at −78 °C. Accordingly, the system using potassium as countercation may correctly be classified as composed of true living polymers.

As a control, we checked the stabilities of polystyryllithium and -potassium under the same conditions. The results are summarized in Table VII, where it can be seen that loss of the living ends is not observed at −78 °C for 24 h and at 30 °C for 30 min. Accordingly, living polystyrene proves to be stable under these conditions where some loss of anions was detected in the living polymers of (alkoxysilyl)styrenes studied here. This strongly suggests the participation of the alkoxysilyl group in the reactions which lead to the loss of active center concentration.

Under the polymerization conditions at −78 °C, the anionic polymerizations appear to be almost instantaneous and complete within a few minutes, whereas side reactions are slow and far from complete after 30 min even in the fastest example. It is therefore considered that the influence of such reactions may be practically negligible on propagation and the side reactions may gradually occur mainly after the conclusion of the polymerization at −78 °C. In fact, well-defined polymers were obtained in quantitative conversions in all cases except for the polymerizations of monomers with methoxy- and ethoxysilyl groups initiated with oligo(α-methylstyryl)dilithium.

Finally, the results presented in Tables IV–VI are of general chemical interest and provide much information for synthesizing block copolymers by the sequential addition method where the use of a long-lived sample of polymer is required at the first polymerization.

Registry No. **1a** (homopolymer), 98542-13-3; **1a**·2K, 105762-17-2; (**1a**)($H_2C{=}CHC_6H_5$) (graft copolymer), 105785-22-6; **1b** (homopolymer), 105785-23-7; **1b**·2K, 105762-18-3; **1c**, 105785-13-5; **1c**·2K, 105762-19-4; **1c**·2Li, 105762-21-8; **1d**·2K, 105762-20-7; **1d**·2Li, 105762-22-9; **1e**, 105785-14-6; **1e**·2K, 105762-24-1; **1e**·2Li, 105762-28-5; **1f**, 105785-15-7; **1f**·2K, 105762-25-2; **1g**, 105785-16-8; **1g**·2K, 105762-26-3; **1h**, 105785-17-9; **1h**·2K, 105762-27-4; **1h**·2Li, 105762-29-6; **2a** (homopolymer), 105785-24-8; **2a**·2K, 105762-23-0; **2b**, 105785-18-0; **2b**·2K, 105762-31-0; **2b**·2Li, 105762-32-1; **3**, 105785-25-9; **3**·2K, 105762-30-9; $H_3C(CH_2)_2OSi(CH_3)_2Cl$, 1825-70-3; $H_3C(CH_2)_3OSi(CH_3)_2Cl$, 1825-72-5; $H_3CCH_2CH(CH_3)OSi(CH_3)_2Cl$, 2725-10-2; $(H_3C)_2CHCH_2OSi(CH_3)_2Cl$, 51986-70-0; $(H_3C)_3COSi(CH_3)_2Cl$, 58566-07-7; 4-$H_2C{=}CHC_6H_4Cl$, 1073-67-2; $H_3CSi(OCH(CH_3)_2)_3$, 5581-67-9; $Cl_2Si(CH_3)_2$, 75-78-5; $HO(CH_2)_2CH_3$, 71-23-8.

References and Notes

(1) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.

(2) Hirao, A.; Nagawa, T.; Hatayama, T.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1985**, *18*, 2101.

(3) Laible, R.; Hamann, K. *Adv. Colloid Interface Sci.* **1980**, *13*, 65.

(4) Morton, M; Rembaum, A. A.; Hall, J. L. *J. Polym. Sci., Part A* **1963**, *1*, 461.

(5) Chappelow, C. C., Jr.; Elliott, R. L.; Goodwin, J. T., Jr. *J. Org. Chem.* **1960**, *25*, 435.

(6) Jenkins, A. D.; Petrak, K.; Roberts, G. A. F.; Walton, D. R. M. *Eur. Polym. J.* **1975**, *11*, 653.

(7) Manami, H.; Nishizaki, S. *Kogyo Kagaku Zasshi* **1960**, *63*, 366.

(8) Hirao, A.; Takenaka, K.; Packirisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157.

(9) $\bar{M}_w/\bar{M}_n$ is calculated based on the method of Tung, which describes the relation of the gel permeation chromatogram and the true molecular weight distribution function: Tung, L. H. *J. Appl. Polym. Sci.* **1966**, *10*, 375.

(10) In our previous paper,[2] we reported that the polymerization of **1a** gave a polymer with a very broad molecular weight distribution in 78% isolated yield. However, after repeated experiments with the use of very carefully and rigorously purified **1a**, **1a** was found to be polymerized quantitatively to afford polymers with $\bar{M}_w/\bar{M}_n$ ratios of 1.6–1.7. Hence, the previous result of the polymerization of **1a** is erroneously obtained, probably due to the impurities in **1a**, and here is to be corrected.

(11) Gilman, H.; Smart, G. N. R. *J. Org. Chem.* **1950**, *15*, 720.

(12) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1.

A Tetramethylene Diradical as the Initiating Species in the Spontaneous Charge-Transfer Copolymerization of *p*-Methoxystyrene with Dimethyl Cyanofumarate

H. K. Hall, Jr.,* Anne Buyle Padias, Ashish Pandya, and Hitoshi Tanaka[†]

C. S. Marvel Laboratories, Chemistry Department, University of Arizona,
Tucson, Arizona 85721. *Received September 15, 1986*

ABSTRACT: The 1:1 alternating copolymerization of *p*-methoxystyrene with dimethyl cyanofumarate proceeds spontaneously in solution at 28 °C. Partitioning of product between copolymer and a dihydropyran cycloadduct favors the small molecule upon dilution, supporting the intermediacy of a tetramethylene diradical. Propagation at the diradical is attested by the increase of molecular weight with conversion. The tetramethylene diradical can be trapped. The equilibrium constant for electron donor–acceptor (EDA) complex formation was determined by NMR spectroscopy. The rate of copolymerization is proportional to the square of the monomer concentrations for equimolar initial concentration. Under these conditions the charge-transfer complex disappears according to first-order kinetics. Comparison of the experimental data with a kinetic scheme, derived with consideration of propagation as proceeding by both free monomer and the EDA complex acting as a monomer, showed that the latter is not significant at our concentrations. These results support and extend our concept of bond-forming initiation in spontaneous charge-transfer polymerizations.

Introduction

Diradical tetramethylenes have been popular intermediates in organic chemistry.[1] They have been generated by a number of different methods, mostly photochemical cleavage of cyclopentanones and in Norrish-2 photoreactions,[2] and are also formed in thermal cycloaddition reactions of olefins. Convincing studies have been those of Bartlett, who studied the cycloadditions of poly(fluoroethylenes),[3] and Pasto, who studied the cycloadditions of alkenes.[4] Recently, captodative substituents have been found to stabilize tetramethylene diradicals.[5,6]

Trapping these diradicals has been difficult and succeeds only with the most reactive trapping reagents, including oxygen and di-*tert*-butyl selenoketone.[7,8] They are very

---

[†] Department of Applied Chemistry, Faculty of Engineering, Tokushima University, Tokushima 770, Japan.

0024-9297/87/2220-0247$01.50/0

transitory intermediates and highly reactive.

We have noted that polymerization provides a powerful method of trapping transitory zwitterions and diradicals.[9] The procedure has two advantages: (1) amplification—if a transitory intermediate initiates polymerization, the polymer is easily identified and isolated; (2) the nature of the polymer, whether homopolymer or copolymer, provides direct evidence as to the identity of the initiating species.

Early in polymer chemistry the tetramethylene diradical formed by combination of two molecules of styrene was postulated by Flory to thermally initiate styrene polymerization at 100 °C.[10] However, this spontaneous polymerization of styrene was later shown by Mayo to involve the formation of phenyltetralin, whose molecule-assisted homolysis with styrene gives monoradicals.[11] Mayo, Pryor,[12] and Solomon,[13] showed that the monoradicals account for the bulk of the styrene homopolymerization. Nevertheless, the formation of 1,2-diphenylcyclobutane in these reactions must still be accounted for in terms of a tetramethylene diradical, as shown by Olaj.[14] α-Methylstyrene behaves similarly.[15] For the thermal polymerization of methyl methacrylate, studies of Meyerhoff[16] identified the tetramethylene diradical as the key intermediate in polymer formation and also cyclodimer formation.

These thermal homopolymerizations occur rather slowly at high temperatures because the molecules necessarily have the same polarity. Spontaneous copolymerizations of monomers of opposite polarities occur more easily as the polarity difference becomes greater. The precise initiating species of these "charge-transfer" polymerizations has not yet been established. The reason they are called charge-transfer polymerizations is that charge-transfer complexes, also known as electron donor–acceptor (EDA) complexes, are clearly visible in these reactions and fade as the reactions proceed. The charge-transfer (EDA) complex plays a role in both initiation and propagation.[17-23]

A detailed examination of the kinetics of spontaneous charge-transfer copolymerization was first carried out by Kokubo, Iwatsuki, and Yamashita.[24] Their kinetic analysis was limited to equal initial concentrations of the two monomers and single-point and low-conversion kinetic runs, with the assumption that the EDA complex was the only propagating species. Under these postulates the observed overall dependence on polymerization rate of 1.5 in each monomer could be explained in terms of a tetramethylene diradical intermediate, although this was not called such. Perhaps this was because no increase in polymer molecular weight with conversion, expected for propagation at diradical, was seen.

More recently, an important series of articles by Nagai delved deeper into these questions for various combinations of donor and acceptor monomers.[25-28] These investigators derived a complete kinetic scheme, again for equal initial concentrations of the two monomers in spontaneous copolymerizations. Again spontaneous radical generation occurred, and again no specific structure was assigned to the initiating species. Nagai found that the molecular weight of the polymer did not increase with conversion and that in the system styrene–α-chloromaleic anhydride, termination occurs through recombination of a donor and an acceptor radical, or two donor radicals.

Otsu has trapped two different radicals by ESR spin trapping in the spontaneous copolymerization of diethyl fumarate and vinyl sulfide.[29] However, it was not proved that these are the true initiators.

It may be noted that Tobolsky[30] calculated that propagation at both ends of a diradical could not take place to a significant extent because the radicals would self-terminate under formation of cyclic structures. However, this was before the advent of conformational analysis and was based only on a freely rotating statistical model.

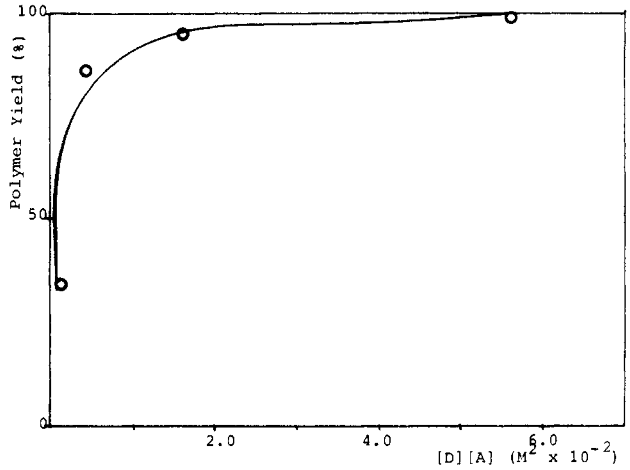


Figure 1. Polymer yield as a function of monomer concentration.

We wished to explore the possible intermediacy of tetramethylene diradicals in these copolymerizations more closely. From our earlier work with electrophilic trisubstituted ethylenes, we selected dimethyl cyanofumarate as an appropriate partner for p-methoxystyrene.[31] They spontaneously and quickly copolymerize at room temperature to give high molecular weight alternating copolymer and are far more reactive than the pairs previously studied. Thus it appeared appropriate to use them for more detailed study.

Results

Polymerization. Mixing the two comonomers, p-methoxystyrene (D) and dimethyl cyanofumarate (A), gave smooth rapid copolymerization. Molecular weights at complete conversion were very high, attesting to high purity for the monomers and clean reaction conditions. Yields were quantitative at high or moderate concentrations. The polymer possessed an alternating 1:1 structure, as established by elemental analysis. This was the case even with 2:1 or 1:2 feed ratios. The polymerization was inhibited by oxygen or by free radical inhibitors. It proceeded in the dark as rapidly as in diffuse laboratory light. Our results were completely reproducible. No indication of their being influenced by adventitious impurities was ever observed.

Competition of Copolymerization with Dihydropyran Formation. As the monomer concentrations decreased to very low values, a dihydropyran cycloadduct, characterized by its NMR spectrum and comparison with earlier results,[32] began to appear at the expense of copolymer (Scheme I). It was characterized in solution by NMR after precipitation of the polymer and addition of free radical inhibitor. The yield of dihydropyran was favored by high dilution, as shown in Figure 1. Experiments were carried out to long reaction times so that no monomer remained when the experiment was worked up (Table I). These results speak for the competitive formation of polymer and dihydropyran from a common intermediate. At higher concentrations the tetramethylene diradical is trapped by monomer. At low concentration it cyclizes to the dihydropyran in a nonconcerted cycloaddition,[32] thereby proving its structure as a tetramethylene diradical (internal trapping).

A similar curve was found by Bevington,[33] who studied the yield of polystyrene from AIBN as a function of the concentration of styrene. High concentrations of styrene

Scheme I

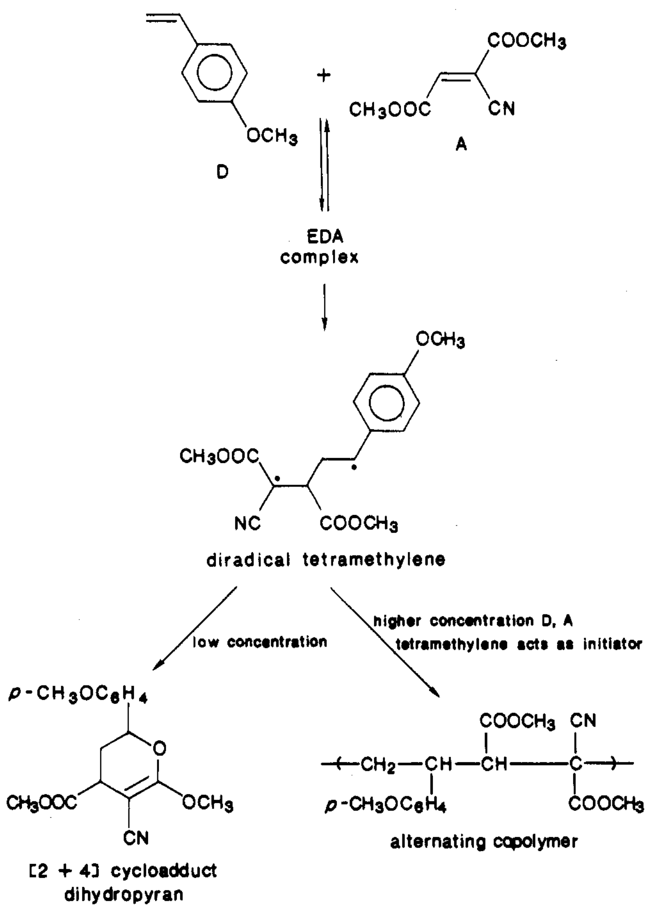


Table I
Dependence of Polymer Yield on the Initial Monomer Concentrations[a]

initial concn of each monomer, M	time, h	yield of polymer,[b] %	yield of dihydropyran,[c,d] %
0.75	24	99	
0.40	36	95	3
0.20	48	86	14
0.10	60	35	65

[a] Conditions: 28 °C in 1,2-dichloroethane under an argon atmosphere. [b] Polymer isolated by precipitation in ether. [c] Yield determined by ^1H NMR. [d] No remaining olefin monomers.

trapped the isobutyronitrile radical to form polystyrene. At low concentrations the polystyrene yield decreased in favor of the small molecule tetramethylsuccinonitrile, formed by dimerization of the isobutyronitrile radical.

No cyclobutane cycloadduct nor cyclodimer of *p*-methoxystyrene was ever found in these experiments.

Trapping the Diradical Tetramethylene Intermediate. An external radical trap, 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO), was added to the reaction of *p*-methoxystyrene and dimethyl cyanofumarate in acetonitrile. A 1:1:1 adduct 1 could be isolated in 23% yield, the structure of which was proved by ^1H and ^{13}C NMR spectroscopy. The mechanism proposed for its formation is shown in Scheme II. The external trapping again proves that the tetramethylene diradical is formed in the reaction mixture.

Scheme II

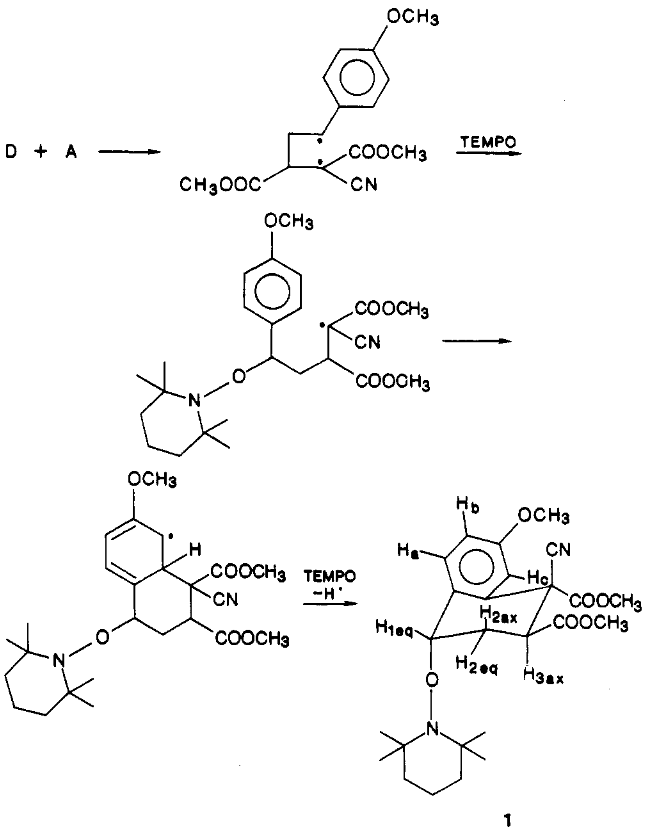


Table II
Increase of Inherent Viscosity and Molecular Weight with Time[a]

time, h	polymer yield, %	η_{inh},[b] dL/g	MW[c]
8	19	0.15	3200
12	31	0.32	31000
16	41	0.64	125000
20	52	0.81	630000

[a] Conditions: 0.1 M each D and A in 1,2-dichloroethane at 28 °C. [b] Inherent viscosity measured on 0.5% dichloromethane solution at 30 °C. [c] Molecular weight determined by SEC vs. polystyrene standard.

Increase of Polymer Molecular Weight during Polymerization. If propagation at diradical were actually occurring, one would expect an increase in polymer molecular weight during the polymerization. This is because as monomer is consumed, termination occurs more significantly than propagation. Termination involves diradical coupling with an attendant increase of molecular weight. The molecular weight and inherent viscosity increase markedly with the conversion, as shown in Table II. This is strong evidence for propagation at diradical. The polymers are monomodal, and this is evidence against formation of any macrocyclic rings.

Charge-Transfer Complex. A yellow charge-transfer (EDA) complex is readily visible upon mixing solutions of the two monomers in organic solvents (λ_{max} 345 nm). We attempted to determine the equilibrium constant *K* for its formation by ultraviolet spectroscopy. An accurate value could not be obtained because of the large competing absorption of the two monomers. Accordingly, we turned to NMR spectroscopy for the determination of the equilibrium constant. This has been shown by Hanna and Ashbough[34] to be the preferred method for determination of EDA equilibrium constants, particularly when there is a clearly visible olefinic hydrogen, as in our case. The data in Table III show the results in deuteriochloroform. We have also determined the equilibrium constant in deuterioacetonitrile and find it to be almost the same: 0.15 L·mol^{-1} in chloroform vs. 0.14 L·mol^{-1} in acetonitrile.

Kinetic Studies. Polymerization was also studied kinetically by investigating the rate of disappearance of

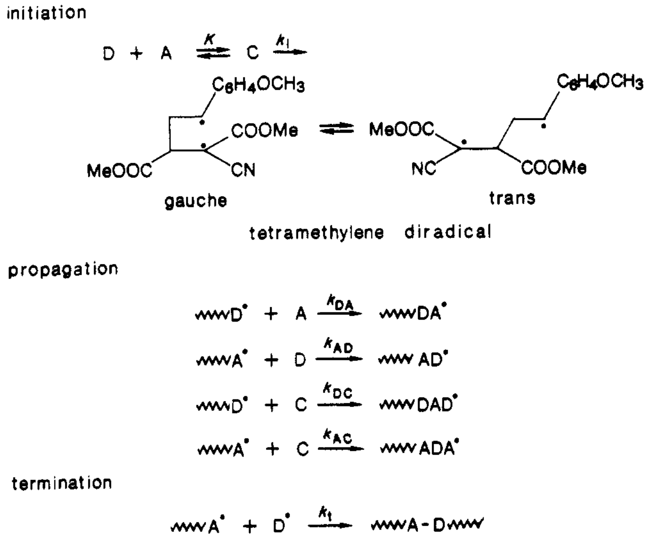
Table III
Determination of K_{EDA} between D and A in $CDCl_3$ at 25 °C

[D], M	[A], M	δ_{obsd}, Hz	Δ_{obsd}, Hz	1/[D], M^{-1}	$1/\Delta_{obsd}$,[a] s
0.00	0.03	1870.1			
0.30	0.03	1860.1	10.0	3.35	0.099
1.04	0.03	1829.9	40.2	0.957	0.024
2.09	0.03	1774.1	96.1	0.478	0.010
2.69	0.03	1725.2	145.0	0.372	0.007

[a] A plot of 1/[D] vs. $1/\Delta_{obsd}$ gives $K = 0.15$ L·mol^{-1}.

monomers. The kinetic studies were carried out at concentrations 5 times greater than those at which dihydropyran formation became significant. Monomer disappearance was followed by size exclusion chromatography using a low molecular weight column. *p*-Methoxystyrene (D) was the monomer more easily followed because of its high ultraviolet absorbance. The rate of polymerization R_p was taken as twice the slope of the plot of *p*-methoxystyrene concentration against time, because one molecule of donor and one molecule of acceptor disappear together. The polymer yield was determined in some cases gravimetrically and found to agree very well with the yield calculated from the monomer disappearance.

Derivation of Kinetic Scheme. We have derived a kinetic scheme for these spontaneous alternating copolymerizations, considering the possibility that propagation occurs both through EDA complex as a monomer and through alternating additions of the free monomers. The following reactions are proposed:



The initiation step to form the tetramethylene diradical could proceed through the EDA complex C or directly from monomers. These two possibilities cannot be distinguished by kinetic methods. The initiation rate can be expressed by either of the following equations:

$$R_i = k_i[C] \Rightarrow R_i = k_iK[A][D] \tag{1}$$

or

$$R_i = k_i[A][D] \tag{2}$$

In this derivation the first equation will be used, in which it is assumed that the EDA complex is on the reaction path. Propagation can occur both through monomer addition and through complex addition in our scheme. Termination is assumed to proceed only through recombination of two different radicals.

The propagation rate is given by the total disappearance of monomer

$$R_p = -\frac{d[D + A]}{dt} = -2\frac{d[D]}{dt} \tag{3}$$

which is equal to twice the disappearance of one of the monomers for these strictly alternating copolymerizations.

The rate of disappearance of the monomers is given by

$$-d[D]/dt = k_{AD}[A^\bullet][D] + k_{AC}[A^\bullet][C] + k_{DC}[D^\bullet][C] \tag{4}$$

$$-d[A]/dt = k_{DA}[D^\bullet][A] + k_{AC}[A^\bullet][C] + k_{DC}[D^\bullet][C] \tag{5}$$

For an alternating copolymerization

$$-d[D]/dt = -d[A]/dt$$

and thus

$$k_{AD}[A^\bullet][D] = k_{DA}[D^\bullet][A] \tag{6}$$

A steady-state assumption is made

$$R_i = R_t$$

$$k_i[C] = k_t[D^\bullet][A^\bullet] \tag{7}$$

Solving (6) and (7) for [D•] and [A•] gives

$$[D^\bullet] = \left(\frac{k_ik_{AD}}{k_tk_{DA}}\right)^{1/2}[C]^{1/2}\left(\frac{[D]}{[A]}\right)^{1/2} \tag{8}$$

$$[A^\bullet] = \left(\frac{k_ik_{DA}}{k_tk_{AD}}\right)^{1/2}[C]^{1/2}\left(\frac{[A]}{[D]}\right)^{1/2} \tag{9}$$

Finally, combining (3), (4), (8), and (9), we obtain

$$-\frac{d[D]}{dt} = \left(\frac{k_i}{k_t}k_{DA}k_{AD}K\right)^{1/2}[D][A] + k_{AC}\left(\frac{k_ik_{DA}}{k_tk_{AD}}K^3\right)^{1/2}[A]^{3/2}[D]^{3/2} + k_{DC}\left(\frac{k_ik_{AD}}{k_tk_{DA}}K^3\right)^{1/2}[A]^{3/2}[D]^{3/2} \tag{10}$$

and

$$R_p = Y([C][D][A])^{1/2} + Z([C])^{3/2} \tag{11}$$

in which

$$Y = 2\left(\frac{k_i}{k_t}k_{DA}k_{AD}\right)^{1/2}$$

and

$$Z = 2\left(\frac{k_i}{k_tk_{AD}k_{DA}}\right)^{1/2}(k_{AC}k_{DA} + k_{DC}k_{AD})$$

The propagation rate can be written in two ways:

$$R_p = YK^{1/2}[D][A] + ZK^{3/2}[D]^{3/2}[A]^{3/2} \tag{12}$$

or

$$R_p = YK^{-1/2}[C] + ZK^{3/2}[D]^{3/2}[A]^{3/2} \tag{13}$$

For equimolar initial concentrations, we can write

$$R_p = -2\frac{d[D]}{dt} = YK^{1/2}[D]^2 + ZK^{3/2}[D]^3 \tag{14}$$

in which the first term describes the contribution of propagation by free monomer, and the second, propagation by EDA complex.

Plotting log R_p vs. log [D] at different times yields a straight line with a slope of 2, proving that the second term in (14) is zero (Figure 2). No propagation occurs via complex in our experiments. Determination of the intercept of these plots yields a value for $YK^{1/2}$, which is the overall polymerization rate coefficient.

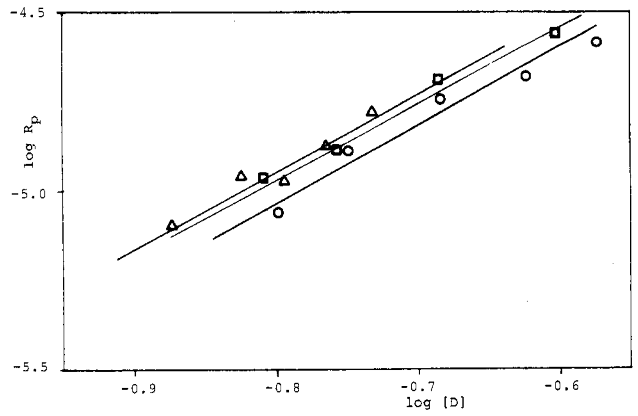


Figure 2. Plot of log R_p vs. log [D] for equal initial concentrations in 1,2-dichloroethane at 28 °C: (△) [D] = [A] = 0.25 M; (○) [D] = [A] = 0.375 M; (□) [D] = [A] = 0.50 M.

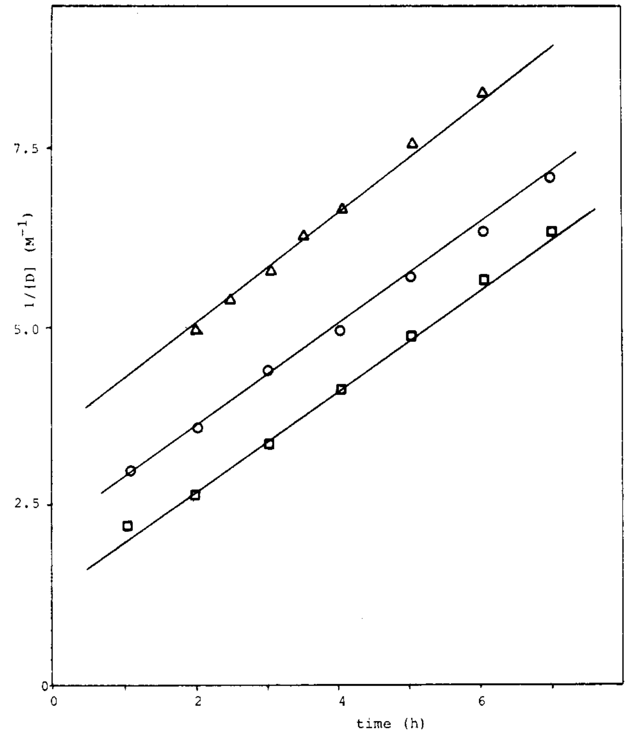


Figure 3. Plot of 1/[D] vs. time for equal initial concentration in 1,2-dichloroethane at 28 °C: (△) [D] = [A] = 0.25 M; (○) [D] = [A] = 0.375 M; (□) [D] = [A] = 0.50 M.

As the second term in (14) is negligible or zero, second-order kinetics in [D] is observed in these runs. Plotting 1/[D] vs. time gives straight lines with a slope equal to $^1/_2 YK^{1/2}$ (Figure 3).

For unequal initial concentrations, the overall polymerization rate coefficient $YK^{1/2}$ can also be derived from eq 12, because Z is zero or negligible.

$$\log R_p = \log (YK^{1/2}) + \log ([D][A]) \qquad (15)$$

Plotting log R_p vs. log ([D][A]) yields a straight line with a slope equal to 1 and an intercept equal to log ($YK^{1/2}$) (Figure 4). The same polymerization rate constants can also be obtained from the integration of the second-order rate law equation:

$$\ln \frac{[A]_0[D]}{[D]_0[A]} = \tfrac{1}{2}([D]_0 - [A]_0)(YK^{1/2})t \qquad (16)$$

Table IV lists the polymerization rate coefficients determined for the different runs and shows that all values for $YK^{1/2}$ are in agreement.

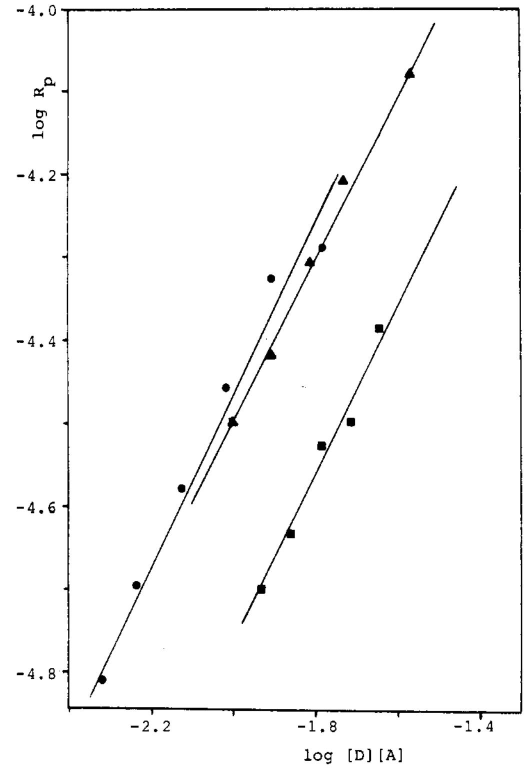


Figure 4. Plot of log R_p vs. log ([D][A]) for unequal initial concentrations in 1,2-dichloroethane at 28 °C: (▲) [D] = 0.75 M, [A] = 0.0375 M; (■) [D] = 0.375 M, [A] = 0.075 M; (●) [D] = 0.50 M, [A] = 0.100 M.

Table IV
Polymerization Rate Coefficients $YK^{1/2}$ ($L \bullet mol^{-1} \bullet s^{-1}$) for the Copolymerization of *p*-Methoxystyrene (D) and Dimethyl Cyanofumarate (A)[a]

Equal Initial Concentrations

[D], M	[A], M	solvent[b]	1/[D] vs. time $YK^{1/2}$	log R_p vs. log [D] $YK^{1/2}$	log R_p vs. log [D] slope
0.50	0.50	DCE	4.8×10^{-4}	4.1×10^{-4}	1.97
0.375	0.375	DCE	3.5×10^{-4}	3.95×10^{-4}	2.00
0.25	0.25	DCE	4.5×10^{-4}	4.6×10^{-4}	1.99
0.40	0.40	MeCN	4.3×10^{-4}	4.1×10^{-4}	1.95

Unequal Initial Concentrations

[D], M	[A], M	solvent[b]	ln {([A]$_0$[D])/([D]$_0$[A])} vs. time $YK^{1/2}$	log R_p vs. log ([D][A]) $YK^{1/2}$	log R_p vs. log ([D][A]) slope
0.75	0.375	DCE	2.6×10^{-4}	3.6×10^{-4}	1.00
0.375	0.75	DCE	2.1×10^{-4}	3.1×10^{-4}	1.08
0.50	1.00	DCE	3.6×10^{-4}	3.7×10^{-4}	1.00
0.40	0.80	MeCN	3.4×10^{-4}	3.2×10^{-4}	1.05

[a] At 28 °C under an argon atmosphere. [b] DCE = 1,2-dichloroethane; MeCN = acetonitrile.

Disappearance of EDA Complex Absorption. The disappearance of the EDA complex was followed by UV spectroscopy at 380 and 400 nm, where there is no interference of monomer absorption. At equimolar initial concentration (0.375 M each), linear first-order plots with rate constant 5.5×10^{-5} s^{-1} were observed (Figure 5). This is in agreement with eq 13, which predicts a first-order relationship for complex concentration if the second term is zero ($Z = 0$). When the initial concentrations were unequal, strongly curved semilogarithmic plots were obtained.

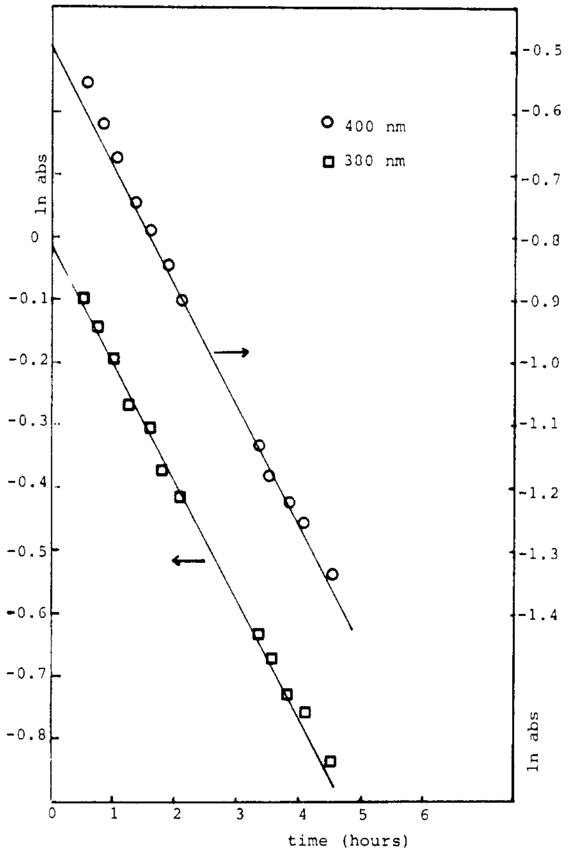


Figure 5. First-order disappearance of EDA complex from equal initial concentrations of donor and acceptor (0.375 M each, 1-mm path length).

Solvent Effect. We wanted to determine whether solvent polarity had a strong effect on reaction. Accordingly two runs were carried out in acetonitrile, as shown in Table IV: one at equal initial concentrations, and one at unequal initial concentrations. The rate constants are the same as in 1,2-dichloroethane.

Discussion

We have presented a large amount of data that are completely consistent with initiation by a tetramethylene diradical. This represents the most comprehensive treatment of charge-transfer initiation of copolymerization and propagation at growing diradical yet reported. The tetramethylene diradical is the only initiating species that can be responsible for those results. The competition experiments show clearly that it competitively initiates polymerization or cyclizes to dihydropyran, thereby proving its structure. External trapping by TEMPO confirmed the structure of this intermediate.

Ion radical initiating species can be excluded on several grounds. First, no cyclobutane homodimer of *p*-methoxystyrene has ever been observed in our reactions. Yet the cation radicals of electron-rich monomers form cyclohomodimers.[35] Second, there is no parallel between affinity, as measured by cyclovoltammetry,[36] and reactivity in polymerization. This again speaks for bond formation between the β-carbons for the formation of tetramethylene intermediates, in which steric hindrance plays a role. Third, the lack of rate change from 1,2-dichloroethane to acetonitrile as solvent speaks strongly against ion radical intermediates.

There is no evidence at all for the participation of excited charge-transfer complexes in these reactions.[37]

When our kinetic scheme is compared with those in the literature, it appears that our kinetic scheme is more comprehensive. It applies throughout the runs and to unequal concentrations of monomers.

The first term in (12) is the same as that derived by Nagai[25,26] if we assume that termination occurs only between two different radicals. The second term in (12) corresponds to the derivation by Yamashita,[24] who only assumes propagation through EDA complex.

The fact that excess *p*-methoxystyrene does not polymerize, meaning a strictly alternating polymer is always obtained independent of the initial monomer concentrations, shows that a *p*-methoxystyrene-ended radical prefers to combine with an electron-deficient radical rather than react with *p*-methoxystyrene. This allows us to simplify our kinetic scheme compared to that of Nagai. Moreover, this point of view offers an explanation as to why no macrocyclic ring formation is observed. The growing diradical will generally possess two like end groups and therefore prefers to grow by polyaddition of the opposite monomer rather than cyclize.

Our analysis of the kinetics allows us to easily establish the fact that no propagation occurs via the EDA complex in our system, compared to the elaborate equations proposed by Shirota and Mikawa.[22,23]

In retrospect, it appears that Yamashita and Nagai had all the evidence for initiation by a tetramethylene diradical in spontaneous copolymerization. Only the fact that molecular weight did not increase with conversion may have kept them from this postulate. Our finding such an increase appears to be due to our choice of highly reactive comonomers.

The key factor determining the partitioning of the tetramethylene intermediate between cyclic small molecule and polymer is clearly dilution, a factor that has been overlooked before. This is in contrast to the explanation offered by Nagai in the 1,3-cyclohexadiene–citraconic anhydride system in which two types of charge-transfer complexes are proposed, a tight one leading to cycloaddition, and a loose one leading to copolymerization.[27,28]

Concentration plays an important role in charge-transfer polymerization in two other ways. A survey of the literature shows that such copolymerizations have in most cases been studied at high initial concentrations, >1 M and as high as 4 M. Even then, propagation is not exclusively by charge-transfer complex. Our choice of highly reactive monomers of opposite polarity enabled us to work at lower concentrations and still have respectable rates of spontaneous polymerization. Second, our kinetics are more nearly independent of medium effects than results carried out at higher concentrations.[38]

Considering the low concentrations used, it is not surprising that we find propagation only through alternating addition of free monomers; the dilution causes the EDA complex to be mostly dissociated in free monomers. Moreover, due to the extreme polarities of the monomers used, the propagating radicals are highly stabilized, thus in some way eliminating the necessity of propagating via the EDA complex. In systems with less polar monomers, one of the radicals is very unstable, and the propagation through EDA complex eliminates the formation of this radical.

In the work of Gotoh,[39] the tetramethylene from *N*-vinylcarbazole and dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate was highly zwitterionic. Formed in the cis or gauche conformation from collapse of the EDA complex, it was held in cis or gauche form by powerful Coulombic attraction. Thus its logical fate was collapse to the cyclobutane. The cyclobutane, being strained, reversibly opened to cis tetramethylene zwitterion, which eventually isomerized to the trans form, which could initiate polymerization. In our present work the tetramethylene diradical is relatively nonpolar. Therefore the cis or gauche tetramethylene readily converts to trans, and we are able to initiate copolymerization effectively from the forward mode of reaction of olefin pairs. We are currently exploring the possibility of generating tetramethylene diradicals from cyclobutanes in order to complete this picture.

Iwatsuki and Yamashita postulated that the magnitude of the EDA complex equilibrium constant determines whether radical or ionic polymerizations will occur.[21] However, this is not quantitatively correct. Gotoh[39] found the equilibrium constant for EDA complex formation between *N*-vinylcarbazole and dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate was 0.19 L·mol^{-1} and observed cationic homopolymerization, while ours is 0.15 L·mol^{-1} for a case that gives strict alternating copolymerization. Nevertheless, the Iwatsuki–Yamashita correlation is highly significant qualitatively and in general terms agrees well with our concept of an "Organic Chemist's Periodic Table".[8]

Experimental Section

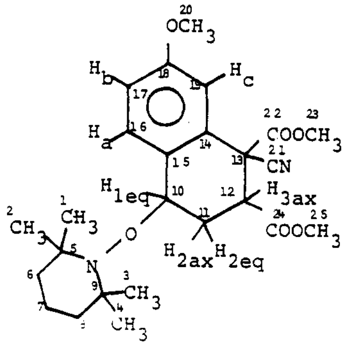
Instrumentation. All melting points were obtained from a Thomas-Hoover capillary melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were taken on Varian EM360L and Bruker WM250 nuclear magnetic resonance spectrometers at 60 and 250 MHz. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Inherent viscosities were determined with an Ostwald–Fenske viscometer. Number-average molecular weights were measured on Du Pont Zorbax PSM 60S, Du Pont Zorbax PSM 300S, and IBM GPC/SEC Pore Type A columns calibrated with polystyrene standards with chloroform as eluent and a Spectra Physics detector at 254 nm. The kinetic data were obtained with the IBM GPC/SEC Type A column with chloroform as eluent, a Spectra Physics detector at 254 nm, and a Hewlett-Packard 3392 A integrator. Elemental analyses were performed by MicAnal, Tucson, AZ.

Solvents. Solvents were dried over calcium hydride and distilled before use.

Reactants. *p*-Methoxystyrene was purchased from Aldrich, distilled from CaH_2, and stored under argon at −15 °C. Methyl glyoxylate hemiacetal (Aldrich), malononitrile, and methyl cyanoacetate (Aldrich) were vacuum-distilled before use.

Dimethyl Cyanofumarate. To a 200-mL round-bottom flask fitted with a Soxhlet extractor containing activated molecular sieves were added 25 g (0.25 mol) of methyl cyanoacetate, 60 g (0.5 mol) of methyl glyoxylate hemiacetal, and 75 mL of dry acetonitrile. The reaction mixture was refluxed for 3 h, and excess glyoxylate and acetonitrile were evaporated. The resulting oil was vacuum-distilled in a Kugelrohr apparatus (100 °C (0.05 mmHg)). The distillate partly solidified. The combined material was recrystallized from a dry ether–petroleum ether mixture to give a white crystalline solid: mp 59.5–60 °C (lit. mp 59–60.5 °C); yield 19.6 g (46.1%); NMR ($CDCl_3$) δ 3.92 (s, 3 H), 3.96 (s, 3 H), 7.47 (s, 1 H); IR (KBr, neat) 2237, 1737–1715, 1634 cm^{-1}.

Trapping Experiment. A mixture of *p*-methoxystyrene (0.4 g, 3 mmol), dimethyl cyanofumarate (0.5 g, 2 mmol), and 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) (0.18 g, 1.15 mmol) was reacted in 5 mL of acetonitrile under an inert atmosphere for 115 h at room temperature. The reaction mixture was analyzed by reverse-phase liquid chromatography (Chemcosorb-5-ODS-H packing; column 4.6 × 150 mm; mobile phase $CH_3CN/H_2O = 7/3$ (v/v); flow rate 9.85 mL/min; refractive index detector). Isolation of the adduct was carried out by thin-layer chromatography (Merck Kieselgel 60 HF_{254}) in chloroform. The product was recrystallized from diethyl ether under an inert atmosphere: mp 130–132 °C; yield 23%; IR (KBr) 2950, 2250 (CN), 1730 and 1710 (C═O), 1630 (N—O), 1608 (aromatic), 1230 cm^{-1}; FAB/MS m/z 459 $(M + 1)^+$, 302 (458 − 156; TEMPO); ^{1}H NMR ($CDCl_3$) δ 0.25, 0.99, 1.19, 1.34 (s, 12 H, TEMPO CH_3), 1.2–1.5 (m, 6 H, TEMPO CH_2), 2.08 (ddd, 1 H, H_{2ax}), 2.80 (ddd, 1 H, H_{2eq}), 3.79, 3.83, 3.95 (s, 9 H, CH_3 ester and methoxy), 4.19 (dd, 1 H, H_{3ax}), 4.92 (dd, 1 H, H_{1eq}), 6.87 (dd, 1 H, H_b), 6.93 (d, 1 H, H_a), 7.54 (d, 1 H, H_c) (the coupling constants were determined from decoupled spectra: $J_{1eq,2ax} = 3.2 \pm 0.2$ Hz, $J_{1eq,2eq} = 2.0 \pm 0.5$ Hz, $J_{2ax,2eq} = -14.2 \pm 0.2$ Hz, $J_{2ax,3ax} = 12.7 \pm 0.5$ Hz, $J_{2eq,3ax} = 2.5 \pm 0.2$ Hz, $J_{1eq,3ax} = 0$, $J_{ab} = 8.5 \pm 0.2$ Hz, $J_{bc} = 2.6 \pm 0.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 17.2 (t, C7), 20.6 (2 q, C1, C2), 27.8 (t, C11), 32.7, 34.7 (2 q, C3, C4), 40.3 (2 t, C6, C8), 42.3 (d, C10), 50.9 (s, C13), 53.5, 54.1, 55.4, (3 q, C23, C25, C20), 59.5, 61.0 (2 s, C5, C9), 74.4 (d, C12), 111.6, 114.3 (2 d, C17, C19), 117.8 (s, C21), 127.8, 131.3 (2 s, C14, C15), 135.2 (d, C16), 160.4 (s, C18), 168.4 (s, C24), 171.6 (s, C22). Anal. Calcd for $C_{25}H_{34}N_2O_6$: C, 65.60; H, 7.42; N, 6.11. Found: C, 65.42; H, 7.43; N, 5.94.



Polymerization. A solution of each monomer was introduced under an argon atmosphere in separate arms of a polymerization Y-tube. Both solutions were degassed twice and mixed after reintroduction of an argon atmosphere. The lemon yellow color of the EDA complex appeared immediately upon mixing. For the kinetic study, aliquots were taken at intervals, diluted, and injected on the SEC. Exposure to air immediately quenched the polymerization. The peak area of the donor peak allowed us to follow the disappearance of monomer as a function of time by using a calibration curve. In a few cases the disappearance of acceptor was also monitored, and A was consumed at the same rate as D. Independent of the monomer ratio, a 1:1 alternating copolymer was always obtained. These runs were reproducible: NMR ($CDCl_3$) δ 6.3–7.0 (broad, 9 H), 1.7–3.1 (broad, 4 H). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.37; H, 5.62; N, 4.62. Found: C, 62.28; H, 5.47; N, 4.56.

Acknowledgment. We are deeply indebted to Du Pont for generous support of this research. Partial support by the National Science Foundation, Division of Materials Research (Grant No. DMR-84-00970), is also gratefully acknowledged. We also wish to thank Professor Michael Szwarc for a critical reading of the manuscript.

Registry No. 1, 106230-81-3; D, 637-69-4; A, 54797-29-4; (D)(A) (alternating copolymer), 77321-33-6; TEMPO, 2564-83-2; dihydropyran cycloadduct, 77321-38-1.

References and Notes

(1) Borden, W. T. *React. Intermed.* **1981**, *2*, 175.
(2) Scaiano, J. C.; Lissi, E. A.; Encinas, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139.
(3) Bartlett, P. D. *Q. Rev. Chem. Soc.* **1970**, *24*, 473.
(4) Pasto, D. J.; Warren, S. E.; Weyenberg, T. *J. Org. Chem.* **1986**, *51*, 2106.
(5) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.
(6) Gundermann, K. D.; Roehrl, E. *Justus Liebigs Ann. Chem.* **1976**, 1661.
(7) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929.
(8) Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1494.
(9) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.
(10) Flory, P. J. *J. Am. Chem. Soc.* **1937**, *59*, 241.
(11) Mayo, F. R. *J. Am. Chem. Soc.* **1953**, *75*, 6133.
(12) Pryor, W. A.; Laswell, L. D. *Adv. Free-Radical Chem.* **1975**, *5*, 27.
(13) Rizzardo, E.; Serelis, A. K.; Solomon, D. H. *Aust. J. Chem.* **1982**, *35*, 2013.
(14) Kauffmann, H. F.; Olaj, O. F.; Breitenbach, J. W. *Makromol. Chem.* **1976**, *177*, 939.

(15) Kauffmann, H. F.; Harms, H.; Olaj, O. F. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2943.
(16) Lingnau, J.; Stickler, M.; Meyerhoff, G. *Eur. Polym. J.* **1980**, *16*, 785.
(17) Shirota, Y.; Mikawa, H. *J. Macromol. Sci., Rev. Macromol. Chem.* **1978**, *C16*, 129.
(18) Shirota, Y. *Encycl. Polym. Sci. Eng.* **1985**, *3*, 327.
(19) Hill, D. J. T.; O'Donnell, J. J.; O'Sullivan, P. W. *Prog. Polym. Sci.* **1982**, *8*, 215.
(20) Cowie, J. M. G., Ed. *Alternating Copolymers*; Plenum: New York, 1985.
(21) Iwatsuki, S.; Yamashita, Y. *Prog. Polym. Sci. Jpn.* **1971**, *2*, 1.
(22) Yoshimura, M.; Nogami, T.; Yokoyama, M.; Mikawa, H.; Shirota, Y. *Macromolecules* **1976**, *9*, 211.
(23) Shirota, Y.; Mikawa, H.; Yoshimura, M. *Macromolecules* **1978**, *11*, 1085.
(24) Kokubo, T.; Iwatsuki, S.; Yamashita, Y. *Makromol. Chem.* **1969**, *123*, 256.
(25) Nagai, K.; Akiyama, K.; Kuramoto, N. *Makromol. Chem.* **1985**, *186*, 1855.
(26) Nagai, K.; Akiyama, K.; Kuramoto, N. *Makromol. Chem.* **1985**, *186*, 1863.
(27) Nagai, K.; Yonezawa, H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 115.
(28) Nagai, K.; Nachida, S.; Nonaka, T. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 773.
(29) Sato, T.; Abe, M.; Otsu, T. *J. Macromol. Sci., Chem.* **1981**, *A15*, 367.
(30) Russell, K. E.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1953**, *75*, 5052.
(31) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22.
(32) Padias, A. B.; Hedrick, S. T.; Hall, H. K., Jr. *J. Org. Chem.* **1983**, *48*, 3787.
(33) Bevington, J. C. *Trans. Faraday Soc.* **1955**, *51*, 1392.
(34) Hanna, M. W.; Ashbough, A. L. *J. Phys. Chem.* **1964**, *4*, 811.
(35) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53.
(36) Mulvaney, J. E.; Cramer, R. J.; Hall, H. K., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 309.
(37) Gaylord, N. G. *J. Polym. Sci., Part C* **1970**, *31*, 247.
(38) Plochocka, K. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981**, *C20*, 407.
(39) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.

Sulfomaleation of EPDM Polymers

Warren A. Thaler,*[†] Stanley J. Brois,[‡] and Francis W. Ferrara[†]

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801, and Paramins Technology Division, Exxon Chemical Company, Linden, New Jersey 07036.

Received June 23, 1986

ABSTRACT: The introduction of polar functionality into hydrocarbon polymers has been studied extensively in our laboratory as a means of producing sulfonate ionomers. Another method for introducing polar functionality is the maleation of hydrocarbon polymers, the anhydride functionality being useful for bonding polar molecules such as amines. Sulfonation is quite vigorous and, under the proper circumstances, is very effective with the low level of unsaturated sites present in a number of hydrocarbon elastomers. Maleic anhydride, to the contrary, exhibits low reactivity, and alternative measures such as prior halogenation–dehydrohalogenation or free radical grafting are required. We wish to report a process called "sulfomaleation" to simultaneously introduce sulfonate ionomer functionality and reactive anhydride groups into elastomers. To accomplish this, we have used sulfonate-substituted maleic anhydrides. The presence of the strongly electrophilic sulfonate activates the maleic group and substantially increases its reactivity with low functionality hydrocarbon rubbers, presumably via an Alder–ene type of reaction. In this preliminary report, we have attempted to elucidate the structures of sulfomaleic anhydride and derivatives and have conducted some screening experiments to demonstrate the formation of polymer adducts and their ability to covalently bond amine to polymers.

The sulfonation[1-3] of low-functionality elastomers such as ethylene–propylene terpolymer (EPDM rubber) has been used extensively in our laboratory to produce ionomers. The introduction of low levels of metal or amine sulfonate results in ionomers[4] with remarkable physical properties. Another chemical modification, the reaction of polymers with maleic anhydride, is used extensively to introduce reactive anhydride functionality into hydrocarbon polymers. An Alder–ene reaction can be utilized to react with the olefin sites of polymers such as low molecular weight ($M_n \sim 1000$) polyisobutylene; however, with many polymers such as EPDM the olefin is not sufficiently reactive. Thus, free radical grafting of maleic anhydride onto saturated hydrocarbon polymers, usually initiated by peroxides, is a major means of introduction of reactive functionality. There are numerous problems connected with free radical grafting of maleic anhydride onto hydrocarbon polymers. The process is nonselective and reactions in solution give extensive maleic grafting to solvent. Furthermore, the hydrocarbon polymer radicals can combine and/or undergo scission, resulting in cross-linking or molecular weight breakdown, depending on the polymer structure. This is a serious disadvantage for some applications.

We wish to report a novel chemical technique that enables us to readily introduce both sulfonate and maleic anhydride functionality in EPDM polymers. The reagents that we have investigated are sulfomaleic anhydride and its derivatives.

A salt derived from sulfomaleic anhydride was first described in 1930,[5] but it was not until 1973 that French workers[6] first reported the preparation of sulfomaleic anhydride free acid (1) by the reaction of SO_3 and maleic anhydride. A search of the literature turned up little regarding this compound. Several patents have been issued covering detergent compositions prepared by reacting alcohols with sulfomaleic anhydride. Some work by Gruzdev[7] on the preparation of some derivatives was published in 1979. No reactions of sulfomaleic anhydride

---

[†] Corporate Research Science Laboratories.
[‡] Paramins Technology Division.

0024-9297/87/2220-0254$01.50/0 © 1987 American Chemical Society