of the above cycloadducts could be detected. As concerted reactions should not be affected by radical trapping agents, this result strongly supports the existence of radical intermediates in their formation.

In the TEMPO experiments, we detected a component with molecular weight 314 in the GC/MS spectra in the product mixture (~14% in peak area). It was identified as the coupling product of the St/AN diradical with TEMPO.



(3)

The fragment peaks $C_6H_5CH_2CH_2^+$ (*m/e* 105) and $C_6H_5CH_2CH_2CNCH^+$ (*m/e* 158) support the proposed coupling of TEMPO with the radical at the AN end, which might be attributed to lower steric hindrance at this end. It was also verified that an AN radical can react with TEMPO, because TEMPO inhibits AN homopolymerization.

One might postulate the existence of a St/St diradical intermediate in the formation of the cis and trans St/St cyclobutane products. However, no such diradical was

Table I
Dependence of Polymer Yield and Dimer Yield on Initial Monomer Concentrations[a]

init concn of each monomer		yield of polymer, %	yield of dimer, %
[St], M	[AN], M		
2.2	3.8	65.7	9.4
1.1	1.9	55.1	18.2
0.44	0.76	45.0	25.0
0.22	0.38	25.3	55.0
0.11	0.19	21.8	68.3

[a] Photoreactions were carried out in CH_3CN; time = 110 h.

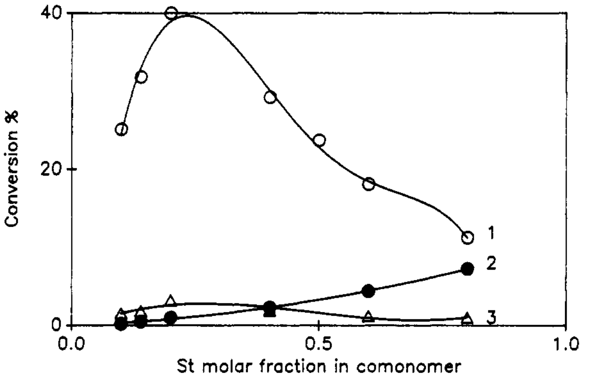


Figure 3. Relationship between the yields of products and St ratio in the comonomer mixture ([St] + [AN] = 5 M, in CH_2ClCH_2Cl, irradiation time = 20 h): (1) copolymer; (2) St/St dimers; (3) St/AN dimers.

trapped by TEMPO, which may be attributed to steric hindrance or a too short lifetime of this diradical.

Effect of Total Monomer Concentration on the Yield of Copolymer and Total Dimers. If 1,4-diradical tetramethylenes are involved in the initiation of polymerization, one would expect a dependence of the ratio of the two competitive reactions, polymerization and cyclization, on the total monomer concentration. At low concentration, the chance of a monomer reacting with the diradical tetramethylene is small, so the diradicals stay in the "cage" and react with each other to form cycloadducts or other small-molecule products. At high concentration, diradicals are trapped by monomers; therefore copolymerization is the main route. This effect is clearly shown in Table I.

Effect of Monomer Feed Ratio on the Yield of the Various Dimers. Figure 3 shows the dependence of the yield of copolymer and dimers on the monomer feed ratio at constant total concentration. Increase of the St mole fraction favors the St/St excimer, while increase of AN ratio favors the St/AN exciplex. At higher St mole fraction, the yield of St/St dimers increases remarkably at the expense of copolymer. St/St diradicals seem to have a shorter lifetime and are more susceptible to cyclization. On the other hand, increase of AN mole fraction rapidly leads to an increase of the yield of copolymer, while the yield of St/AN dimers increases only slightly. So the St/AN diradical is much more reactive in initiating the polymerization than the St/St diradical. The yields of both copolymer and AN/St dimers decrease at low St mole fractions because the whole reaction sequence is dependent upon the light absorption by St.

Effect of Solvent Polarity on Yields of Copolymer and Total Dimers. We first reinvestigated St alone for reference. Figure 4 shows the lack of influence of the polarity of the medium on the photoreaction of St. Both the yields of polymer and dimers are constant.

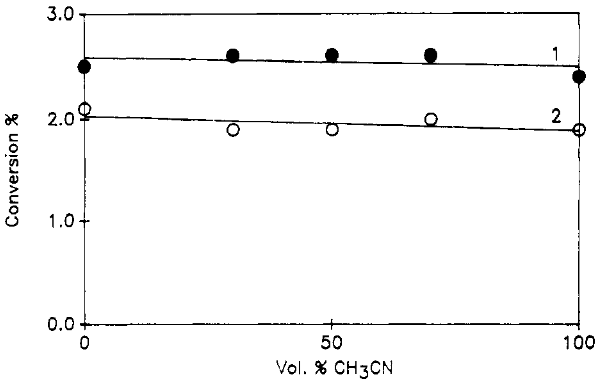


Figure 4. Dependence of the yields of products of polymerization of St on solvent polarity ([St] = 3 M, toluene/acetonitrile solvent, irradiation time = 9 h: (1) copolymer; (2) dimers.

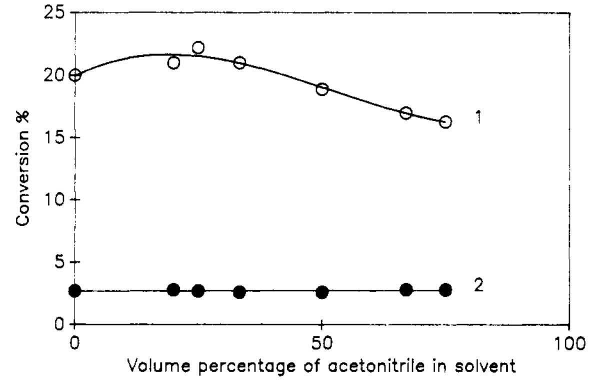


Figure 5. Influence of the solvent polarity on the yields of products of St/AN photoreaction ([St] = 2.2 M, [AN] = 3.8 M, toluene/acetonitrile solvent): (1) copolymer; (2) dimers.

Table II
Photoreaction of St in CH_2ClCH_2Cl[a]

time, h	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
6.5	1.5	1.2×10^5	1.8
18	3.7	1.2×10^5	2.1
24	8.8	1.2×10^5	2.0
49	11.1	1.1×10^5	2.3
73	13.9	1.2×10^5	2.2

[a] [St] = 6 M.

As to the photoreaction of the St/AN system, the rate of polymerization varies slightly with increasing solvent polarity. It increases first, passes through a maximum, and then decreases. The increase of R_p may be attributed to easier formation of exciplex between St and AN in more polar solvents, therefore favoring the St/AN diradical. With further increase of solvent polarity, however, the exciplex may collapse to a tetramethylene intermediate with more zwitterionic character or dissociate into radical ions, so the free radical initiation rate decreases (Figure 5).

Even though in polar solvents the bond formation is somewhat unfavorable, the formed St/AN diradical will exhibit more polar character, leading preferentially to cycloaddition. The overall effect is that the solvent polarity has almost no effect on the yield of cyclodimers. The effect of solvent polarity on thermal cycloadditions has been discussed in a previous paper.[19]

Relationship between Molecular Weight of Copolymer and Conversion. It is known that in diradical initiation and propagation systems, the molecular weight (MW) of polymer will increase with the monomer conversion. This is due to termination by recombination of diradical polymer chains.[9]

We investigated the photohomopolymerization of St first. Table II shows that the MW of PSt does not change with conversion of time. The St/St diradical does not initiate.

Table III
St/AN Photoreaction in $CH_2ClCH_2Cl^a$

time, h	copolymer conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	dimer yield, %
3	2.7	2.2×10^5	2.0	0.4
8	6.4	2.1×10^5	2.4	0.6
15	16.1	2.0×10^5	1.9	1.4
25	20.5	2.3×10^5	2.3	2.0
34	30.6	2.6×10^5	2.0	2.5
42	44.3	1.9×10^5	2.0	3.3

[a] [St] = 5 M; [AN] = 2.93 M.

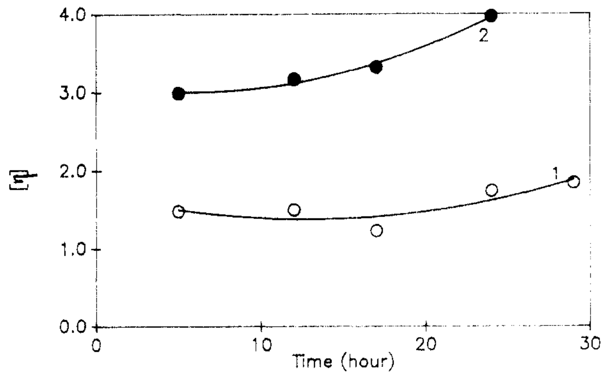


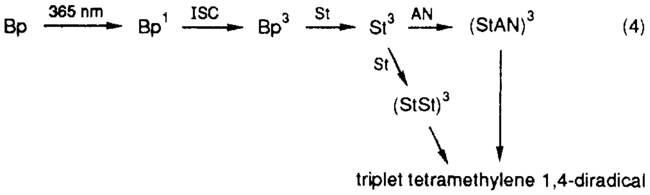
Figure 6. MW–time relationship in St/AN photocopolymerization system ([St] = 0.33 M, [AN] = 7.6 M, in CH_2ClCH_2Cl): (1) without $CuSO_4$ filter; (2) with $CuSO_4$ filter, [benzophenone] = 2×10^{-2} M.

Even though 1,2-diphenylcyclobutanes are formed, neither TEMPO nor monomer can trap it. The initiating radicals are formed mainly by the Mayo mechanism[17] and thus are monoradicals.

Table III shows the relationship of MW with time during the azeotropic copolymerization of St (5 M)/AN (2.93 M). In this case, too, the MW of polymer remains almost unchanged with increasing conversion. The StSt initiation by the Mayo mechanism may still be important in this polymerization, since the St ratio is quite high in the monomer feed.

At high AN ratio, the St/AN diradical would be favored, so we would expect to observe increasing MW with time. This was indeed the case when we carried out the copolymerization with [St] = 0.33 M and [AN] = 7.6 M. The inherent viscosities increase with increasing conversion (Figure 6). These copolymers were insoluble in $CHCl_3$, and no SEC's were run.

Triplet Sensitization. When the copolymerization was carried out at 365 nm in the presence of benzophenone (Bp), the MW increase was more pronounced. In this case, the triplet reaction plays an essential role.



(4)

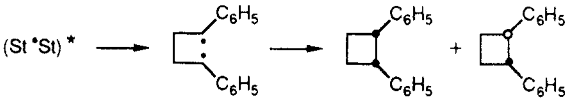
Turro has suggested that a singlet diradical favors "tight" geometries for which the free valences are close together in space, whereas a triplet diradical favors a "loose" geometry for which the free valences are as far apart as possible.[20] The latter has a longer lifetime, so it will be more susceptible to attack by monomer. Therefore, the diradical polymerization character was more pronounced in the presence of Bp, and for this reason perhaps the viscosity is much higher, as shown in Figure 6.

Discussion

In previous papers[8,9] we studied several photoinduced charge-transfer copolymerization systems, in which care was taken to irradiate only the CT complex. This was not very efficient, especially for weak donor/acceptor pairs. St/AN was found to be a suitable system for direct monomer irradiation, because no charge-transfer interaction takes place in the ground state. Only St molecules can absorb light and be excited, producing the initiating species for the polymerization. On the other hand, this system is still complicated because of the St*/St reaction. The excited St is known to form an excimer with another ground-state St molecule, which can produce radical species:

$$\mathrm{St} \xrightarrow{h\nu} \mathrm{St}^* \xrightarrow{\mathrm{D}} \underset{\text{excimer}}{(\mathrm{StSt})^*} \rightarrow \text{initiating radical} \qquad (5)$$

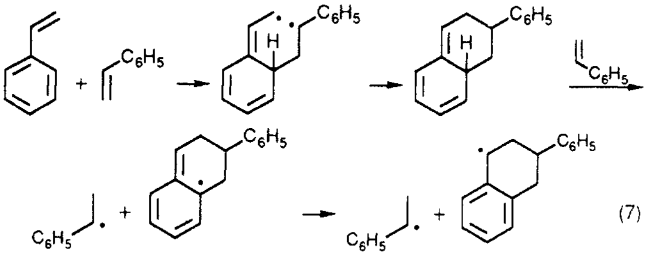
We obtained 1,2-diphenylcyclobutane product in this reaction. One might propose that these cyclobutane adducts were formed by a concerted reaction of two styrenes, but the cis and trans structures support a Flory 1,4-diradical •StSt• intermediate:[21]



(6)

From our investigation of the relationship of MW with time in the St photopolymerization system, we conclude that this diradical cannot initiate. Kopecky[22] studied the thermal decomposition of *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine, which produces the 1,4-diphenyl-1,4-butanediyl diradical. Styrene (60%), *cis*-1,2-diphenylcyclobutane (27%), and *trans*-1,2-diphenylcyclobutane (13%) were formed. This cis or gauche diradical was found to be inefficient in the initiation of St polymerization, but a trans diradical may be more effective.

According to Kauffmann,[17] the initiating monoradicals for the St photopolymerization are thought to originate from the following Mayo reactions.

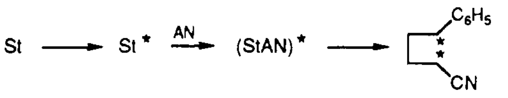


(7)

Dimonie et al.[23] derived a functional relationship between the "instantaneous" degree of polymerization and conversion in normal radical polymerization in which molecular weight (MW) decreases as the monomer is consumed with time. In the photopolymerization of St, the •StSt• diradical cannot be ruled out completely, but the monoradicals from the Mayo reaction dominate. The coupling of monoradical and diradical chains will terminate one end of the diradical propagation chains, thereby reducing the increase of MW with time. The monoradicals reduce the MW like monofunctional compounds in polycondensation reactions.

In the St/AN system, in which the St/AN diradical is an initiation, the monoradicals from St/St reactions are still very important. The increase of MW with time is thus much less remarkable than in a prototypical diradical polymerization system.[5]

In spite of the interference of the St/St reactions, the St/AN diradical can still be detected in our system.



(8)

For the first time, we trapped this tetramethylene intermediate with the radical trapping agent TEMPO. This is direct evidence for the "bond formation" concept. Schlapkohl[18] showed that the Mayo mechanism (Woodward–Hoffmann allowed) is valid for the thermal St/AN reaction, but the photoelectrocyclic [4 + 2] reaction is not allowed, so tetramethylene intermediates become more plausible.

The St/AN diradical can close to cyclobutane, especially in dilute solution, or initiate copolymerization, which is favored in concentrated solution. Initiation of copolymerization and cycloaddition were shown to compete. This supports the existence of a common intermediate, i.e., St/AN diradical tetramethylene, for both of these reaction paths.

No evidence was found for a single-electron-transfer (SET) reaction as the initiation step in the St/AN system. In previous reports on donor/acceptor photoreactions, formation of homodimers of the donor was usually explained by SET, that is, the dissociation of exciplex into anion radicals and cation radicals.[11,24] The latter can add another donor molecule to form a 1,4-cation radical tetramethylene, which closes to cyclodimers or initiates the cationic polymerization. However, this explanation is not available in the St/AN system, in which no StSt cation radical was trapped by methanol and no St cationic polymerization was observed. Moreover, the cyclization reaction of cation radicals is known to be greatly affected by the polarity and basicity of solvents. St cyclodimers, however, were detected in either polar or nonpolar solvents and either basic or nonbasic solvents. The photoreaction of St proves that the cyclodimers of St come from the direct reaction of St/St, and the inhibiting-effect role of the radical scavenger for this reaction indicates the existence of radical intermediates.

Experimental Section

Instrumentation. Electron absorption spectra and fluorescence spectra were recorded with a Perkin-Elmer 983 spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, respectively. NMR spectra were recorded with a Bruker WM-250 nuclear magnetic resonance spectrometer in chloroform-*d*. Chemical analyses were performed by Desert Analytics, Tucson, AZ. GC/MS results were obtained from a Hewlett-Packard GC/MS system. Size-exclusion chromatography was carried out with a Shodex A-804 column calaibrated with polystyrene standards, with chloroform as eluent and a Spectra Physics detector at 254 nm.

Reactants. Acrylonitrile (AN) was purchased from Aldrich and distilled over calcium hydride. Styrene (St) was distilled twice under reduced pressure before use. The solvents were purified by standard procedures.

Procedure. In general, the photoreactions were run in a 15-mL Pyrex tube equipped with a vacuum-line Teflon valve (Chemvac Associates, POR-10). The reaction vessel containing the reaction mixture, usually 10 mL, was placed in a liquid nitrogen bath, degassed under full vacuum (<0.2 mmHg), and then closed off. A 450-W high-pressure mercury lamp served as the light source, and the reactor was located 12 cm from the lamp. The reaction temperature was 35 °C. When the polymerization was carried out with benzophenone as sensitizer, a $CuSO_4$ solution filter was used to cut off the light above 365-nm wavelength[25] (250 g of $CuSO_4{\cdot}5H_2O$/L of H_2O, 1 cm).

After the reaction, the reactants were poured into an excess of methanol/petroleum ether with stirring. The precipitated polymer was filtered off, dried, and weighed. The remaining solution was concentered, and the products were analyzed by GC/MS, NMR, and elemental analysis.

Oligomers of St/AN Photoreaction System. The oligomers were separated into four groups by preparative TLC (1:1:1 hexanes–1,2-dichloroethane–toluene). The first group contains mainly five dimers of styrene. The second and the third groups are the St/AN dimers. The fourth group (very small amount) contains a compound with molecular weight 210, which is a St-$(AN)_2$ trimer.

St/St Dimers. The first group showed mainly five peaks in GC, all with molecular weight 208. Compared with the results from Kauffmann,[17] the structures of the dimers were assigned as follows (the digits in the parentheses show the percentage of the peak area of GC in the total):

2-(2-Phenylethyl)styrene (**1**) (7.2): MS (70 eV) *m/e* (%) 208 (M^+, 10), 117 ($M^+ - C_7H_7$, 100), 91 ($C_7H_7^+$, 23).

cis-1,2-Diphenylcyclobutane (**2**) (44.2): ^1H NMR δ 7.05–6.81 (m, 10 H), 4.01–3.93 (m, 2 H), 2.52–2.40 (m, 4 H); MS (70 eV) *m/e* (%) 208 (M^+, 5), 104 ($M^+ - C_6H_5CH{=}CH_2$, 100), 78 (10).

trans-1,2-Diphenylcyclobutane (**3**) (19.4): ^1H NMR δ 7.32–7.05 (m, 10 H), 3.64–3.50 (m, 2 H), 2.37–2.22 (m, 2 H), 2.20–2.04 (m, 2 H); MS (70 eV) *m/e* (%) 208 (M^+, 3), 104 ($M^+ - C_6H_5CH{=}CH_2$, 100), 78 (10).

1-Phenyl-1,2,3,4-tetrahydronaphthalene (**4**) (8.3): ^1H NMR δ 7.21–6.61 (m, 9 H), 4.03 (m, 1 H), 2.95–2.67 (m, 2 H), 2.22–1.57 (m, 4 H); MS (70 eV) *m/e* (%) 208 (M^+, 100), 180 ($M^+ - CH{=}CH_2$, 90), 165 ($M^+ - C_3H_7$, 40), 130 (M^+ - 78, 80), 104 ($M^+ - CH_2{=}CHC_6H_5$, 25), 91 ($C_7H_7^+$, 40).

2-Phenyl-1,2,3,4-tetrahydronaphthalene (**5**) (5.5): ^1H NMR δ 7.38–6.96 (m, 9 H), 3.20–2.80 (m, 5 H), 2.30–1.90 (m, 2 H); MS (70 eV) *m/e* (%) 208 (M^+, 45), 130 (M^+ - 78, 20), 104 ($M^+ - C_6H_5CH{=}CH_2$, 100), 91 ($C_7H_7^+$, 10), 78 (10).

All the data are completely in agreement with Kauffmann's.[17]

St/AN Dimers. Groups 2 and 3 contain two St/AN dimers each. Group 2 contains **6** and **7**, and group 3 contains **7** and **8**.

1-Phenyl-4-cyanobutane (**6**): ^1H NMR δ 7.50–7.30 (m, 5 H), 5.90–5.70 (m, 1 H), 5.30–5.10 (m, 1 H), 2.90–2.60 (m, 1 H), 2.20–2.10 (m, 2 H); MS (70 eV) *m/e* (%) 157 (M^+, 15), 116 ($M^+ - CH_2CN$, 100), 104 ($M - CH_2{=}CHCN$, 10), 89 (20).

cis-1-Phenyl-2-cyanocyclobutane (**7**): ^1H NMR δ 7.30–7.10 (m, 5 H), 4.00–3.80 (m, 2 H), 2.70–2.20 (m, 4 H); MS (70 eV) *m/e* (%) 157 (M^+, 5), 130 (M^+ - CN, 4), 104 ($M^+ - CH_2{=}CHCN$, 100), 78 ($C_6H_6^+$, 20).

trans-1-Phenyl-2-cyanocyclobutane (**8**): ^1H NMR δ 7.50–7.30 (m, 5 H), 3.60–3.40 (m, 2 H), 2.70–2.20 (m, 4 H); MS (70 eV) *m/e* (%) 157 (M^+, 5), 130 (M^+ - CN, 3), 104 ($M^+ - CH_2{=}CHCN$, 100), 78 ($C_6H_6^+$, 20).

The cis and trans isomers of the cyclobutanes **7** and **8** were assigned based on the chemical shift of the methine ring protons; in analogy to the At/St dimers, the protons at the lowest field were assigned to the cis isomer.

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Photogenerated Tetramethylene Diradicals in Styrene/Fumaronitrile and Related Systems

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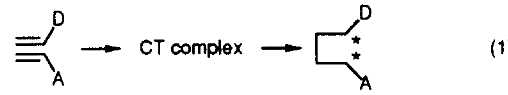
ABSTRACT: The photocopolymerization of styrene/fumaronitrile was studied under irradiation at 365 nm and at 365 + 313 nm. A tetramethylene diradical was produced under either set of conditions, and it initiated the copolymerization or underwent ring closure to form cycloadduct. At 365 + 315 nm the photocycloaddition was favored, while at 365 nm the photocopolymerization was predominant and a molecular weight increase with time was observed. Several related photoinduced "charge-transfer" copolymerizations were also briefly studied.

Introduction

It is known that many electron-donor monomer and electron-acceptor monomer pairs form charge-transfer complexes (CT complexes) and undergo thermal copolymerization spontaneously to produce 1:1 alternating copolymers.[1-3] A bond-formation initiation theory has been postulated to explain the mechanism[3-5]



(1)

where the asterisk represents "+", "−", or "·". The 1,4-diradicals (*,* = ·,·) or zwitterions (*,* = +,−) produced from the collapse of the CT complex, act as the common intermediates for both the small-molecule products (mainly cyclobutanes) and the polymer products.

For the photoinduced charge-transfer copolymerization systems, earlier authors have assumed radical ions as the initiating species.[6-8] Our recent results, however, support the existence of the same tetramethylene intermediates in the photoinduced polymerizations. The tetramethylenes are formed from the excited CT complex and initiate polymerization or cyclize.[9-11]

In previous work, we studied several donor/acceptor copolymerization systems by exclusively irradiating the CT complex.[10-14] This requires strong charge-transfer interaction between the comonomers, so that the UV absorption band of the CT complex can be separated from the adsorption of the components. If the donor/acceptor pair is too weak no, or very few, monomer units are associated into CT complexes, and the initiation is inefficient. If the monomer interaction is too strong, thermal spontaneous reactions may occur, or the CT complex may dissociate to radical ions under irradiation, which are unfavorable for the copolymerization. Thus, only certain selected monomer pairs were suitable for these photoinduced polymerizations by irradiation of the CT absorption band only.

However, the excited complex can also be formed even if there is no charge-transfer interaction in the ground state. Direct excitation of one partner (usually the donor), followed by interaction with the acceptor, produces an exciplex that can also collapse to tetramethylene. We have shown that the styrene/acrylonitrile pair, a weak donor/acceptor pair, undergoes photocopolymerization by such a mechanism.[14]

In this paper, we report the results of photocopolymerization of styrene (St)/fumaronitrile (FN) under irradiation at different wavelengths. The kinetics at 365 nm have already been described in a separate paper.[12] We will discuss the mechanism here, including the role of monomer excitation and CT complex excitation and the diradicals produced in this system. Several related systems will also be briefly examined.

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