Macromolecules 1984, *17*, 2005–2009

C	polymer concentration (percent weight unless otherwise indicated)
f	initiator efficiency
g	grams
[I]	initiator concentration ((g mol)/L)
k	reaction rate constant
l	cell path length (cm)
M	molecular weight
[M]	monomer concentration
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
N	number of species present in the solution
p	weight fraction
R_p	rate of polymerization
R_i	rate of initation
x	mole fraction
ϵ	extinction coefficient (AU)/[(% wt) cm] unless otherwise indicated
λ	wavelength (nm)

Subscripts

i	ith concentration
j	jth wavelength
M	molar
n	nth component
0	initial value
T	overall

Registry No. BPO, 94-36-0; polystyrene (homopolymer), 9003-53-6; poly(butyl methacrylate) (homopolymer), 9003-63-8; poly(isobutyl methacrylate) (homopolymer), 9011-15-8; ethyl benzoate, 93-89-0; benzyl benzoate, 120-51-4; phenyl benzoate, 93-99-2; diphenylmethane, 101-81-5; bibenzyl, 103-29-7; styrene, 100-42-5.

Supplementary Material Available: UV spectra of the model compounds (Appendix I) and Beer–Lambert law for weight-based measurements (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. J. Brussau and D. J. Stein, *Angew. Makromol. Chem.*, **12**, 59 (1970).

(2) B. Stutzel, T. Miyamoto, and H. J. Cantow, *Polym. J.*, **8** (3), 247 (1976).

(3) E. Gruber and W. Knell, *Makromol. Chem.*, **179**, 733 (1978).

(4) L. H. Garcia Rubio, *J. Appl. Polym. Sci.*, **27**, 2043 (1982).

(5) L. H. Garcia Rubio, J. F. MacGregor, and A. E. Hamielec, 181st National Meeting of the American Chemical Society, Atlanta, Mar 29–Apr 3, 1981.

(6) L. H. Tung, "Fractionation of Synthetic Polymers", Marcel Dekker, New York, 1977.

(7) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953.

(8) G. Odian, "Principles of Polymerization", Wiley, New York, 1970.

(9) H. F. Pfann, V. Z. Williams, and H. Mark, *J. Polym. Sci.*, **1**, 14, (1946).

(10) K. E. J. Barrett, *J. Appl. Polym. Sci.*, **11**, 1617 (1967).

(11) K. C. Berger, P. C. Deb, and G. Meyerhoff, *Macromolecules*, **10** (5), 1075 (1977).

(12) M. K. Mishra, *J. Macromol. Sci.*, **C20** (1), 149 (1981).

(13) G. Moad, E. Rhizzardo, and D. H. Solomon, *J. Macromol. Sci.*, **A17** (2), 51 (1982).

(14) G. Moad, D. H. Solomon, S. Johns, and R. I. Willing, *Macromolecules*, **15**, 1188 (1982).

(15) L. H. Garcia Rubio and N. Ro, "Statistical Analysis of Spectroscopy Models", to be published.

(16) D. M. Himmelblau, "Process Analysis by Statistical Methods", Wiley, New York, 1970.

(17) T. L. Sutton and J. F. MacGregor, *Can. J. Chem. Eng.*, **55**, 603 (1977).

(18) H. Martens, Symposium on Applied Statistics, DTH, Lyngby, Denmark (393), Jan 1980.

(19) L. H. Garcia Rubio and K. F. O'Driscoll, in preparation for publication.

(20) F. W. Billmeyer, "Textbook of Polymer Science", Wiley, New York, 1971.

(21) G. Gleixner, O. F. Olaj, and J. W. Breitenbach, *Makromol. Chem.*, **180**, 2581 (1979).

(22) H. H. Jellineck, in "Styrene", R. Boundy and R. Boyer, Eds., Reinhold, New York, 1952.

(23) M. Singh and V. S. Nandi, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 121 (1979).

(24) A. E. Hamielec and N. Fris, "Introduction to Chain Polymerization Kinetics", short course notes, McMaster University, 1980.

(25) S. T. Balke and R. D. Patel, in *ACS Symp. Ser., No. 138*, 1980.

(26) S. T. Balke and R. D. Patel, *Sep. Purif. Methods*,**11** (1), 1–28 (1982).

(27) J. C. Bevington and C. S. Brooks, *J. Polym. Sci.*, **22**, 257 (1956).

Study of the Microstructure of Tetrahydrofuran–3-Methyltetrahydrofuran Copolymers: Computer Simulation of the Copolymerization Reaction

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ABSTRACT: The cationic copolymerization of tetrahydrofuran (A) and 3-methyltetrahydrofuran (B) was studied at 0 °C with acetylhexafluoroantimonate as initiator. The values of the apparent reactivity ratios, calculated by the Kelen–Tüdos method, were $r_A{}^{ap} = 0.78 \pm 0.06$ and $r_B{}^{ap} = 0.15 \pm 0.05$. Values of both the composition and the dyad probabilities were obtained by ^{1}H NMR and ^{13}C NMR spectroscopy, respectively. The microstructure of the copolymers determined from the apparent reactivity ratios differs from that obtained by ^{13}C NMR spectroscopy, indicating that the THF–MTHF system does not obey the classical kinetic scheme in which only four propagation constants are considered. Monte Carlo computer simulations of the copolymerization with complete reversibility were made. Good agreement between the simulated values of both the composition and dyad probabilities with the experimental ones was obtained for the following values of the cross-propagation and depropagation rate constants: $k_{ab} = 6 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$ (both in L mol^{-1} s^{-1}) and $k_{-ab} = 5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$ (both in s^{-1}).

Introduction

The Mayo–Lewis equation has been traditionally used to determine the reactivity ratios of copolymers in which depropagation reactions are absent. The possible use of irreversible copolymerization equations of this type for the description of reversible reactions was studied by O'Driscoll et al.[1,2] in the analysis of some copolymerization systems in which reversibility of the propagation reactions must

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be considered. Other attempts were also made to derive the copolymer composition equation for copolymers with reversibility, the most notable being that of Lowry[3] for one depropagating monomer.[4-6] Treatments were further developed for copolymerizations with reversibility in both homopropagation and cross-propagation reactions.[7-12] However, these methods have not yet been applied to real systems in which the comonomers are heterocycles. The reason may be that the study of this type of copolymerization requires the use of monomers with low ring strain in order that the concentrations of monomer in equilibrium corresponding to the homopolymerization reactions are large enough so that the depropagation rate constants can be easily determined; moreover, it would be convenient that living polymers are formed.

Two monomers specially suitable to study the influence of depropagation reactions on the composition and microstructure of copolymers are tetrahydrofuran (THF) and 3-methyltetrahydrofuran (MTHF). The polymerization of THF has been widely investigated in such a way that the kinetic and thermodynamic parameters are well-known.[13,14] As for MTHF, the cationic polymerization of this monomer ring was recently investigated.[15] These studies showed that living polymers are formed, the ceiling temperature (4 ± 1 °C) being significantly lower than that of THF (86 °C),[13] presumably owing to entropic effects. Although the copolymerization of THF–MTHF was studied by Stratmann et al.,[16] this study was only qualitative in the sense that the influence of the depropagation reactions on the composition and the microstructure of the copolymers was not determined. Therefore, the present investigation focuses on the study of the copolymerization kinetics of THF–MTHF using an oxonium salt with a very stable counterion as initiator which gives rise to living polymers in the case of the homopolymerization of the monomers. The analysis of the microstructure of the copolymers, as determined by ^{13}C NMR spectroscopy, is utilized to estimate the cross-propagation rate constants by Monte Carlo techniques.

Experimental Part

Materials. Tetrahydrofuran was refluxed with potassium hydroxide for 3–4 h, distilled in vacuo, and stored into a sodium mirror. 3-Methyltetrahydrofuran was refluxed successively over potassium hydroxide and over sodium for several hours; it was further distilled in vacuo into a sodium mirror. Acetyl chloride was distilled under a nitrogen atmosphere immediately before use. Silver hexafluoroantimonate was washed in vacuo with SO_2, filtered, and stored in the dark in vacuo.

Initiator. The initiator, acetyl hexafluoroantimonate, was prepared by reaction of silver hexafluoroantimonate and acetyl chloride at −78 °C in tetrahydrofuran solution. The silver chloride formed was eliminated by filtration at this temperature. All these operations were carried out under high vacuum.

Copolymerization Reactions. The copolymerization reactions were carried out in bulk at 0 °C. Thermostatic baths were used in which the temperature precision was ±0.05 °C. The reactions were followed by conventional dilatometric techniques until conversions of about 10% were obtained. The reactions were quenched with an aqueous solution of sodium carbonate, and the copolymers were extracted with benzene, precipitated with methanol, and dried in vacuo.

Characterization. The copolymers were characterized by ^1H NMR and ^{13}C NMR spectroscopy with deuterated chloroform as solvent and tetramethylsilane as internal reference. The ^1H NMR spectra were registered with a Varian XL-100 spectrometer at 100 MHz. The ^{13}C NMR spectra were recorded at the same temperature with a Bruker HX-90E Fourier spectrometer operating at 22.63 MHz; quantitative spectra were obtained by using long pulse delay times (>10 s) and inverse gated decoupling techniques in order to eliminate nuclear Overhauser enhancement. The composition of the copolymers was determined by ^1H NMR spectroscopy from the areas of the resonance signals at about 0.9 ppm, where no overlapping occurs, corresponding to the methyl group of the MTHF structural unit (see Figure 1). The feed compositions and the compositions of the copolymers are shown in Table I.

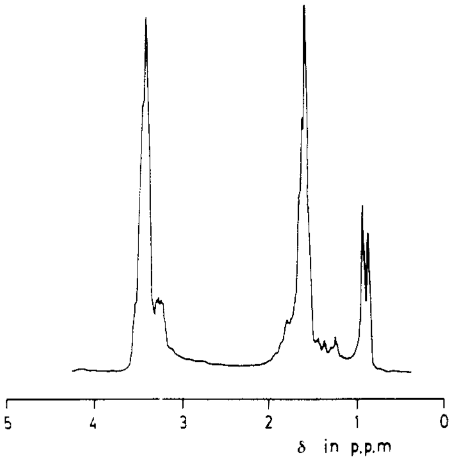


Figure 1. ^1H NMR spectrum of a THF–MTHF copolymer in which the mole fraction of THF is 0.68.

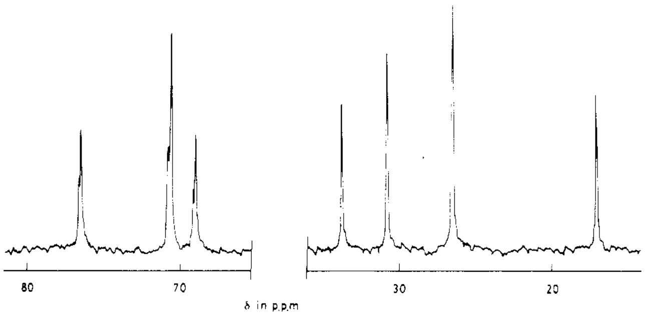


Figure 2. ^{13}C NMR spectrum of a THF–MTHF copolymer in which the mole fraction of THF is 0.47.

Table I
Experimental Results for the Tetrahydrofuran–3-Methyltetrahydrofuran Copolymerization[a]

A, mol L^{-1}	B, mol L^{-1}	F_A	f_A	$M_{n_{theor}}$	$M_{n_{exptl}}$
10.96	1.12	0.91	0.90		
9.37	2.41	0.79	0.80		
8.22	3.35	0.71	0.72	12 900	16 600
7.40	4.02	0.65	0.68		
6.13	5.05	0.55	0.63	19 500	20 200
3.08	7.54	0.29	0.47	13 000	13 500
1.32	8.97	0.12	0.34	12 300	13 800

[a] A and B are, respectively, the mole concentrations of THF and MTHF in the feed. F_A and f_A are the mole fractions of THF in the feed and in the copolymer, respectively.

Number-average molecular weights of the copolymers were measured with a Knauer vapor pressure osmometer in chloroform solutions.

Results and Discussion

Microstructure of the Copolymers. The microstructure of the copolymers was analyzed by ^{13}C NMR spectroscopy. The spectrum of a copolymer, shown in Figure 2, presents several resonance signals, which can be assigned by considering the spectrum of the parent homopolymers. The ^{13}C NMR spectrum of poly(3-methyltetrahydrofuran)[17] shows that the splits of the resonance signals belonging to the two oxymethylene carbons (doublets at 69.04 and 69.21 ppm and at 76.42 and 76.53 ppm) are due to the presence of different structures, head-to-head, head-to-tail, and tail-to-tail, as a consequence

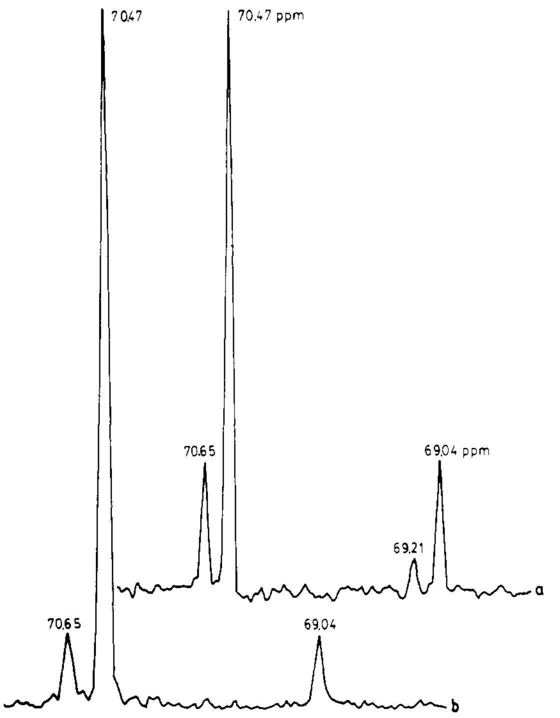
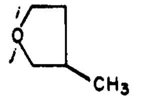


Figure 3. Expanded ^{13}C NMR spectra in the region 68–71 ppm for THF–MTHF copolymers in which the mole fractions of THF are 0.37 (a) and 0.20 (b).

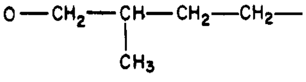
of ring opening through the *i* or *j* bonds in the monomer ring



It is obvious that the ring opening of MTHF through these bonds in the copolymerization with THF may also produce anomalous structures in the chain. Consequently, the THF–MTHF copolymers must be considered as terpolymers with the following structural units:

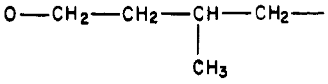
$\text{O—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$

A



$\text{O—CH}_2\text{—}\underset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{—CH}_2\text{—CH}_2\text{—}$

B_i



$\text{O—CH}_2\text{—CH}_2\text{—}\underset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{—CH}_2\text{—}$

B_j

The resonance of the oxymethylene carbons in the structural unit of THF appears as a doublet at 70.65 and 70.47 ppm, corresponding, respectively, to the carbons with or without a methyl group in the δ position with respect to the oxymethylene carbon. Therefore, it is possible to calculate the probabilities of the corresponding dyads, $P(AB_i) + P(B_jA) = P(AB)$, for the copolymers from the areas of the peaks at 70.65 ppm. Moreover, the presence of different dyads BB with head-to-head, head-to-tail, and tail-to-tail structures can be detected from the doublets at 69.04 and 69.21 ppm as was reported elsewhere.[17] The expanded ^{13}C NMR spectra in the region between 68 and 71 ppm are shown in Figure 3 for two copolymers whose mole fractions in MTHF (f_B) are 0.20 and 0.37. The copolymer with higher content in this monomer (labeled a) presents two doublets centered about 69.1 and 70.5 ppm, respectively. The signal at 69.21 ppm corresponds to head-to-tail (or tail-to-head) structures in the dyads BB whereas the signal at 69.04 ppm corresponds to the other possible dyads, including the alternating dyads with the THF structural unit. In the spectrum (labeled b) in Figure 3, the resonance of the oxymethylene carbons of THF appears as a doublet (70.47, 70.65 ppm) whereas only a resonance peak appears at 69.04 ppm, indicating that the structural units of 3-methyltetrahydrofuran are isolated in this copolymer. The peak at 69.21 ppm is not detected for copolymers in which $f_B < 0.20$. The probabilities of the dyads BB and BA, P(BB) and P(BA), can also be calculated from the signals of the doublets centered about 69.1 ppm. The experimental values of the dyad probabilities are indicated in Table II.

Table II
Experimental Dyad Probabilities for Tetrahydrofuran-3-Methyltetrahydrofuran Copolymers

f_A	P(AA)	P(AB)	P(BB)
0.90	0.80	0.10	≈0
0.80	0.60	0.20	≈0
0.63	0.37	0.26	0.11
0.47	0.18	0.29	0.24
0.34	0.12	0.22	0.44

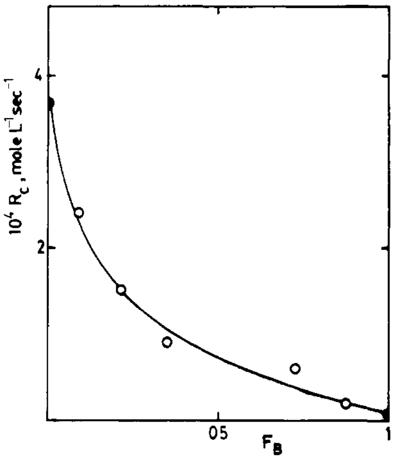


Figure 4. Influence of the mole fraction of MTHF in the feed on the copolymerization rate at 0 °C. Initiator concentration = 7.3×10^{-3} mol L^{-1}.

Kinetics of Copolymerization. Values of the experimental and theoretical number-average molecular weights for some of the copolymers are given in the fifth and sixth columns of Table I. The relatively good agreement between the theoretical and the experimental values seems to suggest that "living copolymers" are obtained, in agreement with what occurs in the homopolymerization of THF[13,14] and MTHF.[15]

The effect of the initial feed mixture on the copolymerization rate is shown in Figure 4, where a great influence of the content of MTHF is observed. The homopolymerization rates were calculated from the values of the propagation rate constants and equilibrium monomer concentrations reported for the bulk polymerizations of THF[13,14,18] and MTHF.[15] It can be seen that small quantities of MTHF greatly decrease the copolymerization rates; for example, when the mole fraction of this monomer in the feed is about 0.15, the copolymerization rate is half of the homopolymerization rate of tetrahydrofuran.

By comparing the feed compositions and the composition of the copolymers given in the third and fourth columns of Table I, one can observe that THF is preferentially incorporated in the copolymer chain when the mole fraction of this monomer in the feed (F_A) is lower than 0.7, the copolymerization being almost azeotropic otherwise. Our results differ from those reported by Stratmann et al.[16] for the same copolymerization carried out at 10 °C with

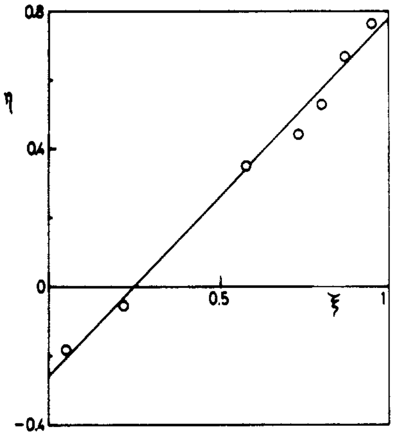


Figure 5. Kelen–Tüdos plot for the copolymerization of THF and MTHF (see ref 19).

$BF_3 \cdot Et_2O$ as initiator. In this case, the content of THF in the copolymers was higher than that obtained in our work, presumably because these workers performed the experiments at higher temperature than the "ceiling temperature" of MTHF,[15] and it is reasonable to assume that under these conditions the addition of THF is much more favored.

The calculation of the reactivity ratios in the THF–MTHF copolymerization presents some problems because the equilibrium monomer concentrations for both monomers are important at the polymerization temperature of 0 °C (about 2 and 8.8 mol L^{-1}, respectively).[18,15] However, Kang and O'Driscoll[1,2] suggested that copolymerization reactions in which depropagation takes place might be adequately described by means of the classical Lewis–Mayo equation in such a way that apparent reactivity ratios could thus be obtained. In this manner, the apparent reactivity ratios were determined from the experimental data at low conversions by the usual procedures. The Kelen–Tüdos plot,[19] shown in Figure 5, is a straight line over the entire composition interval, indicating that the composition of the copolymers obeys the classical copolymerization assuming apparent forward rate constants without considering the possibility of depropagation. The values obtained for $r_A^{ap} = k_{aa}^{ap}/k_{ab}^{ap}$ and $r_B^{ap} = k_{bb}^{ap}/k_{ba}^{ap}$, where k_{ij}^{ap} are the apparent propagation rate constants for homopropagation (k_{aa}^{ap} and k_{bb}^{ap}) and cross propagation (k_{ab}^{ap} and k_{ba}^{ap}), were $r_A^{ap} = 0.78 \pm 0.06$ and $r_B^{ap} = 0.15 \pm 0.05$.

Usually, the microstructure of the copolymers is determined from the apparent reactivity ratios. For instance, the probability of the alternating dyads, $P(AB)$, can be calculated by using the equation

$$P(AB) = f_A/(1 + r_A^{ap}X_A) \qquad (1)$$

where X_A is the monomer ratio (A/B) in the feed mixture. Analogously, the other dyads can be obtained. The experimental values of $P(AB)$, obtained by ^{13}C NMR spectroscopy, and those obtained from the apparent reactivity ratios are shown, as a function of the mole fraction (f_B) of MTHF in the copolymers, in Figure 6. It can be observed that good agreement between both values is obtained only when f_B is lower than 0.3, but for higher content of this monomer the differences are very important, indicating that the apparent reactivity ratios do not explain satisfactorily the copolymerization of systems such as THF–MTHF, in which the depropagation rate constants play an important role.

Monte Carlo Simulation of the Copolymerization. From the analysis of the microstructure of the copolymers,

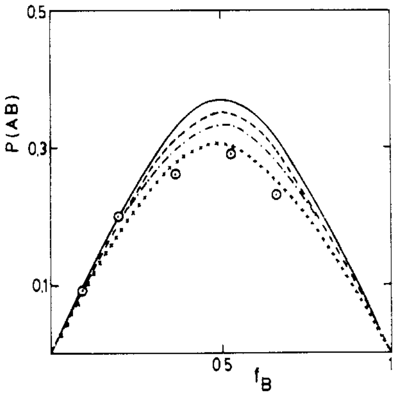


Figure 6. Simulated dyad probabilities obtained by using the following set of cross-propagation and depropagation rate constants: (– – –) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 5.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 16 \times 10^{-3}$; (–·–) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 1.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$; (×) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 5.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$; (—) calculated from the apparent reactivity ratios; (⊙) experimental results from ^{13}C NMR spectroscopy. k_{ab} and k_{ba} are given in L mol^{-1} s^{-1} and k_{-ab} and k_{-ba} are in s^{-1}.

it is clear that the THF–MTHF system does not obey the classical kinetic scheme in which only four propagation rate constants are considered. Therefore, another approach should be used. Since the copolymerization may be considered a stochastic process, Izu and O'Driscoll[20] suggested the application of Monte Carlo techniques to study reversible copolymerization reactions. However, these methods have not yet been applied to real copolymerization systems of heterocyclic monomers. In the case of the so-called dyad model in which the sequence in the terminal dyad affects the fate of the next step, eight constants are defined as shown in the following kinetic scheme:

$$\sim\sim A^+ + A \underset{k_{-aa}}{\overset{k_{aa}}{\rightleftarrows}} \sim\sim AA^+$$

$$\sim\sim A^+ + B \underset{k_{-ab}}{\overset{k_{ab}}{\rightleftarrows}} \sim\sim AB^+$$

$$\sim\sim B^+ + B \underset{k_{-bb}}{\overset{k_{bb}}{\rightleftarrows}} \sim\sim BB^+$$

$$\sim\sim B^+ + A \underset{k_{-ba}}{\overset{k_{ba}}{\rightleftarrows}} \sim\sim BA^+$$

Following Izu and O'Driscoll,[20] the probabilities of occurrence of the events (addition of either monomer and detaching the chain unit) assigned to four different dyads are expressed, for example, for AA dyads as

$$\begin{aligned} P_{AA(+A)} &= k_{aa}[A]/D_1 \\ P_{AA(+B)} &= k_{ab}[B]/D_1 \qquad (2) \\ P_{AA(-A)} &= k_{-aa}/D_1 \end{aligned}$$

where $D_1 = k_{aa}[A] + k_{-aa} + k_{ab}[B]$. Four rate constants were estimated from the homopolymerization reactions of both THF[13,14,18] and MTHF.[15] Their values at 0 °C are $k_{aa} = 5 \times 10^{-3}$, $k_{bb} = 8.2 \times 10^{-4}$ (in L mol^{-1} s^{-1}) and $k_{-aa} = 10^{-2}$, $k_{-bb} = 7 \times 10^{-3}$ (in s^{-1}). The starting values of the two cross-propagation rate constants were obtained by assuming that the values of the apparent and real reactivity ratios are similar. Tentative values of the depropagation rate constants (k_{-ab} and k_{-ba}) were estimated by assuming that the free energy of the cross-propagation reactions is the average of the two free energies of homopropagation.[13,15]

Twenty polymer chains were generated by means of the Monte Carlo method for each of the feed compositions

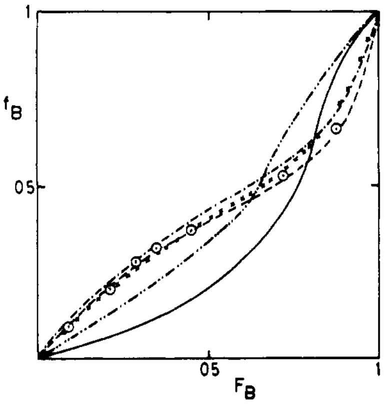


Figure 7. Simulated composition diagram obtained by using the following set of cross-propagation and depropagation rate constants: (—) $k_{ab} = 1.2 \times 10^{-3}$, $k_{-ab} = 5.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$; (- - -) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 5.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 16 \times 10^{-3}$; (-·-) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 1.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$; (-··) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 5.0 \times 10^{-3}$, $k_{ba} = 0.7 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$; (×) $k_{ab} = 6.0 \times 10^{-3}$, $k_{-ab} = 5.0 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$; (⊙) experimental results. k_{ab} and k_{ba} are given in L mol^{-1} s^{-1} and k_{-ab} and k_{-ba} are in s^{-1}.

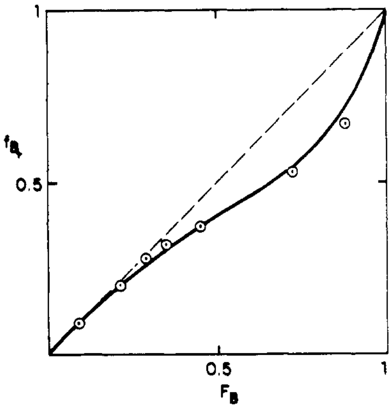


Figure 8. Simulated composition diagram (—) obtained with the following cross-propagation and depropagation rate constants: $k_{ab} = 6 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$ (in L mol^{-1} s^{-1}) and $k_{-ab} = 5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$ (in s^{-1}). (⊙) Experimental values.

given in the first column of Table I. Random experiments were stopped in the case that the number of monomer units exceeded 500. The influence of the cross-propagation and depropagation rate constants is shown in Figures 6 and 7. The results plotted in Figure 7 indicate that the composition of the copolymers is very sensitive to the cross-propagation rate constants, the influence of the cross-depropagation rate constants being in comparison negligible. However, the microstructure of the copolymers is moderately dependent on the values of k_{-ab} and k_{-ba} as can be seen in Figure 6. The calculations show that the best set of values to simulate the composition and microstructure of the copolymers is $k_{ab} = 6 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$ (both in L mol^{-1} s^{-1}) and $k_{-ab} = 5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$ (both in s^{-1}). The values of the composition and the dyad probabilities obtained by using this set of values are shown in Figures 8 and 9. It can be observed that there is very good agreement between the simulated values and the experimental results.

The analysis of the results obtained for the cross-depropagation rate constants shows that the value of k_{-ab} is much lower than k_{-ba}, implying that the back-cyclization of MTHF is favored with regard to that of THF. As for the cross-propagation rate constants k_{ab} and k_{ba}, the simulations suggest that k_{ab} should be somewhat larger than k_{ba}. The reason may be that the nucleophilicity of both monomers is similar and the nucleophilic attack of the oxygen of MTHF on the α carbon of the THF cation is less hindered than in the case of its own monomer. On the contrary, the nucleophilic attack of the oxygen of THF on the α carbon of the MTHF cation is sterically much more disfavored than in the case of the attack on its own monomer.

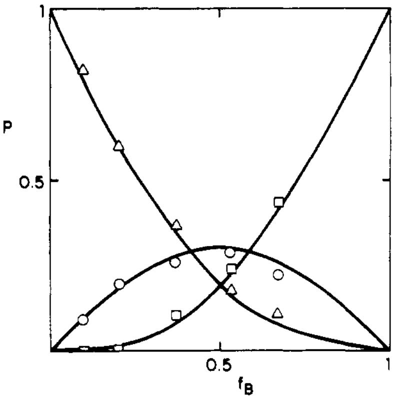


Figure 9. Simulated microstructure (—) of the copolymers using the cross-propagation and depropagation rate constants given in Figure 8. (○), (▲), and (□) represent, respectively, the experimental values of P(AB), P(AA), and P(BB).

Registry No. (Tetrahydrofuran)·(3-methyltetrahydrofuran) (copolymer), 38640-26-5; tetrahydrofuran, 109-99-9; 3-methyltetrahydrofuran, 13423-15-9.

References and Notes

(1) Kang, B. K.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1973**, *A7* (6), 1197.
(2) Kang, B. K.; O'Driscoll, K. F. *Macromolecules* **1973**, *7*, 886.
(3) Lowry, G. G. *J. Polym. Sci.* **1960**, *42*, 463.
(4) Yamashita, Y.; Kasahara, H.; Suyama, K.; Okada, M. *Makromol. Chem.* **1968**, *117*, 242.
(5) Kubisa, P.; Penczek, S. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1509.
(6) Garrido, L.; Guzmán, J.; Riande, E.; de Abajo, J. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3377.
(7) Hazell, J. E.; Ivin, K. J. *Trans. Faraday Soc.* **1962**, *58*, 342; **1965**, *61*, 2330.
(8) Sawada, H. *J. Polym. Sci., Part A-1*, **1967**, *5*, 1383.
(9) Theil, M. H. *Macromolecules* **1969**, *2*, 137.
(10) Howell, J. a.; Izu, M.; O'Driscoll, K. F. *J. Polym. Sci., Part A-1*, **1970**, *8*, 699.
(11) Izu, M.; O'Driscoll, K. F. *Polym. J.* **1970**, *1*, 27; *J. Polym. Sci., Part A-1* **1970**, *8*, 1687.
(12) Harvey, P. E.; Leonard, J. *Macromolecules* **1972**, *5*, 698.
(13) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528.
(14) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1.
(15) Garrido, L.; Guzmán, J.; Riande, E. *Macromolecules* **1981**, *14*, 1132.
(16) Stratmann, H.; Stützel, B.; Feinauer, R. *Angew. Makromol. Chem.* **1978**, *74*, 105.
(17) Garrido, L.; Guzmán, J.; Riande, E. *Macromolecules* **1983**, *16*, 1241.
(18) Matyjaszewski, K.; Slomkowsky, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.
(19) Kelen, T.; Tüdos, F. *J. Macromol. Sci., Chem.* **1975**, *A-9* (1), 1. η and ξ in Figure 5 are related to the mole fraction of monomer in the feed (F_A) and in the copolymer (f_A) by $\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$, where

$$G = \frac{F_A}{1 - F_A}\left(2 - \frac{1}{f_A}\right)$$

$$F = \left(\frac{F_A}{1 - F_A}\right)^2\left(\frac{1 - f_A}{f_A}\right)$$

and $\alpha = (F_m F_M)^{1/2}$, F_m and F_M being, respectively, the lowest and highest values of F in the experimental results.
(20) Izu, M.; O'Driscoll, K. F. *J. Polym. Sci., Part A-1* **1970**, *8* 1675.