Crystalline and amorphous poly[β-(2-cyanoethyl) β-propiolactone] (poly(CEPL)) samples were prepared by ring-opening polymerization of the corresponding monomer with the $(\mathrm{EtAlO})_n$ and $\mathrm{Et(ZnO)_2ZnEt}$ catalysts, respectively, and were fractionated with acetone.[15]

^{13}C-NMR Spectroscopy. ^{13}C-NMR spectra were recorded at 38°C with a Varian Model XL-100 spectrometer at 25.16 MHz with an F-T accumulator. The number of data points utilized for the F-T accumulation was 8192. For the poly(MPL), PHB, and poly(EPL) samples, the spectra were taken in $\mathrm{CDCl_3}$ solution, and for the poly(CEPL) samples the data were taken in $\mathrm{Me_2SO}$-d_6 solutions. The chemical shift values noted in Figures 1–3 were internally standardized from the solvent signals. The errors in the chemical shift values were ±0.04 ppm when the $\mathrm{Eu(DPM)_3}$ reagent was absent and ±0.2 ppm when the shift reagent was present. The separation between meso-dyad and racemic-dyad signals was ±0.04 ppm for the ^{1}C signals, ±0.07 ppm for the ^{2}C signals in the absence of the shift reagent, and ±0.1 ppm for the ^{2}C signals of the poly(MPL) in the presence of the shift reagent. The $\Delta\delta$ values used for describing the induced shift by the shift reagent is in the accuracy of ±0.2 ppm.

The $\mathrm{Eu(DPM)_3}$ shift reagent was found to give the best results among the shift reagents tested. The optimum concentration of the $\mathrm{Eu(DPM)_3}$ reagent was predetermined so as to minimize line broadening and insolubilization and to maximize the signal separation. The mol % concentration was defined as $\mathrm{Eu(DPM)_3}$ mol % of mol monomer unit in the polymers.

Acknowledgments. The authors express their thanks to Dr. K. Lee of our Department for recording ^{13}C-NMR spectra and for helpful discussions. A gift of the PHB sample from Professor Saburo Fukui's laboratory of Kyoto University and encouragement by the late Professor H. Tani are gratefully acknowledged.

References and Notes

(1) F. A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York, N.Y., 1972.

(2) M. Iida, T. Araki, K. Teranishi, and H. Tani, *Macromolecules*, **10**, 275 (1977).

(3) (a) R. Thiebout, N. Fisher, Y. Etienne, and I. Coste, *Ind. Plast. Mod. Elastomeres*, **14**, 1 (1962); (b) J. Cornibert, R. H. Marchessault, A. E. Allegrezza, Jr., and R. W. Lenz, *Macromolecules*, **6**, 676 (1973).

(4) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 452; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance For Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 149; (c) M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).

(5) J. Delsarte and G. Weill, *Macromolecules*, **7**, 343 (1974).

(6) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic Press, New York, N.Y., 1973; R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972).

(7) K. Teranishi, M. Iida, T. Araki, S. Yamashita, and H. Tani, *Macromolecules*, **7**, 421 (1974).

(8) M. Yokouchi, Y. Chatani, H. Tadokoro, and H. Tani, *Polym. J.*, **6**, 248 (1974).

(9) M. Yokouchi, Y. Chatani, H. Tadokoro, K. Teranishi, and H. Tani, *Polymer*, **14**, 267 (1973).

(10) The direction of the shift is normal for Eu ion and is consistent with the case of proton shift in PHB induced by $\mathrm{Eu(fod)_3}$ and $\mathrm{Eu(thd)_3}$ (ref 5).

(11) The polymer structure in solution would be highly sensitive to the solvent used. The fact that the tacticity separation of the poly(CEPL) samples was observed only at high concentration of the shift reagent may be due to high polarity of $\mathrm{Me_2SO}$. For the poly(EPL) sample, benzene was a poor solvent for tacticity separation.

(12) For simplification, the pseudocontact mechanism is considered predominant here, and contact or direct interaction mechanisms are neglected. Validity of the pseudocontact approximation in the ^{13}C NMR has been extensively discussed in ref 13. For the pseudocontact approximation, good correlations between ^{1}H- and ^{13}C-lanthanide shifts are shown in ref 13, though minor deviations due to contact mechanism were observed for the ^{13}C case.

(13) G. E. Hawkes, C. Marzin, D. Leibfritz, S. R. Johns, K. Herwig, R. A. Cooper, D. W. Roberts, and J. D. Roberts ref 6, p 129.

(14) This value was estimated from the shift values at a concentration of the shift reagent of 25 mol % to polymer unit, and the standard χ_i value for the racemic- or meso-dyad unit is not determined. The smaller $\Delta\chi_i$ value (~1°) was determined by assuming the $\chi_i \sim 0°$ or $\sim 180°$. More probable $\Delta\chi_i$ values will be in a range of 2–4°.

(15) T. Araki, S. Hayase, and M. Iida, unpublished results.

Polymerization of α,α-Disubstituted β-Propiolactones and Lactams. 14. Substituent, Solvent, and Counterion Effects in the Anionic Polymerization of Lactones

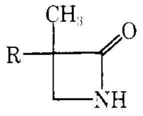
Ebrahim Bigdeli[†] and Robert W. Lenz*

Materials Research Laboratory, Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.

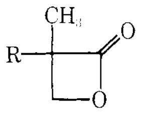
Received November 23, 1978

ABSTRACT: A series of β-propiolactones, substituted in the α position by two alkyl groups, was polymerized in two different dipolar aprotic solvents with two different anionic initiators. The anionic, ring-opening, polymerization reactions involved are bimolecular nucleophilic substitutions which show an apparent steric acceleration, but the increase in propagation rate constants observed with increasing size of the α substituent can be rationalized on the basis of either steric inhibition to ion-pair formation or a favorable hydrophobic interaction. The solvent effects observed are attributed to a greater importance of anion solvation than cation solvation in these ion pair reactions.

Previous publications from this laboratory have described the unusual substituent effects on the rates of anionic, ring-opening, polymerization reactions in dimethyl sulfoxide ($\mathrm{Me_2SO}$) for a series of β-propiolactams which were substituted in the α position with two alkyl groups, Ia–d, as follows.[1]



Ia, R = $\mathrm{CH_3}$
b, R = $\mathrm{CH_2CH_3}$
c, R = $\mathrm{(CH_2)_2CH_3}$
d, R = $\mathrm{(CH_2)_3CH_3}$



IIa, R = $\mathrm{CH_3}$
b, R = $\mathrm{CH_2CH_3}$
c, R = $\mathrm{(CH_2)_2CH_3}$
d, R = $\mathrm{(CH_2)_3CH_3}$

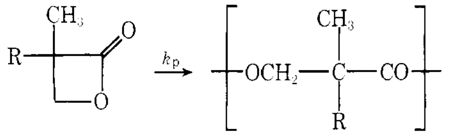
It was observed that when one of the substituents was the methyl group and the other was systematically increased in size within the *n*-alkyl homologous series as shown above, the apparent propagation rate constants unexpectedly increased with increasing size of the alkyl group.

Two possible explanations were offered for this reverse steric effect;[2] these were: (1) the larger alkyl group in the ultimate unit of the active polymer chain increasingly interferes with the approach of the cation to the carboxylate anion end group thereby increasing the reactivity of the carboxylate nucleophile by imparting more free-ion character to the end group ion pair, or (2) the larger alkyl groups in the polymer

---

[†] Department of Chemistry, University for Teacher Education, Tehran, Iran.

Table I
Apparent Propagation Rate Constants for the Anionic Polymerization of α,α-Disubstituted β-Propiolactones



R		Apparent k_p, M^{-1} min^{-1}, in solvent: Me_2SO[a] (22 °C) TEA[b]	Me_2SO[a] (22 °C) K[b]	Me_2SO[a] (37 °C) TEA[b]	THF[a] (37 °C) TEA[b]	ΔE^*, kcal M^{-1}
CH_3	IIa	10.2	9.48			
CH_2CH_3	IIb	11.2	9.97	19.0	28.1	6.4
$(CH_2)_2CH_3$	IIc	11.8	10.5	20.4	31.9	6.6
$(CH_2)_3CH_3$	IId	13.0	11.8	22.9	35.1	6.9

[a] Me_2SO = dimethyl sulfoxide; THF = tetrahydrofuran. [b] TEA = tetraethylammonium; K = potassium

and the monomer can associate with each other with increasing effectiveness by a type of hydrophobic interaction in dipolar aprotic solvents, thereby increasing the local concentration of active end groups and monomers.

For the lactam in this series with the largest substituent group, the methylbutyl monomer, Id, the apparent propagation rate constant in Me_2SO was found to be essentially insensitive to the nature of the counterion for two very different types of counterions: potassium (K) and tetramethylammonium (TMA). Quite different results were observed, however, with the equivalent monomer of the β-lactone series, IId, in which the apparent propagation rate constant for the tetraethylammonium (TEA) counterion was approximately twice that for the potassium counterion in Me_2SO.[3] Furthermore, in this reaction with the TEA counterion, the apparent rate constant was higher in tetrahydrofuran (THF) than in Me_2SO even though the latter is a solvent of considerably higher dielectric constant. This observation led to the tentative suggestion that Me_2SO may reduce the reactivity of the carboxylate anion by some type of specific solvation to be discussed below.[4]

Results

To further investigate the possibility of a specific solvation effect, as well as to determine if the insensitivity to counterion is broadly applicable, and also to ascertain whether the observed steric effects in the lactam series exist in the equivalent lactone series, rate investigations were carried out on all four lactone monomers, IIa–d, in two different aprotic solvents, Me_2SO and THF, with two different counterions, K and TEA. The results of these investigations are collected in Table I.

For each monomer in the series, the apparent propagation rate constant was always slightly, but apparently significantly, higher for the ammonium counterion than for the potassium counterion in Me_2SO solvent. This result, which indicates either a greater free-ion character or less of a structured ion pair character with the TEA counterion, is different from that reported for the equivalent anionic polymerization of the methylbutyl lactam, Id, in which no significant difference was claimed, although the experimental errors in the latter case were considerably greater. In any case, this consistent difference in apparent propagation rate constants throughout the entire series suggests that the nature of the counterion can effect the extent of anion solvation suggested above for the carboxylate anion in Me_2SO.

The solvent effects previously reported for the anionic polymerization reactions of the methylbutyl lactone manomer, IId,[3] and for α-phenyl-α-ethyl-β-propiolactone,[4] which led to the suggestion of a specific solvation mechanism, were observed in the present investigations over the entire series of lactone monomers as seen in the data of Table I. With TEA counterion, the rate constants in THF were 50% higher than those in Me_2SO, again suggesting that the reactivity of the ion-pair end group in the latter solvent is reduced by some undetermined solvation effect. Furthermore, the approximately equal, stepwise increase in the rate constants along the series Et < Pr < Bu for both solvents suggests that, in each case, solvated ion pairs rather than free ions are the active species.

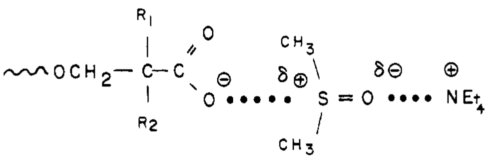


Figure 1. Structured ion pair solvation with specific anion coordination of carboxylate ion to Me_2SO.

The polymerization reactions of three of the monomers were run in Me_2SO with TEA counterion at two different reaction temperatures, 22 and 37 °C. The results of these reactions, while quite limited in extent, permit the calculation of approximate activation energies for the Et, Pr, and Bu monomers, IIb–d, and these are collected in Table I. The data show a small but continuous increase in activation energy with increasing substituent size. The differences observed for the three α substituents are comparable with those reported in closely related bimolecular nucleophilic substitution reactions which, however, undergo steric retardation caused by *n*-alkyl groups.[5] Hence the increase in rate constants with increasing substituent size must, in the present case, be associated with an increase in frequency factor, and either of the possible explanations proposed earlier and discussed below could be rationalized on that basis.

Discussion

In most cases, solvent effects in anionic polymerization reactions involving dipolar aprotic solvents are rationalized on the basis of cation solvation abilities.[6] Much less attention has been given to the possibility of anion solvation effects in such reactions, but this type of effect is most likely the controlling one in the present polymerization reaction.

Gutmann has emphasized the potential importance of anion solvation for a number of reaction types and has placed the effect on a quantitative basis with his concept of solvent acceptor number.[7] The acceptor number, AN, is a dimensionless number expressing the acceptor properties of a given solvent relative to those of a reference standard, and the magnitude of AN can serve to estimate the coordinate bond energy of a given solvent with a specific electron donor: donor → solvent. Me_2SO has a much higher value of this parameter than THF (respective AN values of 19.3 and 8.0), indicating that the former will form a much stronger coordination bond with a nucleophile, such as the carboxylate anion, than the latter, and it is to be expected that the stronger the solvent coordination bond the less reactive the nucleophile.[7]

Hence in the present case, anion solvation would appear to be much more important than cation solvation (even with the K counterion) in controlling reaction rates. If the latter were controlling, it would be expected that Me_2SO would permit higher propagation rate constants than THF because the former is a much better cation-solvating solvent than the latter as indicated by its higher donicity number, DN (29.8 for Me_2SO, 20.0 for THF).[7,8] The specific solvation of anions by Me_2SO has been previously suggested in other studies on the formulation of solvent parameters[9] and on the rates of nucleophilic reactions.[10]

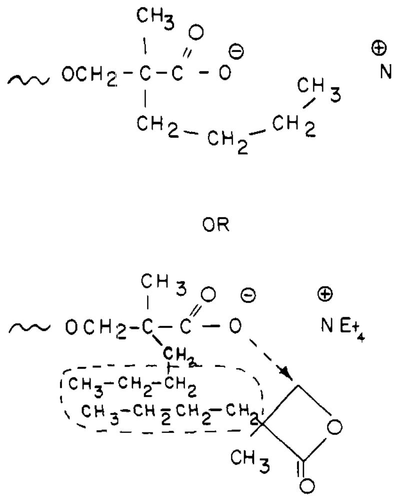


Figure 2. Possible mechanisms for the observed rate increases with increasing size of the α substituent (illustrated for the *n*-butyl group); (above) steric shielding of the approach of the cation to the anion; (below) hydrophobic interaction of the end group and monomer.

Table II
Rate Data for the Polymerization of α-Methyl-α-alkyl-β-propiolactones in Me$_2$SO with TEAB Initiator

Alkyl group	$[M]_0$, mol/L[a]	TEAB $[I]_0$, mol/L[b]	Temp, °C	k_0[c]	k_p, M^{-1} min^{-1} [d]
CH_3 (IIa)	0.248	0.007 34	21–22	0.0717	9.79
	0.248	0.005 88	21–22	0.0585	9.96
	0.178	0.005 13	21–23	0.0555	10.8
C_2H_5 (IIb)	0.167	0.005 8	21–22	0.0664	11.2
	0.163	0.006 73	21–23	0.0673	11.4
	0.180	0.006 48	21–23	0.0712	11.0
C_3H_7 (IIc)	0.153	0.006 60	22–23	0.0759	11.5
	0.135	0.007 26	21–22	0.0858	12.0
	0.151	0.003 44	21–22	0.0389	11.8
C_4H_9 (IId)	0.112	0.007 84	22–23	0.102	13.1
	0.151	0.006 50	22–23	0.0795	12.8
	0.146	0.006 64	22–23	0.0871	13.2

[a] Initial monomer concentration. [b] Initial initiator concentration; TEAB = tetraethylammonium benzoate. [c] Observed rate constant: $k_0 = k_p[I]_0$, obtained directly from plot of log I_0/I vs. time. [d] Apparent or average bimolecular rate constant.

Table III
Rate Data for the Polymerization of α-Methyl-α-alkyl-β-propiolactones in Me$_2$SO with KB Initiator[a]

Alkyl group	$[M]_0$, mol/L	KB[b] $[I]_0$, mol/L	Temp, °C	k_0	k_p, M^{-1} min^{-1}
CH_3 (IIa)	0.193	0.006 40	21–22	0.0612	9.56
	0.188	0.005 92	21–22	0.0562	9.45
	0.189	0.006 20	21–22	0.0584	9.41
C_2H_5 (IIb)	0.163	0.005 92	21–22	0.0580	9.82
	0.158	0.006 12	21–22	0.0616	10.1
	0.144	0.004 62	21–22	0.0461	9.98
C_3H_7 (IIc)	0.130	0.003 96	21–22	0.0413	10.4
	0.271	0.005 94	21–22	0.0615	10.3
	0.181	0.010 1	21–22	0.108	10.6
C_4H_9 (IId)	0.284	0.003 79	21–22	0.0426	11.5
	0.155	0.003 80	21–22	0.049	12.8
	0.159	0.005 89	21–22	0.0658	11.1

[a] See footnotes in Table II. [b] KB = potassium benzoate.

If anion solvation or coordination is indeed the controlling effect in these reactions as suggested above, then it is perhaps surprising that the cation plays an important role as previously discussed. However, the active species in these reactions is most likely a solvated ion pair even in Me$_2$SO with coordination of both the anion and cation occurring because of the strongly dipolar nature of this solvent. This type of dual coordination should result in a very stable solvated ion pair and it could well account for the decreased reactivity of the end group as illustrated in Figure 1. In this structure, the carboxylate anion is shown to be solvated to the sulfur end of the dipole, but Me$_2$SO may be considered to be a donor solvent containing a hard (oxygen) and a soft (sulfur) end, so the reverse orientation of the solvent and the anion is also possible.[11]

An alternate form of the explanation above for the higher reactivity of the carboxylate anion in THF than in Me$_2$SO may be given in terms of the necessity for the anion to be desolvated in the transition state.[12] Because the propagation reaction of this polymerization is an ion-dipole S$_N$2 reaction, it would be expected that solvents of higher dielectric constants or specific anion solvation abilities would decrease the reaction rate because of the necessity for desolvation of the anion to reach the transition state.[13]

The explanation of the unexpected substituent effect is less obvious. Under all conditions, independent of solvent, counterion, or temperature, the rate constants increased with increasing alkyl group size along the series Me < Et < Pr < Bu. The data in Table I indicate that the greatest increase occurred in passing from Pr to Bu substituents, as compared to the differences between the other two consecutive homologues. This pattern is consistent with the two possible routes to steric acceleration previously proposed for the results from the rate investigations on analagous β-lactam monomers.[1,2]

The two mechanisms for this unexpectedly favorable steric effect, counterion shielding and hydrophobic interaction, are illustrated in Figure 2 for the methylbutyl lactone monomer. Both mechanisms are consistent with the apparent decrease in entropy of activation, which is suggested by the apparently increasing frequency factors with increasing alkyl group size, as discussed above. That is, either the increasing accessibility of the carboxylate anion nucleophile resulting from the counterion shielding, or the increasing local concentration of reactants resulting from the hydrophobic interaction, would increase the frequency factor of the bimolecular reaction.

The counterion shielding proposal may seem somewhat inconsistent with the suggestion of a structured ion pair for reactions in Me$_2$SO. However, it is worth noting in Table I that the differences in k_p values along the series of alkyl substituents are considerably greater in THF than Me$_2$SO. That is, for the former where anion solvation should be of little importance, the increased steric hindrance to the approach of the solvated cation possibly becomes more important with increasing size of the α substituent.

It is also interesting to note that the steric effects observed here on the propagation rate constants were not observed earlier by Hall in his determination of the rate constants for reactions of α,α-dialkyl-β-propiolactones (II) with various quaternary ammonium carboxylates. For these reactions carried out in acetonitrile at 35 °C, the order of reactivity as a function of α substituents in II was Me-Me > Me-Et ≃ Me-Pr (IIa > IIb ≃ IIc) and Me-Me > Et-Et ≃ Bu-Bu, and Hall concluded that "substitution by larger alkyl groups resulted in a marked lowering of the rate constant".[14] On the other hand, consistent with the present results, it was observed in that study that the rates of these reactions were higher in THF than in acetonitrile (AN 19.3, DN 14.1).

This last observation adds considerable weight to the suggestion that anion solvation is much more important than

Table IV
Rate Data for the Polymerization of α-Methyl-α-alkyl-β-propiolactones in THF with TEAB Initiator[a]

Alkyl group	$[M]_0$, mol/L	[TEAB] $[I]_0$, mol/L	Temp, °C	k_0	k_p, M^{-1} min^{-1}
C_2H_5 (IIb)	0.164	0.005 10	36	0.1114	28.2
	0.164	0.006 33	36	0.1118	27.8
	0.160	0.006 96	36	0.197	28.3
C_3H_7 (IIc)	0.238	0.005 29	36	0.177	32.7
	0.183	0.006 96	36–38	0.228	31.9
	0.194	0.005 66	36–38	0.175	31.1
C_4H_9 (IId)	0.116	0.006 64	36–38	0.235	35.4
	0.111	0.007 20	36–38	0.251	34.9
	0.121	0.006 07	36–38	0.213	35.2

[a] See footnotes in Table II.

Table V
Rate Data for the Polymerization of α-Methyl-α-alkyl-β-propiolactones in Me_2SO with TEAB Initiator[a]

Alkyl group	$[M]_0$, mol/L	TEAB $[I]_0$, mol/L	Temp, °C	k_0	k_p, M^{-1} min^{-1}
C_2H_5 (IIb)	0.169	0.006 99	36–38	0.132	18.9
	0.182	0.008 33	36–38	0.158	19.0
	0.201	0.004 16	36–38	0.0794	19.1
C_3H_7 (IIc)	0.174	0.008 62	36–38	0.173	20.1
	0.203	0.006 01	36–38	0.121	20.2
	0.102	0.006 56	36–38	0.137	20.9
C_4H_9 (IId)	0.153	0.006 99	36–38	0.201	22.4
	0.164	0.006 80	36–38	0.164	24.1

[a] See footnotes in Table II.

cation solvation in this reaction because the donicity of acetonitrile is less than that of THF, whereas that of Me_2SO is more,[1] yet both Me_2SO and acetonitrile have lower rate constants than THF. In contrast, the greater acceptor capabilities of both Me_2SO and acetonitrile are consistent with the lower reaction rates in these to solvents relative to THF.

Experimental Section

Monomers. Pivalolactone (IIa) was obtained from the Texas Eastman Co. and distilled twice before use. Analysis by gas chromatography indicated greater than 99% purity.

The methylethyl and methylbutyl monomers, IIb and IId, were synthesized from the respective α-alkyl-α-methyl-β-alanines according to the procedure of Testa and co-workers[15,16] and purified by vacuum distillation; IIb, bp 66 °C (16 mm), 68% yield; IId, bp 72 °C (1.1 mm), 62% yield.

The methylpropyl monomer, IIc, was synthesized from 3-bromo-2-methyl-2-propylpropionic acid according to previously published procedures.[14,17]

Initiators. Potassium benzoate (Anal. Calcd: C, 52.4, H, 3.14. Found: C, 52.36, H, 3.08) and tetraethylammonium benzoate (mp 72–75 °C) were used as initiators and prepared and purified as previously described.[3]

Polymerization and Rate Measurements. Polymerization reactions were carried out under an atmosphere of argon as previously described.[1] Rate constants were calculated from data obtained by using IR techniques with a Perkin-Elmer Model 257 spectrometer as previously described.[1] Detailed experimental data so obtained for the four monomers in two solvents with two initiators at two temperatures are collected in Tables II–V. Representative rate plots for the data in Table II are shown in Figure 3.

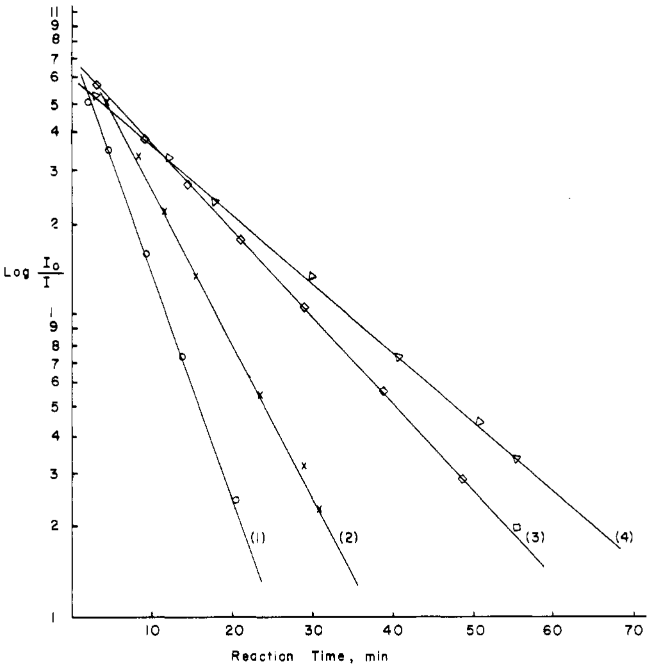


Figure 3. Conversion–time plots of representative polymerization reactions for each monomer in Table II: (1) IId, (2) IIc, (3) IIb, (4) IIa.

Acknowledgment. The authors are grateful to the National Science Foundation for the support of this work under Grant No. GH-38848 and for the use of the facilities of the NSF-sponsored Materials Research Laboratory.

References and Notes

(1) C. D. Eisenbach and R. W. Lenz, *Macromolecules,* **9,** 227 (1976).
(2) C. D. Eisenbach, R. W. Lenz, and H. Sekiguchi, *J. Polym. Sci., Polym. Lett. Ed.,* **15,** 83 (1977).
(3) C. D. Eisenbach and R. W. Lenz, *Makromol. Chem.,* **177,** 2539 (1976).
(4) R. W. Lenz, C. G. D'Hondt, and E. Bigdeli in "Ring-Opening Polymerization", T. Saegusa and E. Goethals, Ed., ACS Symposium Series 59, American Chemical Society, Washington, D.C., 1977, p. 210.
(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1953, p 403 ff.
(6) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers", Interscience, New York, N.Y., 1967, p 424 ff.
(7) V. Gutmann, *Chemtech.,* 255 (1977).
(8) M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Vol. 1, Wiley, New York, N.Y., 1974, p 5 ff.
(9) E. M. Kosower, *J. Am. Chem. Soc.,* **80,** 3253 (1958).
(10) A. J. Parker, Q. Rev., *Chem. Soc.,* **16,** 163 (1962).
(11) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, New York, N.Y., 1968, p 155 ff.
(12) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1960, p 535 ff.
(13) J. F. Coetzee and C. D. Ritchie, "Solute-Solvent Interactions", Marcel Dekker, New York, N.Y., 1969, p 289 ff.
(14) H. K. Hall, Jr., *Macromolecules,* **2,** 488 (1969).
(15) E. Testa, L. Fontanella, G. Cristiani, and L. Mariani, *Justus Liebigs Ann. Chem.,* **639,** 166 (1961).
(16) C. D'Hondt, Ph.D. Thesis, University of Massachusetts, 1975.
(17) J. Cornibert, R. H. Marchessault, A. E. Allegrezza, and R. W. Lenz, *Macromolecules,* **6,** 676 (1973).