Photoinduced Copolymerization and Cycloaddition of 2,3-Dimethyl-1,3-butadiene and Acrylonitrile

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ABSTRACT: The spontaneous photochemical copolymerization of 2,3-dimethyl-1,3-butadiene (DMB) and acrylonitrile was investigated at room temperature. The accompanying cycloaddition was also studied. The free radical copolymerization proceeded slowly at several monomer concentrations under UV irradiation. Higher yields of copolymer were observed in the presence of benzophenone as sensitizer, but the cycloadduct yield was almost unaffected. Maximum copolymer yield was obtained at 1:1 feed ratio. The cycloadducts consisted mostly of cyclobutane adducts as well as the Diels−Alder adduct, and the maximum yield of cycloadduct was obtained at approximately 75 mol % DMB in the feed. A mechanism involving the singlet and triplet excited states of DMB is proposed, in which the initiating species is proposed to be the 6-cyano-2-hexene-1,6-diradical, formed by reaction of the triplet excited *s*-trans DMB with acrylonitrile.

Introduction

We have previously reported on the photoinduced copolymerization of styrene (St) and acrylonitrile (AN).[1] From this investigation we concluded that direct irradiation of St monomer gave the excited St monomer, which then acted as a 1,2-diradical.[2] The excited styrene molecule reacted with St or AN to form St−St and St−AN diradicals, respectively, which could initiate alternating copolymerization or could cyclize. The structure of the found cycloadducts supported this reaction mechanism. Similar results were obtained for the photoinduced copolymerization of St and fumaronitrile.[3] Direct photochemical initiation of free radical polymerization by excitation of the unsaturated monomers and of charge-transfer complexes has been described in a review.[4]

In this work we describe the investigation of another direct photochemical copolymerization and cycloaddition, namely the reaction of 2,3-dimethylbutadiene with acrylonitrile. We will compare these results with the previously described spontaneous copolymerization of these two olefins in the dark.[5]

Results

UV Spectroscopy. The ultraviolet absorption spectrum of DMB was measured. The λ_{max} for DMB was 240 nm, in fair agreement with literature data (λ_{max} 226 nm).[6] The λ_{max} did not change when DMB was mixed with either acrylonitrile, 1,2-dichloroethane, or acetonitrile. No evidence was found for a ground-state charge-transfer complex between DMB and AN, and the solutions were colorless.

Photoinduced Copolymerizations. Two light sources were used for excitation of DMB, namely a xenon lamp and a medium-pressure mercury lamp. Both emit in the region of 240 nm, but the mercury lamp has much greater emitting power at longer wavelengths.

The photoinduced polymerizations of DMB and AN were carried out with either light source in 1,2-dichloroethane as solvent. The polymerization tubes were double-walled quartz and kept at a constant temperature of 20 °C. At this temperature no reaction occurs upon mixing DMB and AN in the dark. At the end of the polymerization, the homogeneous polymerization mixture is added dropwise to methanol, and the precipitated fraction is high molecular weight copolymer. As shown in Table 1, the polymerizations proceeded slowly at different concentrations under UV irradiation. The polymerization yields were independent of the light source but increased with increasing monomer concentration and longer reaction times. At higher concentration and longer reaction times, cross-linking of the copolymer occurred, as witnessed by precipitation of the polymer during the reaction run.

Table 1. Copolymer Yield of DMB and AN in 1,2-Dichloroethane at 20 °C Using Different Light Sources

monomer concentration (mol/L)	irradiation time (h)	copolymer yield (%)	
		using Xe lamp	using Hg lamp
3.0	8	6.2	7.1
	12	6.9	8.2
	24	7.6	9.0
4.2	8	7.3	8.9
	12	10.3	13.0
	24	16.8	20.1
5.4	8	10.7	11.6
	12	18.4	18.3
	24	cross-linked	cross-linked

The free radical character of the photoinduced copolymerization of DMB and AN was verified by the addition of a free radical inhibitor to the mixture during irradiation. Addition of the stable free radical 2,2,6,6-tetramethylpiperidinyloxy (Tempo) greatly retarded the copolymerization.

The reaction of DMB and AN was performed in several solvents with different dielectric constants (polymerization conditions: 3.0 mol/L each, 24 h irradiation with a Xe lamp). Benzene ($\epsilon = 2.2$) as solvent gave a yield of 12.3% copolymer (inherent viscosity 1.07 dL/g); 1,2-dichloroethane ($\epsilon = 10.6$) gave 7.9% copolymer (η_{inh} 1.25 dL/g); and propionitrile ($\epsilon \sim 30$) gave 10.7% yield copolymer (η_{inh} 1.28 dL/g). The inhibition by TEMPO and the lack of a solvent polarity effect point toward

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Table 2. Effect of Irradiation Time and Initial Concentration on Copolymer and Cycloadduct Yield from an Equimolar Mixture of DMB and AN in 1,2-Dichloroethane at 20 °C

monomer concentration (mol/L each)	time (h)	copolymer yield[c] (%)	η_{inh}[d] (dL/g)	small molecule yield[e] (%)
3.0[a]	4	2.7	1.10	5.1
	8	6.5		9.0
	12	7.1	1.21	11.0
	24	7.9	1.26	11.2
	32	9.3		11.3
	36	11.0	1.33	11.3
4.1[b]	4	3.1	1.09	
	8	6.6	1.12	
	12	8.0	1.14	
	24	8.4	1.19	
	32	10.1	1.20	
	36	11.7	1.20	

[a] Xe lamp. [b] Hg lamp. [c] The wt % of high molecular weight product precipitated in methanol. [d] Measured in chloroform at 30 °C; concentration 50 mg in 10 mL. [e] The wt % of nonvolatile ether-soluble fraction.

the free radical character of the copolymerization and exclude electron-transfer initiation.

The copolymerization parameters of DMB and AN are reported in the literature as $r_1 = 0.03$ and $r_2 = 0.09$.[7] The copolymer obtained from the photoinduced copolymerization was analyzed and contained 50.7% DMB and 49.3% AN, in agreement with the reported copolymerization parameters. The NMR spectrum confirms the nearly perfect alternating character of the obtained copolymer and also indicates that the copolymer is almost exclusively formed by 1,4-addition of the diene, as also found for the thermal spontaneous copolymerization.[5] No peaks for terminal vinyl groups could be detected in the NMR spectrum.

Effect of Irradiation Time. Equimolar solutions of DMB and AN at 3.0 and 4.1 mol/L each were irradiated for extended periods of time at 20 °C. As shown in Table 2, the copolymer yields increase slowly as a function of time, reaching about 10 wt % after 36 h. More concentrated solutions result in somewhat higher yields, but the polymer becomes insoluble, resulting in heterogeneous reaction mixtures. The inherent viscosity of the formed copolymers is approximately constant as a function of time.

The methanol-soluble fraction from the 3 mol/L solutions was analyzed. The small molecules can be separated from the oligomers by precipitation of the latter in ether. The term “small molecules” refers to the ether-soluble fraction after removal of the solvent and unreacted monomers under vacuum and consists of a mixture of cycloadducts (see below). The yield of small molecules remains constant after 12 h, reaching a maximum of about 11 wt %.

Effect of Feed Ratio. The copolymerizations were run at different feed ratios at different starting monomer concentrations. The copolymer yield reaches its highest value around equimolar feed ratio, as shown in Table 3 for several concentrations. The inherent viscosity of the resulting copolymer is somewhat higher for monomer feeds rich in AN.

The yields of small molecules (methanol-soluble, ether-soluble fractions) are also included in Table 3. These yields are clearly higher for the monomer feeds rich in DMB.

Table 3. Effect of the Feed Ratio on the Copolymer and Small Molecules Yields (1,2-Dichloroethane as Solvent; Temperature 20 °C)

total monomer concn (mol/L)	benzophenone added	time (h)	molar feed ratio DMB/AN	copolymer yield[a] (%)	η_{inh}[b] (dL/g)	small molecule yield[c] (%)
8.2	no	24	20/80	6.1	1.27	
			40/60	7.7	1.23	
			50/50	8.4	1.16	
			60/40	7.4	1.08	
			80/20	6.7	0.93	
7.2	no	24	33/67	6.0	1.28	2.2
			40/60	11.3	1.23	5.0
			50/50	10.6	1.16	
			59/41	9.3	1.09	9.2
			78/22	4.5	0.93	10.0
6.4	no	36	0/100	0		0
			20/80	6.5		2
			40/60	10.1		4.8
			50/50	9.8		6.8
			60/40	9.0		9.7
			74/26	5.8		10.9
			80/20	4.2		10
			90/10	1.8		8.4
			100/0	0		3.4
5.4	yes[d]	24	20/80	20	1.30	1.0
			35/65	41	1.31	5.8
			50/50	43	1.28	
			65/35	46	1.24	6.4
			80/20	28	1.08	10.2

[a] Methanol-insoluble fraction. [b] Measured in chloroform at 30 °C; concentration 50 mg in 10 mL. [c] Nonvolatile ether-soluble fraction. [d] 2 mol % vs total monomer.

Table 4. Effect of Photosensitizer Benzophenone on the Photoinduced Reaction of DMB and AN, Equimolar Monomer Feed, Time 24 h in 1,2-Dichloroethane at 20 °C

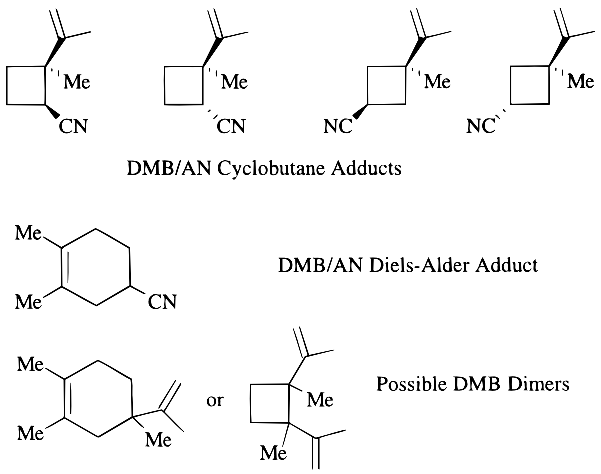
benzophenone (mol % vs total monomer concn)	monomer concn (mol/L each)	copolymer yield[a] (%)	η_{inh}[b] (dL/g)	smal molecule yield[c] (%)
0	2.0	5.0	1.06	7.2
0	2.9	7.4	1.22	5.8
0	4.2	21.3	1.31	3.0
0	5.3	cross-linked		
2.0	2.2	35.0	1.07	7.7
2.0	3.1	41.2	1.30	5.9
2.0	4.0	63.4	1.33	3.2
2.0	5.1	cross-linked		
0.5	2.7	33.0		7.1
1.1	2.7	36.6		6.8
1.5	2.7	40.1		6.6
2.0	2.7	42.7		6.2
2.6	2.7	49.0		5.7
3.0	2.7	52.0		5.1
3.5	2.7	59.4		4.3

[a] Methanol-insoluble fraction. [b] Measured in chloroform at 30 °C; concentration 50 mg in 10 mL. [c] Nonvolatile ether-soluble fraction.

Effect of Photosensitizer. 2,3-Dimethyl-1,3-butadiene is a weak chromophore, which may explain the low yields obtained, even after rather long irradiation times. The effect of added benzophenone (BPh) as sensitizer on the reaction of DMB and AN is summarized in Table 4. The experiments were run on equimolar monomer mixtures at several concentrations in the presence and in the absence of BPh. The yields of copolymer and small molecules were determined as described above.

Addition of BPh greatly increases the yield of copolymer, while the small molecule yield is not affected. A series of experiments run at constant monomer concen-

Chart 1



tration (2.7 mol/L each in 1,2-dichloroethane) shows the effect of increasing sensitizer concentration. The copolymer yield steadily increases with sensitizer concentration, while the yield of small molecules drops slightly. The latter could be due to depletion of the reactants by the dominant copolymerization, and the yield of small molecules can be considered constant and insensitive to the sensitizer concentration.

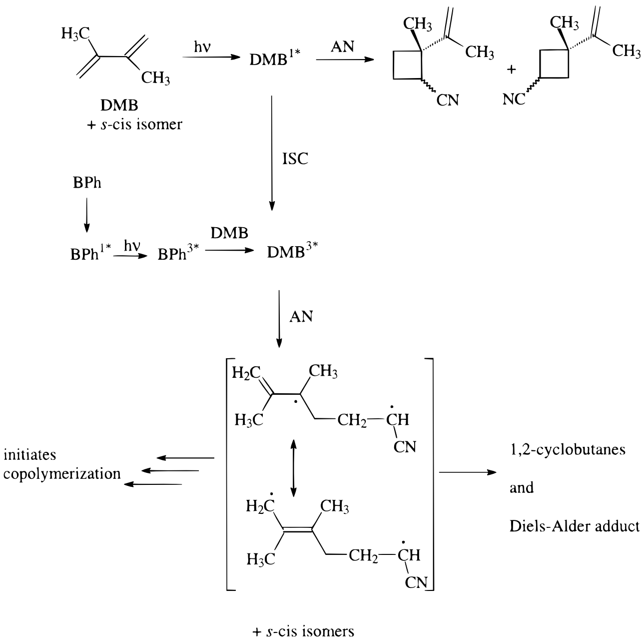
The effect of changing monomer feed ratio on reactions in the presence of benzophenone are also included in Table 3. The presence of BPh results in an enhancement of the copolymer yield, but no noticeable effect on the yield of small molecules is observed. The maximum yields for copolymer are still observed close to a 50/50 monomer feed ratio.

Identification of the Small Molecules. As mentioned, the methanol-soluble fraction is composed of oligomeric material and a mixture of cycloadducts. The cycloadducts are separated from the oligomers by precipitation of the latter in ether. The ether-soluble fraction is submitted to GC-MS analysis and the cycloadducts are identified by their mass spectra. The cycloadducts were adducts of DMB and AN or DMB dimers. The structures are shown in Chart 1 and include DMB/AN cyclobutane and Diels–Alder adducts, along with DMB dimers.

A typical GC spectrum from the GC/MS analysis contains peaks at 4.76, 4.92, 4.95 and 5.01 min retention time, which correspond to the four possible DMB/AN cyclobutane adducts, namely 1,2-cis- and -trans- and 1,3-cis- and -trans-substituted cyclobutanes. A large peak at 5.78 min corresponds to the Diels–Alder DMB/AN adduct, while the smaller peaks around 5.4 min correspond to DMB dimers. The four cyclobutane peaks add up to 60% of the total in most runs, while the DMB/AN Diels–Alder adduct is about 25–30% of the total small molecules. All four cyclobutane isomers showed similar decomposition patterns: the loss of HCN and of propene from the molecular ion led to a base peak $M = 67$ in all cases, which corresponds to a methylcyclobutene cation. The Diels–Alder adduct was identified by comparison with a spectrum of an authentic sample.[5] The DMB dimers are only minor contributors, usually about 5% total, and their structure could not be identified from the MS spectra.

As mentioned above, the total yield of small molecules increases with reaction time, but levels off after about 12 h (Table 2). With varying feed ratios the yield of the small molecules is higher in excess DMB, the maximum yield is obtained at about 75/25 DMB/AN molar feed ratio (Table 3). This may be due to the tendency of DMB to dimerize. The yield of small molecules however is insensitive to the presence of photosensitizer (Tables 3 and 4).

Scheme 1



Discussion

No thermal reaction of DMB with AN is observed at room temperature. However, under photochemical irradiation, both cycloaddition and copolymerization do occur. These must be due to excitation of DMB. We note that the yield of the copolymer goes through a maximum around a 1:1 feed ratio, while the cycloadduct yield is greatest at about 75:25 DMB/AN feed ratio.

As far as the mechanism is concerned, we offer the simple interpretation depicted in Scheme 1. The UV light from either lamp is capable of exciting both the predominant *s*-trans and the *s*-cis forms of the diene.[8] According to the Woodward–Hoffmann rules, a concerted $\pi^2s + \pi^2s$ cycloaddition involving the excited singlet states is photochemically allowed. Because DMB^{1*} is highly energetic and indiscriminate, and because no intermediates requiring resonance stabilization are involved in a concerted reaction, both 1,2- and 1,3-isomers of the cyclobutane adducts, each as cis–trans mixtures, are formed. This is evidence that both *s*-trans and *s*-cis DMB were excited. In this interpretation the cyclobutane adducts are generated mainly from the singlet excited state of DMB.

The singlet excited DMB*'s can also undergo intersystem crossing (ISC) to form their triplets, which will act as either cis or trans diradicals. These diradicals can add to AN to form extended diradicals in several conformations. They prefer to add AN rather than DMB because the polarity difference favors cross-addition.

When benzophenone is added, it preferentially absorbs the light. Its excitation is immediately followed by facile ISC to BPh^{3*}, which then transfers its triplet energy to both *s*-cis and *s*-trans DMB. This represents an alternate route to DMB^{3*} by lower energy sensitizers as reported earlier by Hammond and Herkstroeter.[9b]

Our experimental data show that benzophenone BPh greatly accelerates copolymerization, while leaving cycloaddition yields almost unaffected. We propose that the excited triplet BPh^{3*} excites both *s*-trans and *s*-cis DMB to form the corresponding π-allyl diradicals.[9] After addition of AN, these can initiate the copolymerization. To a minor extent they can also close to cyclobutanes or, in the *s*-cis case, to the cyclohexene. Photochemical formation of this Diels−Alder adduct, 1,2-dimethyl-4-cyanocyclohexene, is not concerted, according to the Woodward−Hoffmann rules, so the *cis*-2-hexene-1,6-diradical is proposed as the intermediate in its formation.

We also noted that the copolymer maximum yield occurs at a 1:1 feed ratio, while the cycloadduct maximum yield occurs at higher DMB concentration. We propose that the copolymer maximum yield is determined by the propagation, which is greatest at 1:1 feed ratio, while the cycloadduct yield is more dependent on the excitation of the DMB molecules and is therefore greater at greater DMB concentrations. The cycloadduct yield decreases at DMB feeds greater than 75% because, as both DMB^{1*} and DMB^{3*} preferentially react with AN, as shown by the fact that DMB/AN cycloadducts far outnumber DMB dimers. We can constrast our results with the data obtained by Hammond and co-workers in their investigation of the photosensitized cycloadditions of 1,3-butadiene.[9] They obtained diene cyclodimers only from the triplet state, while in our work most of the cyclobutane adducts come from reaction of the singlet excited state. We propose that the polarity difference between the reactants allows the cross-cycloaddition with AN to proceed from the singlet excited state.

It may also be of interest to contrast these photochemical results for DMB and AN with those of their thermal reaction, without any additives[6] or in the presence of the Lewis acid $ZnCl_2$.[10] The thermal reactions lead to both cycloadduct and copolymer by parallel competitive second-order reactions. The photochemical results, in contrast, involve competitive reactions of AN and DMB with excited DMB. Again AN is more effective in this regard than DMB, as evidenced by the relative yields of cycloadducts. Accordingly, DMB, DMB^{1*}, and DMB^{3*} should all be regarded as electron-rich, nucleophilic species.

Experimental Section

Methods and Instrumentation. Elemental analyses were obtained from Desert Analytics, Tucson, AZ. The inherent viscosities were measured at 30 °C in chloroform in an Ostwald viscometer. GC/MS analyses were obtained using a Hewlett-Packard GC/MS system (electron impact). NMR spectra were recorded on a Bruker AM-250 at 250 MHz in deuterated chloroform using tetramethylsilane as standard. The Xenon lamp was a PEK xenon short arc lamp X-75 at 75 W, average luminance 80 000 cdla/cm^2. The mercury lamp was a Conrad-Hanovia immersion lamp, medium-pressure quartz mercury-vapor lamp, 450 W, 27 W in the 220−280 nm region.

Reactants. Acrylonitrile (AN) and 2,3-dimethyl-1,3-butadiene (DMB), purchased from Aldrich, were purified by distillation over calcium hydride. Benzophenone (Aldrich) was used without any further purification. 1,2-Dichloroethane was distilled from calcium hydride.

Polymerization Procedure. The comonomers are mixed with 1,2-dichloroethane and the mixture is degassed by two freeze−thaw cycles. The double wall quartz polymerization tube is exposed to the UV light and kept at a constant temperature. At the end of the polymerization the mixture is precipitated in methanol. The precipitate is filtered off, after centrifugation if necessary, dried overnight under vacuum, and weighed. The copolymer NMR spectrum corresponds to the data reported in an earlier paper.[5] The methanol solution is concentrated on a rotary evaporator and dried. The residue is dried overnight under vacuum at room temperature. The residue is dissolved in chloroform and precipitated in ether. The precipitate consists of oligomers. The solvent is evaporated and the residue is submitted to GC/MS analysis.

GC/MS Data. The temperature profile of the analysis is as follows: 1 min at 70 °C, increase to 300 °C at a rate of 20 °C/min, and 5 min at 300 °C. The four relatively equal peaks at 4.7−5.0 min correspond to the four DMB/AN cyclobutane isomers, the smaller peaks at 5.4 min are DMB dimers and the large peak at 5.8 min is the Diels−Alder adduct of DMB and AN.

Typical MS for DMB/AN Cyclobutane Adducts. MS: *m/e* 135 (M^+, <5%), 120 (M − Me, 10%), 106 (M − CH_2CH_2, 20%), 93 (M − Me − HCN, 20%), 82 (M − AN, 50%), 67 (base peak, $C_5H_7^+$), 54, 39.

DMB Dimer. MS *m/e* 164 (M^+, 20%), 149, 135, 121 (60%), 107 (50%), 91 (25%), 82 (65%), 67 (base peak), 53, 41, 28.

DMB/AN Diels−Alder Adduct 4-Cyano-1,2-dimethylcyclohexene. NMR ($CDCl_3$): 2.75 (m, 1H), 2.24 (br s, 2H), 2.17−1.75 (m, 4H), 1.62 (s, 6H) ppm. MS: *m/e* 135 (M^+, 35%), 120 (M − Me, 30%), 93 (M − Me − HCN, 60%), 82 (55%), 67 (base peak, $C_5H_7^+$), 53, 39 (85%).

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References and Notes

(1) Li, T.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1990**, *23*, 3899.

(2) Unett, D. J.; Caldwell, R. A. *Res. Chem Int.* **1995**, *21*, 665.

(3) Li, T.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1990**, *23*, 3904.

(4) Li, T.; Lee, C.; Hall, H. K., Jr. *Adv. Polym. Sci.* **1990**, *97*, 1.

(5) Li, Y.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1993**, *58*, 7049.

(6) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; J. Wiley & Sons: New York, 1981; p 313.

(7) Koningsberger, C.; Salomon, G. *J. Polym. Sci.* **1946**, *1*, 201, 353.

(8) Ruecker, C.; Lang, D.; Friege, H.; Sustmann, R. *Chem. Ber.* **1980**, *113*, 1663.

(9) (a) Liu, R. S. H.; Turro, N. J. Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 3406. (b) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.

(10) Mikhael, M.G.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1994**, *27*, 7499.

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