3904 *Macromolecules* **1990**, *23*, 3904-3909

(9) Li, T.; Luo, B.; Chu, G.; Hall, H. K., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1735.
(10) Raetzsch, M.; Chomiakov, K. *Acta Polym.* **1980**, *30*, 577.
(11) Raetzsch, M. *Prog. Polym. Sci.* **1987**, *13*, 277.
(12) Bowman, M.; Terence, R. *J. Am. Chem. Soc.* **1974**, *96*, 692.
(13) Tazuke, S. *J. Phys. Chem.* **1970**, *74*, 2390.
(14) Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley and Sons: New York, 1981; Chapter 6.
(15) Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Macromolecules* **1982**, *15*, 960.
(16) Kirchner, K.; Riederle, K. *Angew. Makromol. Chem.* **1983**, *111*, 1.
(17) Kauffmann, H. F. *Makromol. Chem.* **1979**, *180*, 2649.
(18) Kirchner, K.; Schlapkohl, H. *Makromol. Chem.* **1976**, *177*, 2031.
(19) Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1987**, *52*, 4536.
(20) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978; Chapter 11.
(21) Flory, P. J. *J. Am. Chem. Soc.* **1937**, *59*, 241.
(22) Kopecky, K. R.; Evani, S. *Can. J. Chem.* **1969**, *47*, 4041.
(23) Dimonie, M.; Oprescu, C. R.; Hubca, Gh. *Rev. Roum. Chim.* **1976**, *21*, 763.
(24) Yamaguchi, K.; Oh, S.-C.; Shirota, Y. *Chem. Lett.* **1986**, 1445.
(25) Murov, S. L. *Handbook of Photochemistry*: Marcel Dekker, Inc.: New York, 1973; p 90.

Registry No. **1**, 72197-20-7; **2**, 7694-30-6; **3**, 20071-09-4; **4**, 3018-20-0; **5**, 29422-13-7; **6**, 30154-21-3; **7**, 128023-45-0; **8**, 128023-46-1; St, 100-42-5; AN, 107-13-1.

Photogenerated Tetramethylene Diradicals in Styrene/Fumaronitrile and Related Systems

Tong Li,[*,†] **Anne Buyle Padias, and H. K. Hall, Jr.**[*]

C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received October 4, 1989; Revised Manuscript Received February 14, 1990

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.

[†] Visiting scholar from Fudan University, Shanghai, People's Republic of China.

0024-9297/90/2223-3904$02.50/0

Results

UV-vis Spectra. Figure 1 shows the electron-absorption spectra of the St/FN system. FN has no absorption at 365 nm and St has only very little. When they are mixed together, however, the spectrum shows a broadening toward longer wavelengths, leading to a notable absorption at 365 nm. The new absorption is attributed to the CT complex.

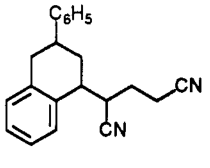
Thus, when we irradiate the system with 365-nm light (with a $CuSO_4$ solution filter), the CT complex excitation should play a major role in the photoreaction. If, on the other hand, the system is irradiated with (365 + 313)-nm light (without a $CuSO_4$ solution filter), both CT complex excitation and monomer excitation could produce intermediates for further reactions.

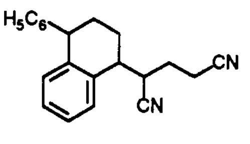
Photocopolymerizations and Cycloadditions. At room temperature, the St/FN system does not undergo spontaneous copolymerization in the dark. Under irradiation with (313 + 365)-nm light, the photoreaction takes place, and copolymer and cycloadduct are formed.

A trace of TEMPO (2,2,6,6-tetramethylpiperidinyloxy radical (2×10^{-3} M)), a well-known radical scavenger, completely inhibits the polymerization. The presence of O_2 in the system prolongs the induction period and reduces the polymerization rate. These results support the radical mechanism of this copolymerization. We determined the reactivity ratio of the St (M_1)/FN (M_2) system at conversions below 10%, and the copolymer compositions were calculated from elemental analysis data. The values $r_1 = 0.2 \pm 0.02$, $r_2 = 0$ are the same as the literature values ($r_1 = 0.19$, $r_2 = 0$[15]), which means that the obtained copolymer is not an exact alternating copolymer. The structure of St/FN copolymer has been thoroughly studied. This copolymerization does not produce copolymers containing more than 40 mol % FN. The presumed structure FN·St·St·FN·St·St·FN·St·FN·St·St·FN·St·FN·St·St,[16] in which the sequence FN·St·St alternates with FN·St, would reduce the steric and polar interactions.

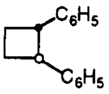
In our case, the copolymerization is accompanied by the formation of olgiomers. The $(St)_2FN$ trimers and $(St)_2$ dimers are the main products. Small amounts of St/FN dimers and $St(FN)_2$ trimers are also observed.

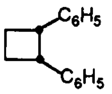
For the $(St)_2FN$ trimers, the following structures were proposed, based on mass spectral data only (see Experimental Section):

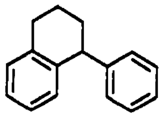




The structures of $(St)_2$ dimers are







At 365 nm or 313 + 365 nm, the structures of the cycloadducts were almost identical as derived from NMR, GC/MS, and HPLC data. If TEMPO was added to the reaction system, none of the above cycloadducts were obtained. Therefore, they must be formed through radical intermediates, and a concerted reaction is unlikely.

Photoreactions at Different Wavelengths. Figure 2 shows the time-conversion plots of the St/FN photocopolymerization system in the presence of and without a $CuSO_4$ filter. As shown in Table I, without a $CuSO_4$ filter (both 313 and 365 nm) the copolymer yield was lower, but more cycloadduct was obtained, resulting in an overall higher yield than when the mixture was irradiated with only 365-nm light. This indicates that 313-nm light favors cycloadduct formation.

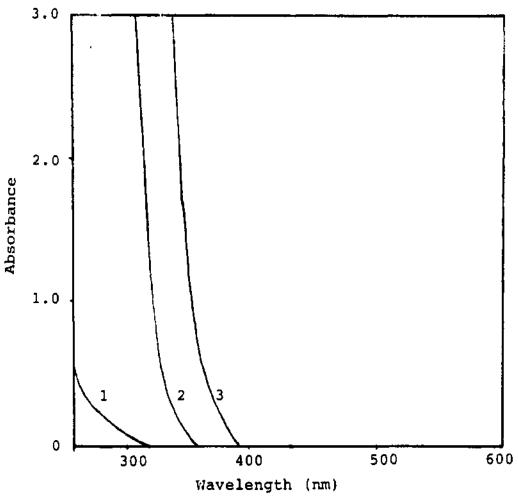


Figure 1. UV-vis spectra of the St/FN system (in CH_2Cl_2): (1) [FN] = 0.3 M; (2) [St] = 3 M; (3) [St] = 3 M, [FN] = 0.3 M.

Figure 3 shows the relationship between the copolymer/cycloadduct ratio and the monomer concentration. This ratio increases with the monomer concentration as was also found in the previous investigation.[11] This implies the existence of a common intermediate for the copolymer and the cycloadduct formation. Figure 3 also shows that the copolymer/cycloadduct ratio was much higher when the photoreaction was carried out with a $CuSO_4$ filter (365 nm only). This means copolymerization was favored at this wavelength.

Effect of Monomer Feed. The results of the photocopolymerization and photocyclization at different monomer feeds are shown in Tables II and III. When [FN] > [St], copolymer yield > cycloadduct yield, and when [St] > [FN], cycloadduct yield > copolymer yield.

Relationship between Molecular Weight and Polymerization Time. The molecular weight of the copolymer shows a different relationship with time at 365 nm and at 313 + 365 nm (Figure 4). When the monomer feed is 1:1, the polymer MW does not change with time at 313 + 365 nm, while it increases with time at 365 nm and is higher than at 313 + 365 nm.

Figure 5 shows the dependence of molecular weight on time at different monomer feeds at 313 + 365 nm. When [FN] > [St], MW increases with time, and if [St] > [FN], MW decreases with time. In the case of [St] = [FN], MW is almost independent of the monomer conversion.

Effect of Solvent Polarity. Table IV shows the influence of solvent polarity on the copolymer yield and cycloadduct yield. With increasing polarity, the yields increase at first, pass through a maximum, and then decrease. The copolymer yield is much more sensitive to the medium polarity than the cycloadduct yield.

With further increase of solvent polarity, the dissociation of the exciplex into solvated radical ions increases. These radical ions do not initiate radical polymerization, so the polymer yield decreases. FN is a less polar monomer than AN, so the decrease of R_p in the St/FN system appears at higher solvent polarity than for the St/AN system. The effect of solvent polarity on the polymerization of monomers with different polarity has been discussed before.[17]

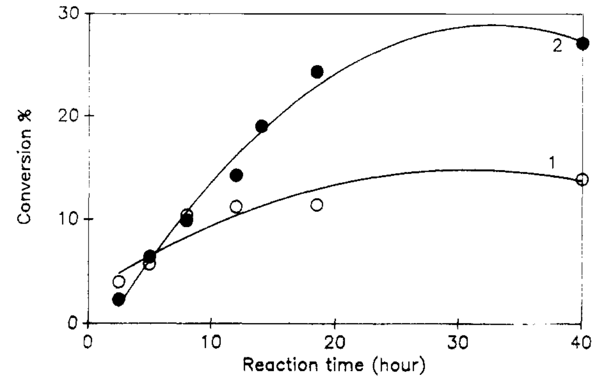


Figure 2. Conversion–time plots of the St/FN photopolymerization system ([St] = [FN] = 0.8 M, in benzene): (1) without $CuSO_4$ filter; (2) with $CuSO_4$ filter.

Photoreactions of St with Other Acceptor Olefins. Table V shows the photoreaction of St with different acceptor olefins. As the electron-accepting ability of the olefins increases, both the copolymer yield and the oligomer yield increase, and the copolymer starts to show an alternating tendency. With strong electron acceptors the copolymer yield and cycloadduct yield decrease. This is very much like the effect of solvent polarity.

Photoreactions of FN with Other Donor Olefins. FN photocopolymerizes with other donor monomers such as α-methylstyrene, 2-vinylnaphthalene (2-VN), and *p-tert*-butylstyrene. Among these, Shirota has already reported the photoinduced copolymerization of the 2-VN/FN system and proposed radical ions as the initiating species.[8] We reinvestigated this system, and in our view, the results support a diradical mechanism.

Shirota observed the cycloaddition products as well as copolymer in the 2-VN/FN system. Our experiments are in agreement with Shirota's observations. However, as shown in Table VI, we also observed an increase of copolymer yield and decrease of cycloadduct yield with increasing monomer concentration. We propose that these facts are indications for a diradical mechanism.

We also observed an increase of the molecular weight (MW) with conversion (Figure 6). This again is evidence for a diradical polymerization.[5] In the polymerization of 2-VN, initiated by AIBN, the MW decreases with increasing monomer conversion. Dimonie et al.[18] derived the relationship between the "instantaneous" degree of polymerization and conversion in normal radical polymerization and showed that the MW decreases as the monomer is consumed with time.

When the copolymerization is carried out in the presence of benzophenone (Bp), the MW of the polymer increases. In this case, the triplet reaction plays an essential role:

$$Bp \xrightarrow{h\nu} Bp^1 \xrightarrow{ISC} Bp^3 \xrightarrow{2\text{-VN}} (2\text{-VN})^* \xrightarrow{FN} (2VN\text{-}FN)^3 \text{ triplet 1,4-diradical} \quad (2)$$

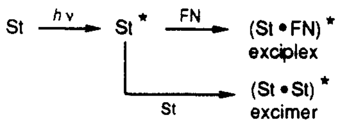
The triplet diradicals have longer lifetimes, so they favor monomer addition.

The photopolymerization of 2-VN alone is much slower than the 2-VN/FN system. Thus the formation of the diradical dimer •VNVN• is not very important in the initiation of the copolymerization.

Discussion

In the previous paper,[9] we studied the photoinduced copolymerization and cyclization reactions of the St/AN system. Evidence was given for the existence of a diradical intermediate for both reactions. In this system, the excited complex is produced through excitation of St, followed by interaction with AN. The collapse of the exciplex produces a 1,4-diradical capable of polymerization initiation or cycloadduct formation.

The stronger donor/acceptor pair St/FN system can undergo photoreactions not only by excitation of St but also by excitation of the CT complex. The 313-nm light is mainly absorbed by St, and the excited St* can react either with FN or with another St.



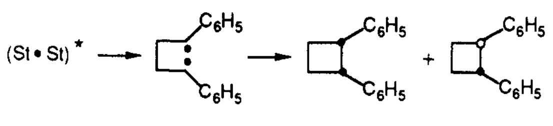
$$\begin{tikzcd} St \arrow[r, "h\nu"] & St^* \arrow[r, "FN"] \arrow[dr, "St"'] & (St\bullet FN)^* \text{ exciplex} \\ & & (St\bullet St)^* \text{ excimer} \end{tikzcd} \quad (3)$$

In contrast, the 365-nm light is absorbed by the CT complex, resulting in the following reaction:

$$St + FN \rightarrow \underset{\text{CT complex}}{(ST\cdot FN)} \xrightarrow{h\nu} \underset{\text{excited complex}}{(St\cdot FN)^*} \quad (4)$$

The obtained excited CT complex should be identical with the exciplex formed at 313 nm and should undergo the same follow-up reactions.

When the photopolymerization is carried out with a $CuSO_4$ filter, both the excimer and the exciplex are produced. The former can cyclize to the cyclobutane dimers:

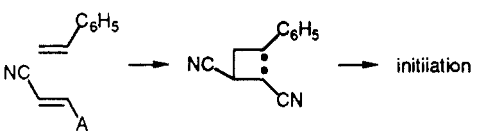


(5)

It is known that the •StSt• diradical intermediate is an inefficient initiator for the polymerization.[19]

Another outcome of the St/St reaction is depicted in Scheme I. The two monoradicals can either initiate polymerization or couple to form $(St)_2FN$ trimers.

In the absence of a $CuSO_4$ filter, the St/FN system can produce the 1,4-diradical which is mainly responsible for the initiation. Almost no St/FN dimers were detected.



(6)

It is known that a diradical polymerization shows an increase of the molecular weight (MW) of polymer with time.[5] In our system the monoradicals produced in Scheme I can terminate one end of the diradical propagating chains by radical–radical coupling. This reduces the contribution of the diradical propagation, and no increase with time is observed. Only if [FN] > [St] does the reaction of St with FN become important enough to observe the MW increase with time.

When the photopolymerization is carried out in the presence of a $CuSO_4$ filter eq 4 becomes the main route to produce initiating radicals. St/St reactions can still be detected because of a slight absorption of St at 365 nm (especially at high concentration). In these conditions, the cycloadduct yield is much lower, and the MW clearly increases with time.

The St/FN ratio plays the same role in controlling the outcome of the photoreactions. At a high ratio of St/FN, St/St reactions become more important: The cycloadduct formation is favored and no MW increase is observed.

Table I
Photoreaction of St/FN[a]

monomer concn, M	time, h	with $CuSO_4$ filter (365 nm)			without $CuSO_4$ filter (313 + 365 nm)		
		% polymer	% cycloadducts	% total	% polymer	% cycloadducts	% total
0.4	46	14.2	6.5	20.7	5.7	20.5	26.2
0.2	52	11.1	12.0	23.1	4.3	22.3	26.6
0.1	72	3.9	6.8	10.7	0.6	20.9	21.5

[a] [St] = [FN], in benzene.

Table II
Photoreaction of St (0.2 M)/FN (0.8 M) (without $CuSO_4$ Filter)

time, h	copolymer yield, %	cycloadduct yield, %
6	2.4	4.3
18	10.8	8.0
30	12.0	8.6
48	21.6	16.1
95	36.0	20.6

Table III
Photoreaction of St (0.8 M)/FN (0.2 M) (without $CuSO_4$ Filter)

time, h	copolymer yield, %	cycloadduct yield, %
8	6.7	6.7
16	10.7	9.5
30	15.4	17.8
40	16.4	24.9
64	23.7	28.9

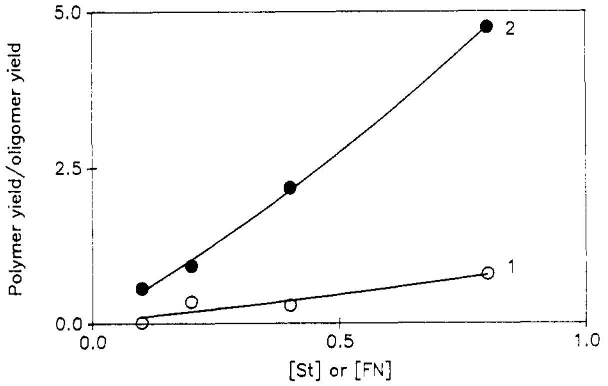
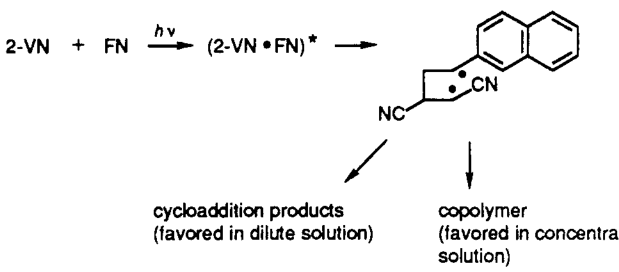


Figure 3. Relationship between polymer yield/oligomer yield and monomer concentration ([St] = [FN]): (1) without $CuSO_4$ filter; (2) with $CuSO_4$ filter.

In this paper, we briefly extended our investigations of photopolymerizations to some other donor/acceptor systems (Tables IV and V). The "bond-formation initiation" theory is also applicable to them; for example:



(7)

Experimental Section

Instrumentation. Electron-absorption spectra were recorded with a HP 8542 Diode Array spectrophotometer. NMR spectra were recorded with a Bruker WM-250 nuclear magnetic resonance spectrometer. Chemical analyses were performed by Desert Analytics, Tucson, AZ. GC/MS spectra were obtained with a Hewlett-Packard GC/MS system.

Size-exclusion chromatography was carried out with a Shodex A-804 column calibrated with polystyrene standards, using chloroform as eluent and a Spectra Physics detector at 254 nm.

Table IV
Influence of Solvent Polarity on Photoreaction of St/FN (without $CuSO_4$ Filter)[a]

solvent toluene/CH_3CN	polymer yield, %	cycloadduct yield, %
1:0	7.9	12.6
2:1	19.5	19.0
1:1	38.6	19.0
1:2	44.6	19.5
0:1	41.9	15.7

[a] [St] = [FN] = 0.8 M, irradiation for 8 h.

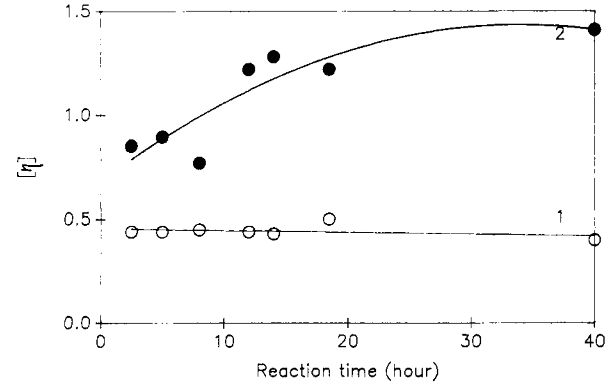


Figure 4. Relationship between MW and polymerization time ([St] = [FN] = 0.8 M, in $ClCH_2CH_2Cl$): (1) without $CuSO_4$ filter; (2) with $CuSO_4$ filter. [η] was measured in DMF; 30 °C.

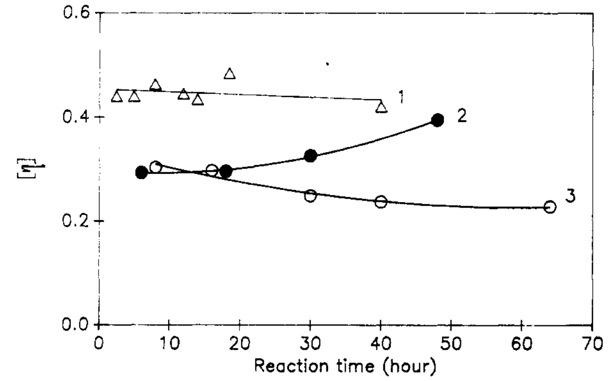


Figure 5. Dependence of MW on polymerization time for the St/FN system in $ClCH_2CH_2Cl$: (1) [St] = [FN] = 0.8 M; (2) [St] = 0.2 M, [FN] = 0.8 M; (3) [St] = 0.8 M, [FN] = 0.2 M. [η] was measured in DMF; 30 °C.

Reactants. Fumaronitrile (FN) was recrystallized from benzene. Styrene (St) was distilled under reduced pressure twice before use. 2-Vinylnaphthalene (2-VN) was recrystallized from alcohol/water and further purified by sublimation. All other monomers and solvents were purified by standard procedures.

Procedure. The photoreactions were run in 15-mL Pyrex tubes equipped with a vacuum-line Teflon valve. The reaction vessel containing the reaction mixture 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 radiation source, and, when needed, a $CuSO_4$ solution filter (250 g of $CuSO_4 \cdot 5H_2O$/L of H_2O 1 cm) was used to cut off the light above 365 nm.[20] The reactor was located 12 cm from the

Table V
Photoreaction of St with Different Acceptors

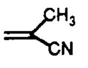
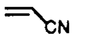
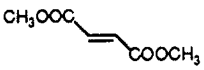
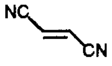
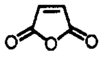
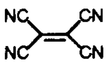
A	yield of copolymer, %	A/D in copolymer	yield of cycloadduct, %	structure of cycloadduct
 MAN	2.4	1.5/1	3.6	MAN/St·(St)$_2$ (trace)
 AN	4.0	1.4/1	5.0	(St)$_2$·St/AN
 DEF	7.0	1/1	5.0	(St)$_2$·St(DEF)$_2$·(St)$_2$DEF
 FN	10.7	1/1	14.4	(St)$_2$·(St)$_2$FN·St/FN (trace)
 MAn	80.1	1/1	3.0	(St)$_2$·St(MAN)$_2$
 TCNE	0		28.2	St/TCNE and other unidentified products

Table VI
Dependence of Polymer and Oligomer Yield on the Initial Monomer Concentration (without CuSO$_4$ Filter)[a]

init concn of each monomer, M	yield of copolymer, %	yield of cycloadduct, %
0.5	48.2	19.8
0.25	23.3	41.9
0.1	11.9	66.7
0.05	9.5	66.7

[a] In benzene, irradiation for 60 h.

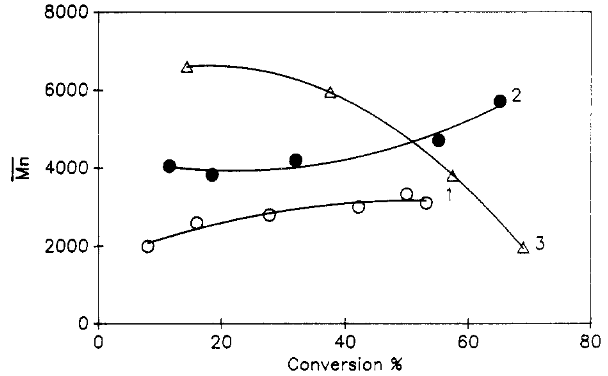
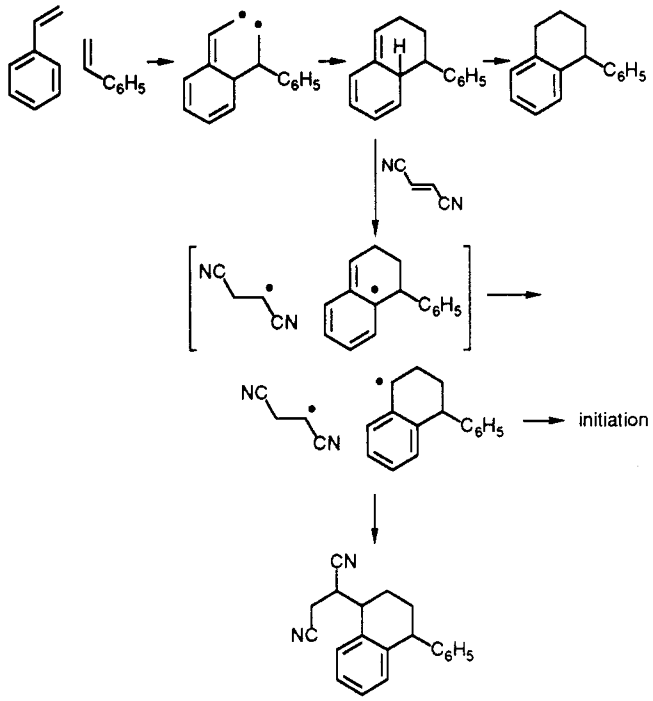


Figure 6. MW-conversion plots ([2-VN] = [FN] = 0.5 M, in benzene): (1) 2-VN/FN, without CuSO$_4$ filter; (2) 2-VN/FN/benzophenone (10^{-2} M), with CuSO$_4$ filter; (3) 2-VN/FN/AIBN (10^{-2} M), 80 °C.

Scheme I



lamp, and the reaction temperature was 35 °C. The photoreactions were carried out with stirring.

After the reaction, the reactants were poured into an excess of methanol. The precipitated polymer was filtered off, dried, and weighed. The remaining solution was concentrated at 90 °C under vacuum until all the monomer was removed, and the residue was examined.

Oligomers of the St/FN Photoreaction System. The oligomers were separated by preparative TLC (1:1:1 hexanes–1,2-dichloroethane–toluene). They consisted mainly of St/St dimers and St$_2$/FN trimers.

The structures of the dimers were assigned as follows: *cis*-1,2-Diphenylcyclobutane: ^{1}H NMR δ 7.05–6.81 (m, 10 H), 4.01–3.93 (m, 2 H),2.51–2.40 (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: ^{1}H 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: ^{1}H NMR δ 7.21–6.61 (m, 9 H), 4.03 (m, 1 H), 2.95–2.69 (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).

The following structures for the (St)$_2$/FN trimers have been proposed: 1-(1,3-dicyanopropyl)-3-phenyl-1,2,3,4-tetrahydronaphthalene and 1-(1,3-dicyanopropyl)-4-phenyl-1,2,3,4-tetrahydronaphthalene. Two peaks are observed in the GC with the same mass spectrum: MS *m/e* 286 (M$^+$, 35), 207 (M$^+$ − $CNCHCH_2CN$, 44), 129 (M$^+$ − $CNCHCH_2CN$ − C_6H_5, 60), 91 ($C_7H_7^+$ 100). Due to limited amounts, no useful NMR spectrum could be obtained.

Acknowledgment. We are deeply indebted to the National Science Foundation, Division of Materials Research, for partial financial support of this research.

Macromolecules **1990,** *23,* 3909-3915 **3909**

References and Notes

(1) Cowie, J. M. G. *Alternating Copolymers*; Plenum Press: New York, 1985.

(2) Shirota, Y. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1985; Vol. 3, p 327.

(3) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 440.

(4) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986,** *108,* 4902.

(5) Hall, H. K., Jr.; Padias, A. B.; Pandya, A.; Tanaka, H. *Macromolecules* **1987,** *20,* 247.

(6) Retzsch, M. *Prog. Polym. Sci.* **1987,** *13,* 277.

(7) Oh, S.-C.; Yamaguchi, K.; Shirota, Y. *Polym. Bull.* **1987,** *18,* 99.

(8) Yamaguchi, K.; Oh, S.-C.; Shirota, Y. *Chem. Lett.* **1986,** 1445.

(9) Li, T.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules*, preceding manuscript in this issue.

(10) Lee, C.; Hall, H. K., Jr. *Macromolecules* **1989,** *22,* 21.

(11) Li, T.; Luo, B.; Chu, G.; Hall, H. K., Jr. *J. Polym. Sci., Polym. Chem. Ed.*, **1990,** *28,* 1735.

(12) Li, T.; Zhou, C.; Dai, L. *Chinese Sci. Bull.* **1989,** *34,* 702.

(13) Li, T.; Pan, J.; Zhang, Z. *Makromol. Chem.* **1989,** *190,* 1319.

(14) Li, T.; Zhou, C. *Chinese Polym. Acta* **1989,** *3,* 316.

(15) Greenley, R. Z. *J. Macromol. Sci., Chem.* **1980,** *A14,* 445.

(16) Ham, G. G. *Vinyl Polymerization*; Marcel Dekker: New York, 1967; Vol. 1, Part 1, Chapter 1.

(17) Li, T.; Cao, W.; Feng, X. *Sci. Sin. B* **1987,** *5,* 685.

(18) Dimonie, M.; Oprescu, C. R.; Hubca, Gh. *Rev. Roum. Chim.* **1976,** *21,* 763.

(19) Kopecky, K. R.; Evani, S. *Can. J. Chem.* **1969,** *47,* 4041.

(20) Murov, S. L. In *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 90.

Registry No. (MAN)(St) (copolymer), 33961-16-9; (AN)-(St) (copolymer), 9003-54-7; (DEF)(St) (copolymer), 29058-33-1; (FN)(St) (copolymer), 27882-58-2; (MAn)(St) (copolymer), 9011-13-6; (2-VN)(FN) (copolymer), 83094-11-5.

Electron Pair Donors in Carbocationic Polymerization. 2. Mechanism of Living Carbocationic Polymerizations and the Role of in Situ and External Electron Pair Donors[†]

G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Received November 15, 1988; Revised Manuscript Received February 12, 1990

ABSTRACT: A new mechanism is proposed for the living carbocationic polymerization [LC$^+$Pzn) of isobutylene (IB) initiated by tertiary ester/MtCl$_n$ (MtCl$_n$ = BCl$_3$ or TiCl$_4$) complexes (Scheme I). According to this mechanism, the initiating systems, e.g., tertiary ester/MtCl$_n$ (I), first yield *tert*-C$^+$···OCORMtCl$_n^-$ ion pairs (II) which may initiate IB polymerization by monomer addition to the *tert*-C$^+$···OCORMtCl$_n^-$ species (III). Species III eventually will undergo collapse with the counteranion, yielding a tertiary chloride capped PIB chain (IV) plus MtCl$_{n-1}$OCOR, an in situ electron pair donor (ED). In line with previous observations, excess MtCl$_n$ will reionize IV, yielding the active propagating species PIB$^+$···MtCl$_{n+1}^-$ (V). Thus the temporarily dormant species IV are in dynamic equilibrium with the propagation-active species V. The function of the EDs, both in situ and external ones, is to stabilize the active carbocations, affecting beneficially the course of polymerization. The transitory formation of tertiary chlorides by collapse of the "mixed" counteranion OCORMtCl$_{n-1}^-$ (II → VI), however, may also occur prior to polymerization. The exact route leading to the final IV $\rightleftharpoons$ V equilibrium depends on reaction conditions, i.e., the nature of initiator and MtX$_n$, stability of the mixed counteranion, solvent polarity, temperature, etc. The latter equilibrium accounts for the presence of tertiary Cl end groups (PIB-Cl^t) upon quenching. This is a crucial deviation from the earlier mechanistic view according to which the dormant species are tertiary ester or tertiary ether terminated PIB. These propositions have been substantiated by a variety of means: (1) by demonstrating the existence of reversible termination in the PIB-Cl^t/excess BCl$_3$/IB system; (2) by analysis of literature sources dealing with the transformation of tertiary ester and tertiary ether/MtCl$_n$ complexes to the corresponding tertiary chlorides; (3) by observations that the equimolar 2-acetyl-2,4,4-trimethylpentane (TMPOAc)/TiCl$_4$ system is totally inactive; (4) by polymerizations induced by equimolar mixtures of cumyl acetate (CumOAc) + cumyl methyl ether (CumOMe)/excess TiCl$_4$ and CumCl + CumOMe/excess TiCl$_4$ systems, both of which give living polymerizations and narrow molecular weight distribution (MWD) PIBs; (5) by polymerizations of IB induced, on the one hand, by TMPOAc/excess TiCl$_4$ and, on the other hand, by TMPCl/excess TiCl$_4$/ethyl acetate (EtOAc) systems, where only the latter give narrow-MWD product; and (6) by comparing the MWDs of PIBs prepared by CumCl/excess TiCl$_4$ and CumCl/excess TiCl$_4$/EtOAc and demonstrating the MWD narrowing effect of the deliberately added external ED (EtOAc). The information generated in these studies has been analyzed, and a mechanistic interpretation of the observed facts is offered.

A. Introduction

In the course of our systematic investigations on LC$^+$Pzn, particularly those on the LC$^+$Pzn of IB,[1-3] evidence has increasingly been accumulating that the initial views concerning the mechanism of these polymerizations[4,5] are insufficient and must be revised. According to the original proposition, the LC$^+$Pzn of IB induced by tertiary ester/BCl$_3$[4] or tertiary ether/BCl$_3$[5] complexes involves initiation and propagation by monomer insertion into polarized non-

---

* To whom correspondence should be addressed.

[†] Paper 26 in the series "Living Carbocationic Polymerization". For paper 1, see: Kaszas, G.; et al. *Polym. Bull.* **1988,** *20,* 413.

0024-9297/90/2223-3909$02.50/0