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## Solvent effects in the anionic polymerization of [alpha], [alpha]-disubstituted-[beta]-propiolactones.

Eileen M. Minter  
*University of Massachusetts Amherst*

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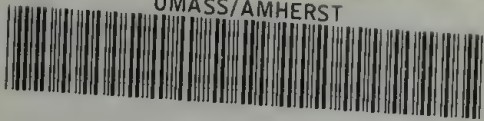
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SOLVENT EFFECTS IN THE ANIONIC POLYMERIZATION OF  
 $\alpha, \alpha$ -DISUBSTITUTED- $\beta$ -PROPIOLACTONES

A Dissertation Presented

By

EILEEN M. MINTER

Submitted to the Graduate School of the  
University of Massachusetts in partial fulfillment  
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 1983

Polymer Science and Engineering

Eileen M. Minter

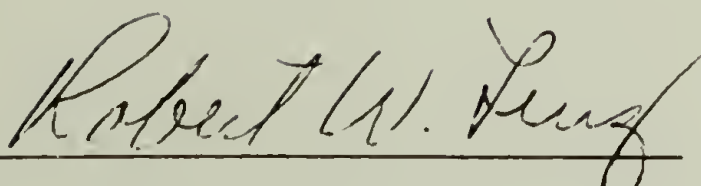
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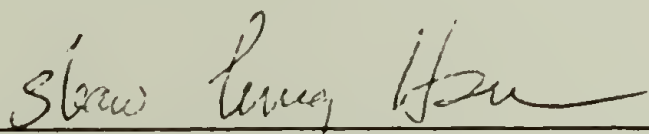
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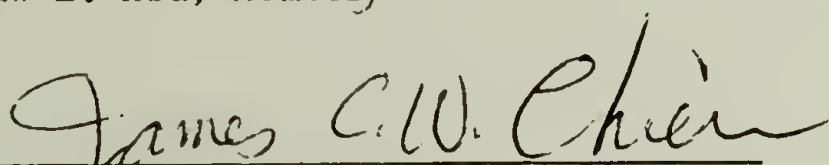
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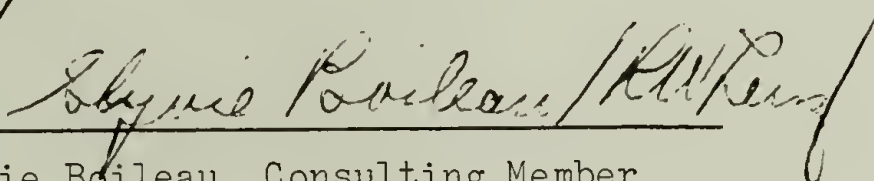
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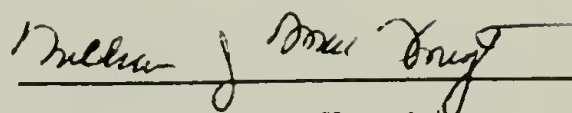
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Finally and most importantly, I acknowledge that without God's help all of my efforts would have been in vain.

"Trust in the Lord with all your heart and lean not on your  
own understanding  
In all your ways acknowledge him, and he will make your  
paths straight"

(Prov. 3:5 & 6)

# A B S T R A C T

## SOLVENT EFFECTS IN THE ANIONIC POLYMERIZATION OF $\alpha$ , $\alpha$ -DISUBSTITUTED- $\beta$ -PROPIOLACTONES

(May, 1983)

Eileen M. Minter, B.A., Wells College

M.S., University of Massachusetts, Ph.D., University of Massachusetts

Directed by: Professor Robert W. Lenz

The effect of solvent polarity on the anionic polymerization rates of  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones was studied. Polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in tetrahydrofuran was a living polymerization. In dimethyl sulfoxide, however, nucleophilic attack on the monomer by the sulfoxide oxygen initiated polymerization, obscuring the study of solvation effects. Similar behavior was observed in N, N-dimethylformamide. When other dipolar aprotic solvents were used, living polymerization systems were obtained. Polymerization rates were greatest in solvents of high dielectric constant, where cation solvation is greatest.

Unlike  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone,  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone is unreactive towards dimethyl sulfoxide. When  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was polymerized in dimethyl sulfoxide, the polymerization rate decreased abruptly at low conversions because of

gelation of the growing polymer. The decrease in overall polymerization rate upon gelation was caused by a sudden decrease in the number of polymer chains capable of growth. The polymerization rate of the active chain ends was unaffected by gelation. Bimodal molecular weight distributions arose because two types of chain ends were present after gelation.

Anionic polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-methylpyrrolidone continued despite precipitation of the growing polymer at low conversions. N-Methylpyrrolidone is a better solvent than dimethyl sulfoxide despite its lower dielectric constant. Solvent-solvent interactions in dimethyl sulfoxide compete with cation-solvent interactions, resulting in decreased cation solvation.

The polymerization rate of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-methylpyrrolidone was substantially less than that of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone. Either the increase in substituent size or the decrease in polymer solubility may have been responsible.



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# C H A P T E R    I

## INTRODUCTION

### 1.1   Historical   Perspective

Previous investigators found that the anionic polymerization rate of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was greater in tetrahydrofuran than in dimethyl sulfoxide, a more polar solvent. If the polymerization rate was affected only by cation solvation, the opposite behavior would be expected. When  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was polymerized in dimethyl sulfoxide, the polymerization rate decreased abruptly at low conversions, and the molecular weight distribution of the resultant polymer was bimodal.

### 1.2   The   Dissertation   Problem

There are two aspects to the dissertation problem: first, to understand how solvent polarity affects the anionic polymerization rate of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone, and second, to determine the cause of the anomalous behavior of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in dimethyl sulfoxide. The polymerization rates of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone were determined by infrared spectroscopy in several dipolar aprotic solvents and the results were explained in terms of nonspecific cation solvation.  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was polymerized in several dipolar aprotic solvents. Gelation of the polymerizing solution caused this monomer's unusual behavior in

dimethyl sulfoxide.

### 1.3 Organization of the Dissertation

This dissertation is organized as follows: Chapter II discusses the literature relevant to cation solvation and to polymer gelation. Chapter III presents the experimental results of solvent effects in the anionic polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone. Chapter IV discusses the anionic polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in dimethyl sulfoxide and in N-methylpyrrolidone. Conclusions and suggestions for further work are contained in Chapter V. Experimental methods are presented in Chapter VI. Five appendices are included: error analysis, kinetic analysis, computer program used for kinetic analysis, heat conduction calculations, and kinetics from molecular weight distribution data.

## C H A P T E R   I I

### SURVEY OF THE RELEVANT LITERATURE

#### 2.1 Solvent Effects on Dissociation

Anionic polymerization rates are greatly affected by reaction solvent. The equilibrium between free ions and ion pairs, as well as their rates of propagation and termination, depend on the nature of the reaction medium. There are many types of ion pairs, from tight ion pairs and solvent-separated ion pairs, to loose ion pairs, each with its own characteristic rate constant.

The reaction solvent does not act as an inert medium where polymerization takes place. Its electrophilicity and nucleophilicity play an important role in the polymerization process. When an electrolyte is placed in solution, the degree of dissociation depends on the solvent's ability to stabilize the resulting ions. A solvent that can donate electrons will readily solvate cations, facilitating dissociation into free ions. Ion pairs and free ions may coexist in solvents of moderate solvating ability.

Szwarc considered solvation in terms of free energy changes {1}, dividing the dissociation process into three steps {2}:

1. transfer of an ion pair into evacuated space,
2. separation of the ions in vacuum, and
3. immersion of the two isolated ions into the solvent while still keeping them far apart.

The first two steps are endothermic and the last is exothermic. In order for dissociation to occur, the free energy change of the final step must be negative and exceed the positive energy requirements of the first two steps. Both the enthalpy and entropy of dissociation determine the value of this free energy change.

The entropy of solvation is usually negative because ions tend to order solvent molecules in their solvation spheres. The enthalpy of dissociation is negative because of ion solvation. Dissociation into free ions can occur when sufficient energy is released on solvation, which occurs when there are specific solute-solvent interactions, such as electron pair donation, electron pair acceptance, or hydrogen bonding. Ion pairs are formed in weakly electrophilic or nucleophilic solvents, where ions are stabilized only by nonspecific interactions.

In structured solvents the degree of dissociation is sometimes less than expected {3}. The energy gained by solvation is offset by the energy required to disrupt the solvent structure and rearrange the solvent molecules around an ion. Free ions disrupt the solvent structure to a greater extent than ion pairs, so the proportion of free ions may be less than expected. In highly structured solvents, the energy requirements for dissociation may be too great and ion pairs will predominate.

The polymerization rate is greatly affected by the degree of dissociation of the propagating species. In propagation reactions involving ion pairs, the monomer must compete with the counterion for the propagating anion. In an anionic polymerization, the



nucleophilicity of the propagating chain end is enhanced when it dissociates into free ions, and the influence of the counterion is removed. The rate of polymerization is almost always greater for free ions than for ion pairs.

The nucleophilicity of a free anion is decreased in electrophilic solvents because the anion must be desolvated before it can attack the monomer. The polymerization rate will decrease with increasing solvent electrophilicity. Thus, when determining how a solvent will affect the polymerization rate, both the solvent's ability to facilitate dissociation and to solvate the propagating anion must be considered.

## 2.2 Solvent Polarity Scales

The ionizing power of a solvent is not always described by its dielectric constant because this solvent property does not take into account specific solute-solvent interactions. Many investigators have established empirical scales of solvent polarity by determining solvent effects on a measurable property of a probe molecule. Empirical solvent polarity scales have been reviewed by Griffiths and Pugh {4}, Dack {5}, and Reichardt {6} and are summarized in Table I.

Solvent parameters are roughly proportional to solvent dielectric constant only when nonspecific electrostatic solute-solvent interactions, such as ion-dipole interactions, occur between the probe molecule and the solvent (see Figure 1).

Two empirical measurements of solvent polarity are the acceptor number (AN) and the donor number (DN) {10}. The acceptor number

Table 1 {7}

## Empirical Solvent Polarity Scales

	Dielectric Constant	Dipole Moment	$\epsilon^{(a)}$	$E_T^{(b)}$
Chloroform	4.8 (20°C)	1.15	63.2	39.1
Methylene Chloride	8.9 (25°C)	1.55	64.2	41.1
Tetrahydrofuran	7.6 (25°C)	1.75	58.8	37.4
Acetone	20.7 (25°C)	2.69	65.7	42.2
N-Methylpyrrolidone	33.0 {8}	4.1 {8}		42.2 {8}
Nitromethane	35.9 (25°C)	3.56	71.2	46.3
Acetonitrile	37.5 (20°C)	3.44	71.3	46.0
N, N-Dimethylacetamide	37.8 (25°C)	3.72	66.9	43.7
N, N-Dimethylformamide	38.3 (20°C)	3.86	68.5	43.8
Dimethyl Sulfoxide	46.4 (23°C)	4.3	70.2	45.0
Propylene Carbonate	70 (20°C)	4.98		46.6 {8}

(a) Based on solvatochromism of pyridinium iodide

(b) Based on solvatochromism of pyridinium N-phenol betaines

Table 1 (cont'd.)

Solvent	DN <sup>(c)</sup>	AN <sup>(d)</sup>	log $k_{ion}$ <sup>(e)</sup>
Chloroform		23.1	
Methylene Chloride		20.4	
Tetrahydrofuran	20.0	8.0	
Acetone	17.0	12.5	
N-Methylpyrrolidone	27.3	13.3 {8}	
Nitromethane	2.7	20.5	-3.921
Acetonitrile	14.1	19.3 {8}	
N, N-Dimethylacetamide	27.8	13.6	
N, N-Dimethylformamide	26.6 {8}	16.0	-4.298
Dimethyl sulfoxide	29.8	19.3	-3.738
Propylene Carbonate	15.1	18.3	

(c) Based on enthalpy of coordination of the donor  
and  $SbCl_5$

(d) Based on  $^{31}P$  NMR chemical shift in the presence of  
the acceptor

(e) Based on the rate of ionization of p-methoxyneophyl-  
p-toluenesulfonate

Table 1 (cont'd.)

Solvent	$\Delta\nu_D^{(f)}$	$\Delta\nu_A^{(g)}$	$\pi^*^{(h)} \{9\}$
Chloroform	-17		0.760
Methylene Chloride	-12		0.802
Tetrahydrofuran	90	0.2	0.576
Acetone			0.683
N-Methylpyrrolidone			0.921
Nitromethane	6	4.8	
Acetonitrile	49	1.9	0.713
N, N-Dimethylacetamide	113		0.882
N, N-Dimethylformamide	107		0.875
Dimethyl Sulfoxide	141	8.2	1.000
Propylene Carbonate			

(f) Based on change in IR absorbance of -OD in MeOD relative to benzene

(g) Based on change in IR absorbance of C=O in acetophenone

(h) Based on solvatochromism of five indicators



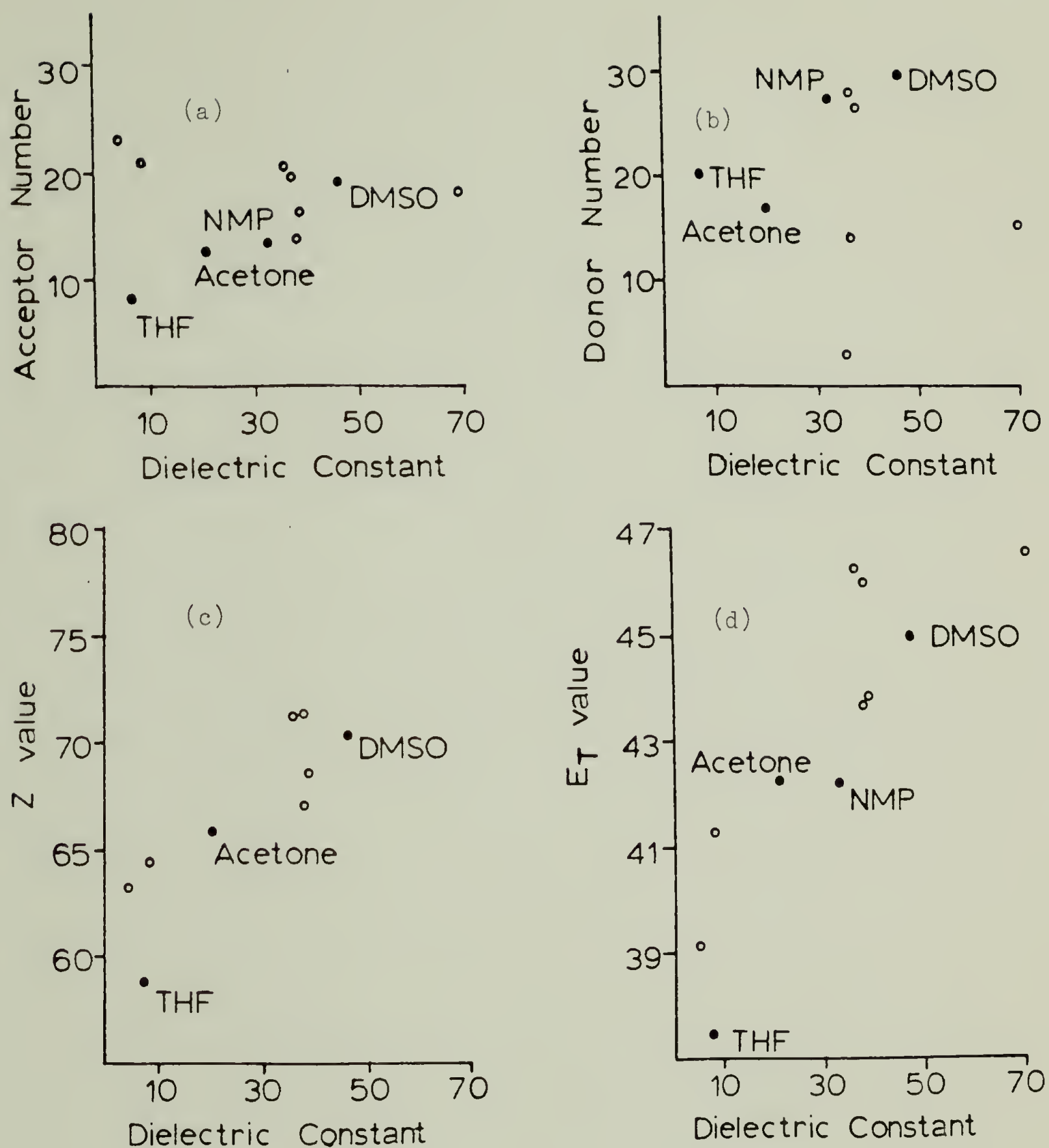


Figure 1. Correlation of empirical solvent polarity parameters and dielectric constant. Closed circles correspond to relevant solvents. A. Acceptor Number B. Donor Number C. Z Value D.  $E_T$  Value. From Reference {7}.

NMP = N-Methylpyrrolidone THF = Tetrahydrofuran  
DMSO = Dimethyl sulfoxide.

describes the electrophilic properties of a solvent and is equal to the  $^{31}\text{P}$  NMR chemical shift of  $\text{Et}_3\text{PO}$  relative to  $(\text{C}_6\text{H}_5)_2\text{POCl}$  in the presence of the solvent molecule in an inert medium (hexane). The donor number is a measure of the nucleophilicity of a solvent molecule and is equal to the negative enthalpy of interaction between antimony pentachloride and the solvent in an inert medium (dichloroethane).

### 2.3 Application of Polarity Scales to Ion Solvation

High rates of propagation in anionic polymerization reactions occur in solvents that favor dissociation through cation solvation. Solvents of high donor number readily donate electrons to the cation and, thus, favor cation solvation. The application of Gutmann's scale of donor numbers to ionization assumes that similar solute-solvent interactions occur in both the reference and reaction systems. If so, there should be a linear free energy relationship between the two processes, as follows:

$$\Delta G_{\text{Diss}} = m\Delta G_{\text{D}\cdot\text{SbCl}_5} + c \quad (2.1)$$

where  $\Delta G_{\text{Diss}}$  is the Gibbs free energy of dissociation,  $\Delta G_{\text{D}\cdot\text{SbCl}_5}$  is the Gibbs free energy of coordination of the donor solvent and  $\text{SbCl}_5$ , and  $m$  and  $c$  are constants. Then, because

$$\begin{aligned} \Delta G_{\text{Diss}} &= \Delta H_{\text{Diss}} - T\Delta S_{\text{Diss}}, \\ \Delta G_{\text{Diss}} &= m\Delta H_{\text{D}\cdot\text{SbCl}_5} + mT\Delta S_{\text{D}\cdot\text{SbCl}_5} + c. \end{aligned} \quad (2.2)$$

Because

$$\ln K_{\text{Diss}} = \frac{-\Delta G_{\text{Diss}}}{RT}, \quad (2.3)$$

$$\ln K_{\text{Diss}} = \frac{-m\Delta H_{\text{D}\cdot\text{SbCl}_5}}{RT} - \frac{m\Delta S_{\text{D}\cdot\text{SbCl}_5}}{R} + c'' \quad (2.4)$$

$$= \frac{m \text{ DN}}{RT} - \frac{m S_{\text{D}\cdot\text{SbCl}_5}}{R} + c'' \quad (2.5)$$

Gutmann has shown {11} that the entropy of coordination is constant for  $\text{SbCl}_5$ , so the following relationship should hold:

$$\ln K_{\text{Diss}} = \frac{m \text{ DN}}{RT} + c' \quad (2.6)$$

Polymerization rates are affected not only by the degree of dissociation but also by the degree of coordination of the anion. According to Gutmann {10}, the extent of coordination of the anion by the solvent is described by the acceptor number. Thus, high rates of anionic polymerization will be found in solvents of high donor numbers and low acceptor numbers.

Solvation of ion pairs is not always quantitatively described by the solvent donor number. Steric interactions {12} as well as entropic effects {13} can alter this relationship. In the case of tetraalkylammonium counterions, which are coordinately saturated, solvation occurs by ion-dipole interactions {14}, a different solvation mechanism than in the  $\text{SbCl}_5$ -solvent systems.

## 2.4 Effect of Solvent Structure on Dissociation

Solvent donor numbers are determined in dilute solution. Under these conditions it is not possible to establish the effects of the solute on solvent structure. For example, dimethyl sulfoxide is believed to possess some order because of dipole-dipole interactions between solvent molecules {15}{16}{17}. When an ion is placed in dimethyl sulfoxide, the ion affects the intermolecular structure already present and imposes a different structure in its vicinity {18}. This reordering requires energy and affects the solvation entropy, so less dissociation occurs than in the absence of solvent order. Dimethyl sulfoxide in dilute solution is free of the influence of other solvent molecules and may appear to be a better solvating agent than is realized in the bulk solvent.

Cox and coworkers {19} measured the free energy, enthalpy, and entropy of transfer of univalent electrolytes from water into a series of solvents including propylene carbonate ( $\epsilon = 70$ ), dimethyl sulfoxide ( $\epsilon = 46.4$ ), N, N-dimethylformamide ( $\epsilon = 38.2$ ), N-methylpyrrolidone ( $\epsilon = 33.0$ ), and acetonitrile ( $\epsilon = 37.5$ ). These results were used to estimate the free energies, enthalpies, and entropies of transfer of the individual cations and anions comprising the electrolyte. The changes in free energy can be related to changes in ion solvating properties {20}. The negative free energy of transfer of  $\text{Et}_4\text{N}^+$  decreased in the following order: dimethyl sulfoxide > N, N-dimethylformamide > acetonitrile. The enthalpy of transfer is less exothermic when an ion is placed in a structured solvent where solute-solvent



interactions must be destroyed and replaced by ion-solvent interactions. The exothermic enthalpy of transfer of  $\text{Et}_4\text{N}^+$  decreased in the following order: acetonitrile  $\approx$  propylene carbonate  $\approx$  N, N-dimethylformamide  $>$  dimethyl sulfoxide, and for  $\text{Bu}_4\text{N}^+$  the order was as follows: N-methylpyrrolidone  $>$  propylene carbonate  $\approx$  N, N-dimethylformamide  $>$  acetonitrile  $>$  dimethyl sulfoxide. Likewise, more entropy is gained when an ion is placed in a structured solvent. The relative order of the gain in entropy for the various solvents upon transfer of  $\text{Et}_4\text{N}^+$  was: dimethyl sulfoxide  $>$  N, N-dimethylformamide  $>$  acetonitrile.

The usefulness of donor numbers for prediction of rates of substitution on nickel (II) ion by 4-phenylpyridine, 2, 2'-bipyridine, 1, 10-phenanthroline and 2, 2', 2''-terpyridine was assessed by Coetzee and Umemoto {21} and Coetzee and Karakatsanis {22}. Solvents used were acetonitrile ( $\epsilon = 38$ , DN = 14.1), propylene carbonate ( $\epsilon = 69$ , DN = 15.1), and dimethyl sulfoxide ( $\epsilon = 45$ , DN = 29.8). Rate measurements obtained with a stopped-flow spectrophotometer revealed that the rate of substitution was greatest in propylene carbonate and least in dimethyl sulfoxide. Both steric interference with coordination and the sheetlike structure of dimethyl sulfoxide were thought to contribute to rate retardation. The authors emphasized that donor numbers were measured relative to a standard acceptor and may not apply to other systems.

The degree of dissociation in dimethyl sulfoxide is affected more by the donor properties of dimethyl sulfoxide than by its acceptor properties. Exner and Steiner {23} measured the limiting equivalent conductivity of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{Cl}^-$  in dimethyl sulfox-

ide. These measurements revealed that small cations are solvated more strongly than large cations by dimethyl sulfoxide. Conductivity was unaffected by anion size because the anions were weakly solvated.

Dissociation of tetraalkylammonium salts is incomplete in dimethyl sulfoxide. Solvation of  $\text{Et}_4\text{N}^+$  is greater in acetone and in N-methylpyrrolidone than in dimethyl sulfoxide, and so the degree of dissociation of tetraethylammonium salts is greater.

4-Bromoisophorone undergoes an  $\text{S}_{\text{N}}2$  reaction with pivalate anion {24} to give a mixture of 4- and 2-pivaloxyisophorone. The rate of consumption of the starting material and the product distribution are dependent on the reactivity of the anion, which is determined by the extent of ion pairing. For the  $\text{K}^+$ ,  $\text{Li}^+$ , and  $\text{Na}^+$  salts, the reactivity of the anion increases as the donor number of the solvent increases, indicating that increasing cation solvation favors dissociation. The  $\text{Et}_4\text{N}^+$  salt was less reactive and showed little change in reactivity as the solvent was changed from dimethyl sulfoxide (DN = 29.8) to N, N-dimethylformamide (DN = 30.9) to hexamethylphosphoramide (DN = 38.8), indicating that cation solvation is ineffective and that tetraethylammonium pivalate is predominately an ion pair in these solvents.

Gal'pern and coworkers {25} measured the conductance of tetraethylammonium halides in N-methylpyrrolidone. The degree of dissociation depended on the anion;  $\text{Et}_4\text{NI}$  was completely dissociated, while  $\text{Et}_4\text{NCl}$  was partially associated. Anion mobility was greater than cation

mobility because of greater cation solvation. Mobilities of both cations and anions were greater in N, N-dimethylformamide and N, N-dimethylacetamide than in N-methylpyrrolidone, but less in propylene carbonate. This result was attributed to differences in solvent viscosity, although calculation of ion mobilities from conductivity data already account for solvent viscosity. A better explanation might be that cations are less solvated in N, N-dimethylformamide and N, N-dimethylacetamide than in N-methylpyrrolidone.

According to Krumgalz {26} tetraalkylammonium ions, unlike inorganic ions, cannot form donor-acceptor bonds. Solute-solvent interactions occur through ion-dipole interactions. As the size of the alkyl substituent increases, the positive charge is dispersed. Cation solvation decreases as the size of the solvation shell decreases. From conductance measurements, Krumgalz found when the alkyl substituent is larger than n-propyl, little solvation occurred, and the Stokes radii are solvent independent. For  $\text{Et}_4\text{N}^+$ , the radii are solvent dependent and the size of the solvation shell decreases in the series N, N-dimethylformamide > acetonitrile > nitromethane  $\approx$  N-methylpyrrolidone {25}  $\approx$  N, N-dimethylacetamide > dimethyl sulfoxide.

Kabish {27} used proton magnetic resonance spectroscopy to determine the equilibrium constants of tetraalkylammonium salts. In formamide the salts were completely dissociated, in acetonitrile, a mixture of ion pairs and free ions was present, while in acetone, ion pairs predominated. In chloroform, little dissociation was discernible and the degree of dissociation depended upon the anion.

## 2.5 Solvent Effects on Anionic Polymerization

2.5.1 Vinyl Monomers. Miertus and coworkers used quantum mechanics to calculate the most energetically stable anion-to-counterion distance in the anionic polymerization of styrene {28}. Both anion-counterion and solute-solvent interactions were considered. As the dielectric constant of the solvent increased, the anion-to-counterion distance increased. Calculations involving the initial state as well as the activated complex revealed that the activation energy of propagation involving ion pairs increased with solvent polarity because of the increased stabilization of the initial state. The activation energy of propagation involving free ions was less than that of propagation involving ion pairs. Increases in polymerization rate with solvent polarity were attributed to dissociation of the ion pairs into more reactive free ions.

Empirical measurements of solvent effects support these conclusions. Schmitt and Schulz {29} polymerized styrene with sodium naphthalene in dimethoxyethane, tetrahydrofuran, and 3-methoxytetrahydrofuran. The propagation rate constant of free ions,  $k_p^-$ , was unaffected by the reaction solvent while the propagation rate constant of ion pairs,  $k_p^+$ , was greater in dimethoxyethane (a more polar solvent) than in tetrahydrofuran. Despite the greater basicity of the oxygen of 3-methoxytetrahydrofuran when compared to tetrahydrofuran,  $k_p^+$  was lower in the former than in the latter. This result was attributed to steric hindrance of cation solvation by the methyl substituent on the solvent molecule. The anion remained unsolvated in these ethers. Increases in the overall



polymerization rate with solvent polarity were attributed to increased dissociation of free ions.

Dainton and coworkers {30} studied the anionic polymerization kinetics of styrene and  $\alpha$ -methylstyrene. The kinetics were followed dilatometrically in dioxane ( $\epsilon = 2.21$ ), tetrahydrofuran ( $\epsilon = 7.42$ ), and tetrahydropyran ( $\epsilon = 5.52$ ). The polymerization rate increased while the activation energy for both processes decreased as the dielectric constant of the solvent increased. Polymerization was faster than expected in benzene ( $\epsilon = 2.3$ ).

2.5.2  $\beta$ -Propiolactone and  $\alpha, \alpha$ -Dialkyl- $\beta$ -propiolactones. Kazanskii {31} discussed the roles of monomeric and polymeric solvation of the counterion in the anionic polymerization of heterocycles. Quantum mechanical calculations revealed that, during the anionic polymerization of ethylene oxide, the polymer chain can compete with the alkoxide chain end for coordination of the counterion. Substitution weakened these interactions. Evidence for self-solvation was based on chain length effects on both polymerization rates and on electrical conductivities.

In the case of  $\beta$ -propiolactone, there was only indirect evidence for solvation by the macromolecule. When dibenzo-18-crown-6 was complexed with the counterion in the polymerization of this monomer, the equilibrium constant of complexation of the  $\text{Na}^+$  counterion was low, implying the existence of a weak shielding, or coordination, of the counterion by the polymer. Solvation of the counterion by monomer was also important, as shown by the dependence of both the extent of ion pair dissociation and polymerization rate on monomer concentration.

Slomkowski and Penczek {32}{33} polymerized  $\beta$ -propiolactone with potassium acetate-dibenzo-18-crown-6-ether in methylene chloride. The presence of the crown ether, a cation complexing agent, eliminated proton transfer reactions from monomer, enabling the occurrence of living polymerization. The polymerization kinetics were followed by dilatometry and the ion pair dissociation constant measured conductometrically. Free ions propagated one hundred times faster than ion pairs. At lower monomer concentrations, the rate of free ion propagation increased slightly while the rate of ion pair propagation remained unchanged. The monomer solvated the growing anion and, in order for propagation to occur, desolvation of the anion had to occur first. The activation energy was, thus, higher at higher monomer concentrations.

In contrast to Kazanskii {31}, Slomkowski and Penczek did not mention solvation of the counterion by the growing macromolecule. They felt that the low equilibrium constant of complexation of  $\text{Na}^+$  counterion was due to the inability of this counterion to fit into the dibenzo-18-crown-6-ether. In the case of  $\text{K}^+$ , the cation was almost completely complexed by the crown ether.

Boileau {34}{35} studied the anionic polymerization of propylene sulfide and of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in the presence of cryptates. Kinetic measurements showed that, in the polymerization of propylene sulfide,  $k_p^+$  increased rapidly with counterion size, while  $k_p^-$  was unaffected. In the presence of cryptates,  $k_p^+$  is slightly greater than  $k_p^-$ , but in the absence of cryptates,  $k_p^+$  was less than  $k_p^-$ . Similar behavior was observed when  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was polymerized. Polarization of the monomer preceding ring cleavage during

propagation was increased by the presence of large counterions. In such a case, the polymerization rate of ion pairs was enhanced. When ordinary counterions were used, the degree of dissociation of the propagating chain end determined the nucleophilicity of the anion and the polymerization rate.

Solvent effects on both the anionic and the cationic polymerization of  $\beta$ -propiolactone and  $\alpha, \alpha$ -dialkyl- $\beta$ -propiolactones have been reported. Belen'kaya and Lyudvig {36} observed solvent effects in the cationic polymerization of  $\beta$ -propiolactone initiated by  $(C_2H_5)_2HO^+SbF_6^-$ . The polymerization rate was greater in methylene chloride ( $\epsilon = 8.9$ , AN = 20.4) than in nitromethane ( $\epsilon = 36.7$ , AN = 20.5).

Khomyakov and Lyudvig {37} investigated the effect of medium polarity on the rate of initiation in the cationic polymerization of  $\beta$ -propiolactone. Initiation was accomplished by ester interchange with triethyloxonium hexachloroantimonate and was faster in media of low dielectric constant. Electrical conductivity measurements revealed that dissociation of ion pairs into free ions was greater in solvents of high dielectric constant. The initiation rate constant involving free ions,  $k_{in}^+$ , and the initiation rate constant involving ion pairs,  $k_{in}^\pm$ , depended strongly on dielectric constant. Above a critical dielectric constant ( $\epsilon = 23$ ) ion pairs were more reactive than free ions. Below it, free ions were more reactive.

Markevich and Enikolopyan {38} polymerized  $\beta$ -propiolactone in toluene, tetrahydrofuran, acetonitrile, and nitrobenzene. Initiation by triethylamine was shown by IR and NMR spectroscopy to occur by

hydrogen abstraction followed by alkyl-oxygen ring cleavage. The polymerization rate increased as solvent polarity increased.

Hall {39} measured the rate constants in the anionic polymerization of many  $\alpha$ ,  $\alpha$ -dialkyl- $\beta$ -propiolactones. Differential calorimetry was used to determine these rate constants. Hall was limited to the study of oligomers, since calorimetry requires a homogeneous, nonviscous solution. Hall found that the rate of initiation was slightly greater than the rate of propagation, and that the polymerization was a living polymerization. The polymerization process was described by first order reaction kinetics. The polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was studied in acetonitrile, with tetraethylammonium pivalate as initiator, and in tetrahydrofuran, with tetrabutylammonium pivalate as initiator. The polymerization rate was greater in tetrahydrofuran. The effect of solvent polarity on reaction rate could not be determined because two different counterions were used in the two solvents.

Eisenbach and Lenz {40} determined the rate of polymerization of  $\alpha$ -methyl- $\alpha$ -butyl- $\beta$ -propiolactone in tetrahydrofuran and in dimethyl sulfoxide. The initiator was tetraethylammonium benzoate. A first order rate equation, neglecting termination, was used to describe the process. The conversion was determined by measuring the infrared absorbance of the monomer carbonyl group as a function of time.

Eisenbach and Lenz found that  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone polymerized faster in tetrahydrofuran than in dimethyl sulfoxide. On the basis of donicity {10}, they had expected that dimethyl sulfoxide



(DN = 29.8) would solvate the counterion to a greater degree than tetrahydrofuran (DN = 20.0) and greater polymerization rates would be observed. The authors explained their findings by postulating that a highly polar compound such as dimethyl sulfoxide would interact strongly with both anions and cations, increasing the tightness of an ion pair, and the polymerization rate would decrease.

This work was extended to include other  $\alpha$ ,  $\alpha$ -dialkyl- $\beta$ -propiolactones {41} including  $\alpha$ ,  $\alpha$ -dimethyl- $\beta$ -propiolactone,  $\alpha$ -methyl- $\alpha$ -ethyl- $\beta$ -propiolactone,  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone, and  $\alpha$ -methyl- $\alpha$ -n-butyl- $\beta$ -propiolactone. Tetrahydrofuran and dimethyl sulfoxide were the reaction solvents. In all cases, the polymerization rate was greater in tetrahydrofuran than in dimethyl sulfoxide. Bigdeli and Lenz believed that anion solvation was more important than cation solvation. Dimethyl sulfoxide is a better electron acceptor (AN = 19.3) than tetrahydrofuran (AN = 8.0) and should form stronger coordinate bonds. The reaction rate of a nucleophile would be less in dimethyl sulfoxide than in tetrahydrofuran.

Side reactions that compete with polymerization may obscure rate measurements. The polymerization reactions of many heterocyclic monomers have been initiated with organic sulfides, sulfoxides, and sulfonium salts {42} such as dimethyl sulfide, dimethyl sulfoxide, and trimethylsulfonium bromide. Among the compounds polymerized were  $\alpha$ -methyl- $\alpha$ -alkyl- $\beta$ -propiolactones,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone,  $\epsilon$ -caprolactam, and ethylene oxide. High molecular weight polymers were prepared at 20°C. Block copolymers were prepared by sequential monomer

addition.

While these authors did not discuss the mechanism of these reactions, Cohen and Tsuji {43} reported that epoxides such as cyclohexene oxide could be oxidized to  $\alpha$ -hydroxyketones by dimethyl sulfoxide with boron trifluoride catalysis. The same reaction occurred at lower rates with reduced yields in the absence of catalyst. This reaction proceeds by nucleophilic attack of the dimethyl sulfoxide oxygen on the epoxide ring to cause ring cleavage {44} (see Figure 9a). The sulfonium ion formed then splits to form the  $\alpha$ -hydroxyketone and dimethyl sulfide. Any of these compounds could initiate polymerization.

Bigdeli and Lenz {41} observed a correlation between alkyl substituent size of  $\alpha$ ,  $\alpha$ -dialkyl- $\beta$ -propiolactones and polymerization rate. They had expected that the bulky substituents would sterically interfere with nucleophilic attack by the propagating anion, and the polymerization rate would decrease. In both tetrahydrofuran and dimethyl sulfoxide, the order of reactivity of  $\alpha$ -methyl- $\alpha$ -alkyl- $\beta$ -propiolactones was n-butyl > propyl > ethyl > methyl. The effect was greater in tetrahydrofuran. Two explanations were proposed. Either bulkier substituents could more effectively block approach of the counterion, loosening the ion pair, or alternatively, hydrophobic interactions between substituents on the growing polymer and on the incoming monomer could increase the local monomer concentration or could position the incoming monomer for facile nucleophilic attack. Both counterion shielding and hydrophobic interactions would increase the polymerization rate. In a later paper {45}, Lenz reported that these steric effects were associated with an increase in activation entropy.

## 2.6 Gelation Phenomena

2.6.1 Gelation in Anionic Polymerization.  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was polymerized in dimethyl sulfoxide by Hvilsted and coworkers {46}. Tetraethylammonium benzoate was the initiator. Analysis of the polymerization kinetics was difficult because gelation occurred at low conversions. By using high initiator-to-monomer ratios, it was possible to measure the polymerization rate. Plots of conversion as a function of time showed that the polymerization rate decreased abruptly after about fifteen minutes. The molecular weight distributions of polymers formed after the rate decrease were multimodal.

2.6.2 Gelation in Polymeric Systems. Gelation has been observed in many polymer-solvent systems, including gelatin-water {47}, poly(acrylonitrile co-vinyl acetate)-N, N-dimethylacetamide {48}, poly(methyl methacrylate)-N, N-dimethylformamide {49}, polystyrene-decalin {50}, poly(vinyl alcohol)-water {51}, poly(vinyl chloride-dimethylphthalate {52}, and poly(pivalolactone)- $\gamma$ -butyrolactone {53}. Gelation in these systems does not result from chemical crosslinking but is associated with crystallization of segments of the polymer chain. Atactic poly(vinyl chloride) forms gels in both polar and nonpolar solvents {52} {54} {55}. X-ray diffraction revealed that the crosslinks are composed of syndiotactic sequences which crystallize into a fringed micellar morphology. Crystallinity was limited by the low degree of stereoregularity of the polymer.

Mixtures of isotactic and syndiotactic poly(methyl methacrylate),

as well as block copolymers, can form gels in N, N-dimethylformamide, although neither of the homopolymers gelled in the absence of the other {49}. Gelation is thermally reversible because of the non-covalent nature of the crosslinks. Coherent x-ray scattering disappeared above the melting point. Tacticity determinations by IR and NMR spectroscopy revealed that, as the syndiotactic content of the polymer increased, the melting point also increased because gelation was caused by crystallization of syndiotactic sequences.

The kinetics of the gelation of gelatin in water were followed by differential scanning calorimetry {47}, and were consistent with rapid nucleation of crystallization and fibrillar growth, followed by slow improvement of crystallinity.

Frequently, the degree of crystallinity in polymer gels is too low for detection by x-ray diffraction {56}, since diffuse scattering by solvent may obscure the crystalline diffraction pattern. By orienting the molecules in the gel, Paul {48} was able to distinguish between the anisotropic scattering of the gel and the diffuse isotropic scattering from the solvent. Increasing the concentration of the crystallizable component by altering polymer concentration, molecular weight, or tacticity {51} enhances coherent diffraction intensity.

The number of crosslinks in a polymer gel is affected by the solvent and the gelation conditions. Gels formed at low temperatures contain a greater number of crosslinks which melt at lower temperatures than those formed at higher temperatures {47}.

The type of solvent can affect the conformation of the dissolvent polymer and so alter the extent and the rate of gelation. Gels of



poly(vinyl chloride) exhibit two types of crystalline morphology. One type corresponds to fringed micellar crystallization and was shown to be load bearing by x-ray diffraction studies on stretched samples. The other type corresponds to lamellar crystallization. The properties of the two crystalline morphologies are solvent dependent.

Gels with low moduli are obtained in good or in poor solvents (as described by the solubility parameter,  $\delta$ ); gels with high moduli are obtained in medium solvents which optimize the polymer-polymer inter-chain interactions needed for crystallization {52}.

Once the gel has formed, the solvent swells the amorphous material between crosslinks. In poly(vinyl alcohol) gels {57}, the x-ray diffraction pattern is unaffected by a change in solvent since solvent molecules are excluded from the crystallites. Many polymer gels exude solvent (syneresis) {48}{56} as crystallinity increases, because the solvent is squeezed out by crystallization.

## C H A P T E R   I I I

### SOLVENT EFFECTS IN THE ANIONIC POLYMERIZATION OF $\alpha$ -METHYL- $\alpha$ -PROPYL- $\beta$ -PROPIOLACTONE

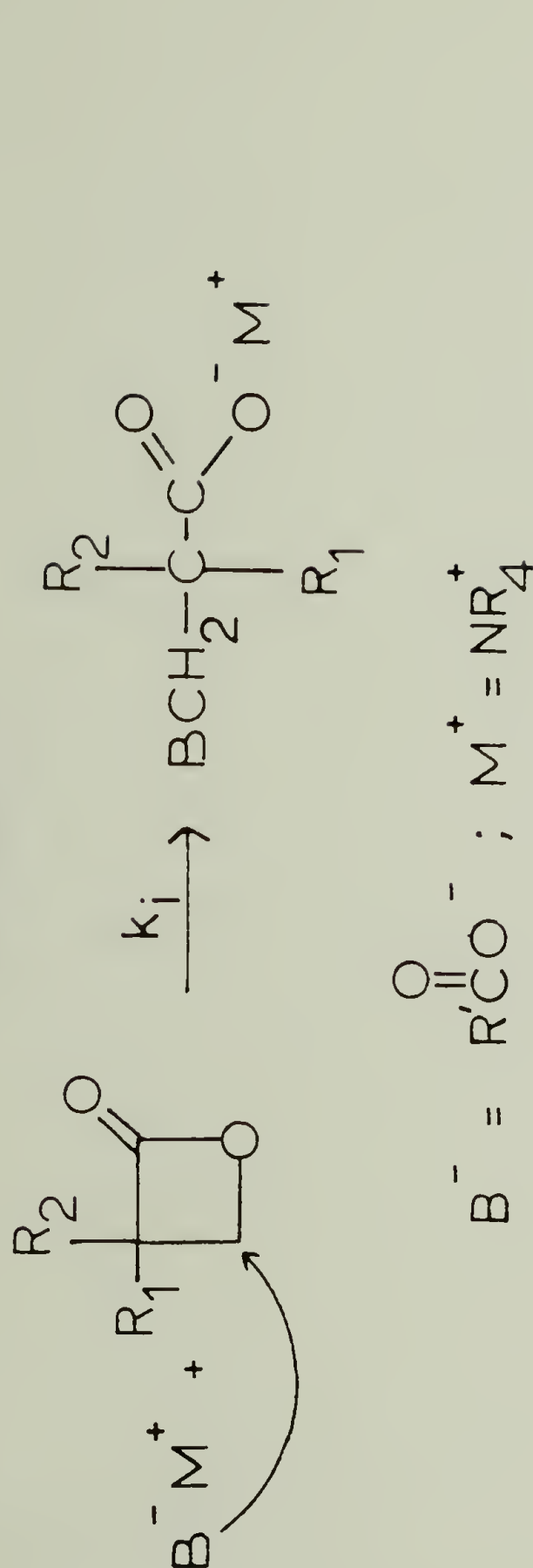
#### 3.1 Polymerization Kinetics

The anionic polymerization of  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones is an  $S_N2$  reaction (see Figure 2). Initiation and propagation occur by nucleophilic attack at the unsubstituted  $\beta$  carbon atom, which causes ring cleavage between the  $\beta$  carbon atom and the ring oxygen {58}{59}. Weak nucleophiles, such as carboxylate salts, can initiate polymerization because ring strain enhances the electrophilicity of the unsubstituted carbon atom. Chain transfer to monomer does not occur, so in the absence of impurities, a living polymerization system can be obtained.

Reaction conversion can be determined with infrared spectroscopy by measuring the monomer carbonyl group absorbance periodically throughout the course of the polymerization reaction. This band was selected because its large extinction coefficient enabled accurate determination of small concentration of monomer and because this absorbance is distinct from absorbances of the carbonyl group in the polymer chain (see Figure 3).

The polymerization reaction is described by a first order rate equation without termination or transfer. The rates of initiation and propagation are similar because both the initiating and the propagating species are carboxylate ion {39}, hence, the rate of initiation can be

### Initiation



### Propagation

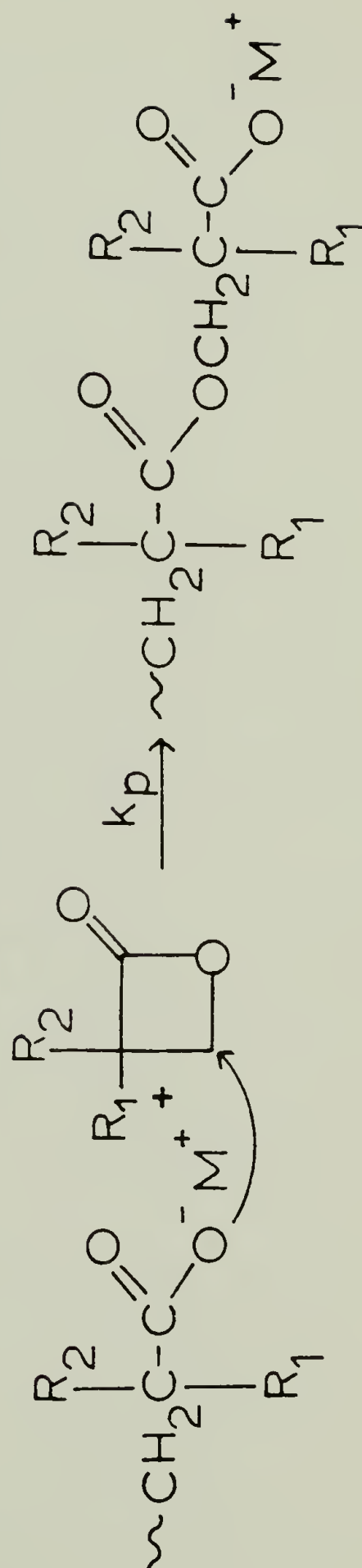


Figure 2. Polymerization reactions in the anionic polymerization of  $\alpha$ ,  $\alpha$ -dialkyl- $\beta$ -propiolactones.

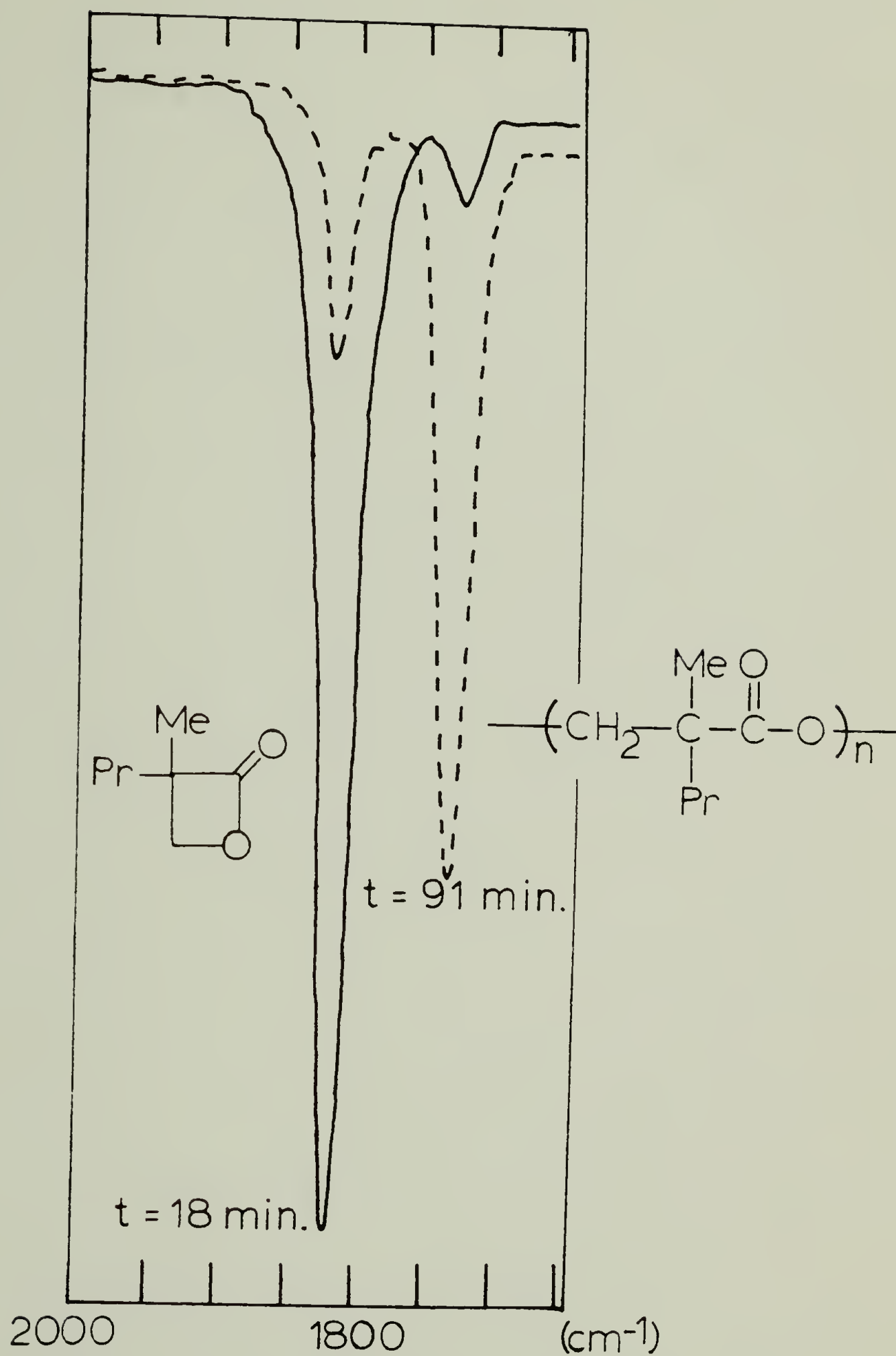


Figure 3. Monomer and polymer carbonyl group infrared transmittances at different conversions.

neglected when describing the rate of disappearance of monomer. Then,

$$-\frac{d\{M\}}{dt} = k_p \{M\} \{LE\} \quad (3.1)$$

where  $\{M\}$  is the monomer concentration at any time  $t$ ,  $k_p$  is the composite (or global) rate constant for ion pairs and free ions, and  $\{LE\}$  is the concentration of living ends.

$$k_p = (1 - f) k_p^+ + f k_p^- \quad (3.2)$$

where  $f$  is the fraction of free ions,  $k_p^+$  is the propagation rate constant of ion pairs, and  $k_p^-$  is the propagation rate constant of free ions.

$$\{LE\} = \{I_o\} \quad (3.3)$$

where  $\{I_o\}$  is the initial initiator concentration. Integration of Equation 3.1 and substitution of Equation 3.3 gives the following equation:

$$\ln \{M\} = \ln \{M_o\} - k_p \{I_o\} t . \quad (3.4)$$

Beer's law relates the measured absorbance to the monomer concentration, as follows:

$$A = ab\{M\} \quad (3.5)$$

where  $A$  is the absorbance,  $a$  is the extinction coefficient,  $b$  is the path length, and  $\{M\}$  is the monomer concentration. Substitution of Equation 3.5 into Equation 3.4 gives the following:

$$\ln A = \ln \{M_o\} + \ln (ab) - k_p \{I_o\} t . \quad (3.6)$$



The composite rate constant,  $k_p$ , can be determined from the slope of a plot of  $\ln$  absorbance as a function of time, provided that the initial initiator concentration is known.

### 3.2 Anionic Polymerization of $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone in Tetrahydrofuran

3.2.1 Beer's Law in Tetrahydrofuran. One of the important assumptions in the kinetic analysis is that the absorbance of a species is proportional to its concentration (Beer's law). This is true when no concentration-dependent associations occur between the species in solution {60}. Beer's law is obeyed in tetrahydrofuran by the monomer under study, both in the absence and in the presence of polymer (see Figure 4).

3.2.2 Living Nature of the Polymerization. In principle it should be possible to obtain living polymers in tetrahydrofuran, and such systems were obtained under the experimental conditions. Samples were removed periodically from the polymerizing reaction mixture and their conversions were measured spectroscopically. When all of the monomer had been consumed, additional monomer was added and its rate of disappearance was determined (see Figure 5). The second batch of monomer was consumed at approximately the same rate as the first (see Table 2), indicating that the number of growing chain ends probably did not change.

Molecular weights of samples obtained periodically throughout the polymerization reaction were determined by gel permeation chromatography and agree well with molecular weights calculated from the relationship  $\overline{DP}_n = \{M\} / \{I_0\}$  (see Table 3). The ratio of  $\overline{M}_W / \overline{M}_N$

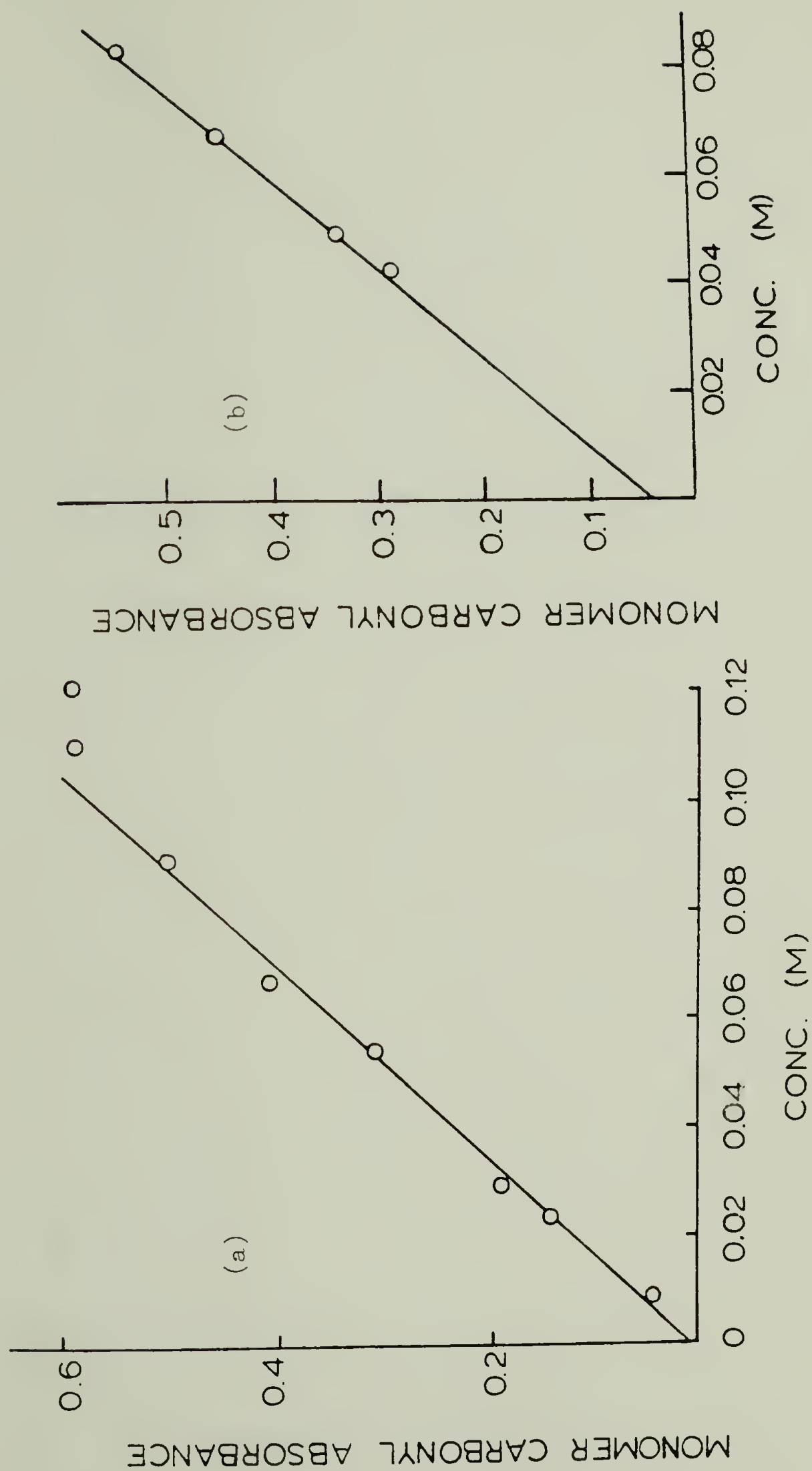


Figure 4. Monomer carbonyl group infrared absorbance as a function of molar concentration. A. In the absence of polymer. B. In the presence of polymer.

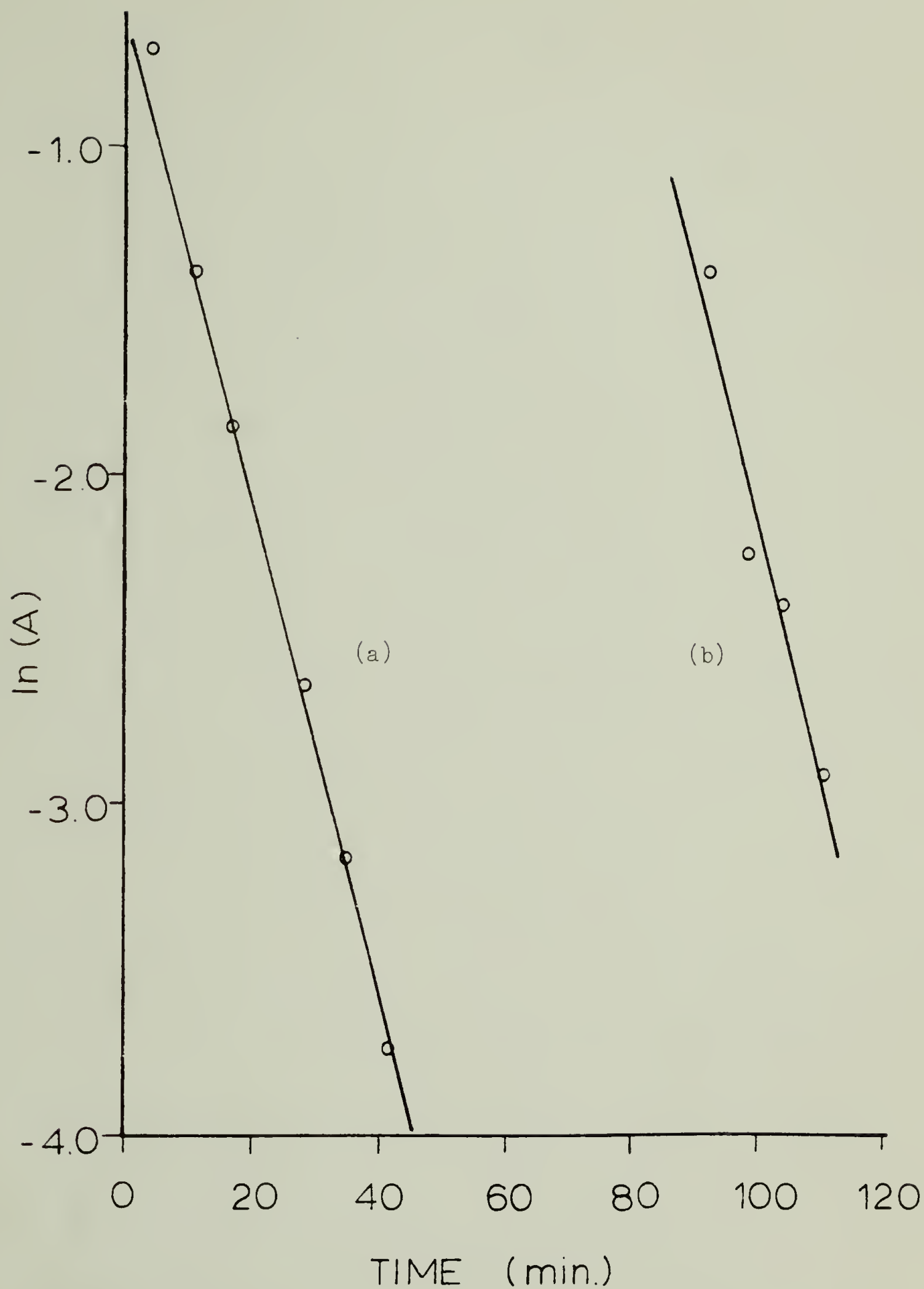


Figure 5. Conversion as a function of time in the living anionic polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in tetrahydrofuran at  $34^{\circ}\text{C}$ . A. After initiation  
B. After addition of additional monomer.

approached the theoretical value of 1.00 at higher conversions.

Table 2

Polymerization Rates of Living  
Poly( $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone)\*

Time of monomer addition	$k_p \{I_o\}$ ( $\text{min.}^{-1}$ )	$k_p$ ( $\text{M}^{-1}\text{min.}^{-1}$ )
0 min.	0.07474	$34.8 \pm 0.7$
88.4 min.	0.0792	$37 \pm 3$

\* in tetrahydrofuran with tetraethylammonium benzoate at  $34^\circ\text{C}$

Table 3

Calculated and Experimental Molecular Weights of  
Poly( $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone) Prepared in Tetrahydrofuran\*

$\{I_o\}$ (M)	$\{M_o\}$ (M)	Polymer- ization Time (min.)	Calculated MW	Observed $\bar{M}_W$	$\bar{M}_N$	$\bar{M}_W / \bar{M}_N$
0.000878	0.2264	12.39	11000	15000	9000	1.56
0.000871	0.2629	20.83	19000	17000	15000	1.15
0.000879	0.1955	25.19	16000	18000	17000	1.06
0.000870	0.2731	29.20	24500	25000	23000	1.09

\* with tetraethylammonium benzoate at  $34^\circ\text{C}$

3.2.3 Heat Conduction in IR Cells. Previously, kinetic measurements were made on unquenched reaction systems, exposing the still-polymerizing



solution to temperature changes as the solution left its constant temperature environment to enter an IR cell at room temperature. The rate of heat conduction from the solution to the IR cell can be estimated from Fourier's law of heat conduction {61} (see Appendix II). It was estimated that the solution in the cell should have reached room temperature in approximately five seconds when the reaction solvent was diethyl ether. Less time would be required for more polar solvents, which have higher thermal conductivities. The polymerization rate constants obtained from unquenched samples were variable, because polymerization rates are temperature sensitive. When an unquenched sample was held even a few seconds longer at room temperature before its conversion was determined, the measured rate constant was greatly affected (see Figure 6 and Table 4). Therefore, quenched samples must be used for kinetic measurements by infrared spectroscopy. A suitable quenching agent is methanol.

Table 4

Effect of Sampling Technique on  
Polymerization Rate\*

Sample time at room temperature	$k_p \{I_o\}$ (min. <sup>-1</sup> )	$k_p$ (M <sup>-1</sup> min. <sup>-1</sup> )
8 sec.	0.062	39.0
12 sec.	0.041	25.8

\*  
in tetrahydrofuran with tetraethyl-  
ammonium benzoate

3.2.4 Rate Measurements in Tetrahydrofuran. All of the reagents were

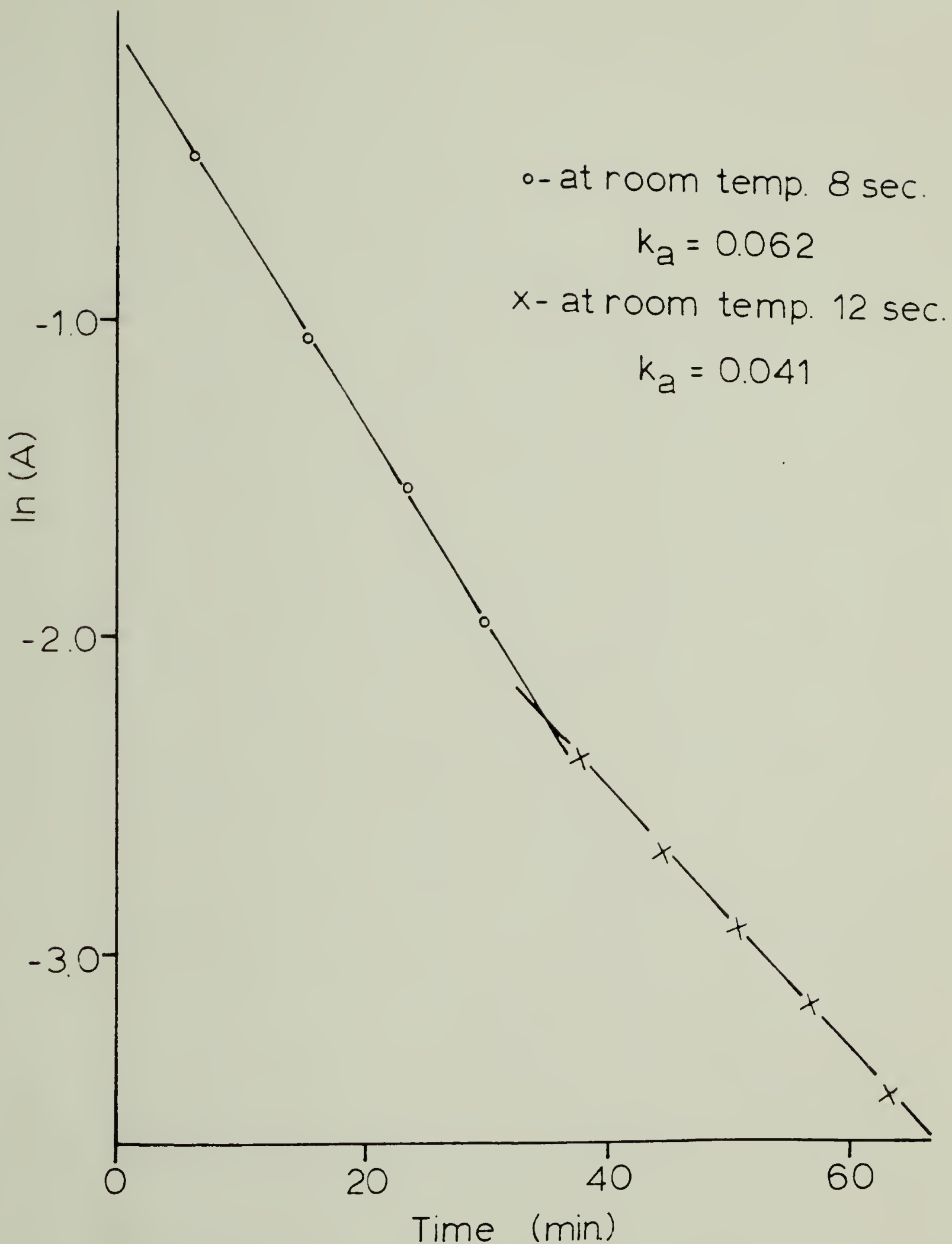


Figure 6. Conversion as a function of time of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in tetrahydrofuran from measurements on unquenched samples.

carefully purified and dried (see Chapter 6 for experimental details). The polymerization vessels were dried with a Bunsen burner flame while under vacuum, then filled with argon. Manipulations of the initiator, tetraethylammonium benzoate, were performed in a nitrogen-filled glove box. A weighed amount of a stock initiator solution was injected into each polymerization vessel, and the reaction mixture was allowed to reach 34°C in a constant temperature bath. A weighed amount of monomer,  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone, was added and allowed to polymerize a given length of time, after which polymerization was quenched with a known amount of methanol. The absorbances of the unreacted monomer were determined and normalized to the same initial monomer concentration. A plot of  $\ln$  absorbance as a function of time was found to be linear (see Figure 7), indicating that the monomer disappeared by a first order process. The overall polymerization rate constant,  $k_p$ , was  $37 \pm 0.67 \text{ M}^{-1} \text{ min.}^{-1}$ . This is similar to that reported by Bigdeli and Lenz {41} ( $31.9 \text{ M}^{-1} \text{ min.}^{-1}$  at 34°C). The molecular weight distributions of these samples were narrow, as expected for a living system. The molecular weights observed agreed with the calculated values (see Table 3).

### 3.3 Polymerization Reactions in Dimethyl Sulfoxide

Dimethyl sulfoxide acts as an initiator as well as a solvent and reacts with  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone to initiate an anionic polymerization. This reaction occurred despite all attempts to further purify the solvent and could not be quenched by addition of methanol. The molecular weight of the polymer was low and the distribution was somewhat broad ( $\bar{M}_W = 3800$ ,  $\bar{M}_N = 3200$ ,  $\bar{M}_W / \bar{M}_N = 1.2$ ), as expected when new

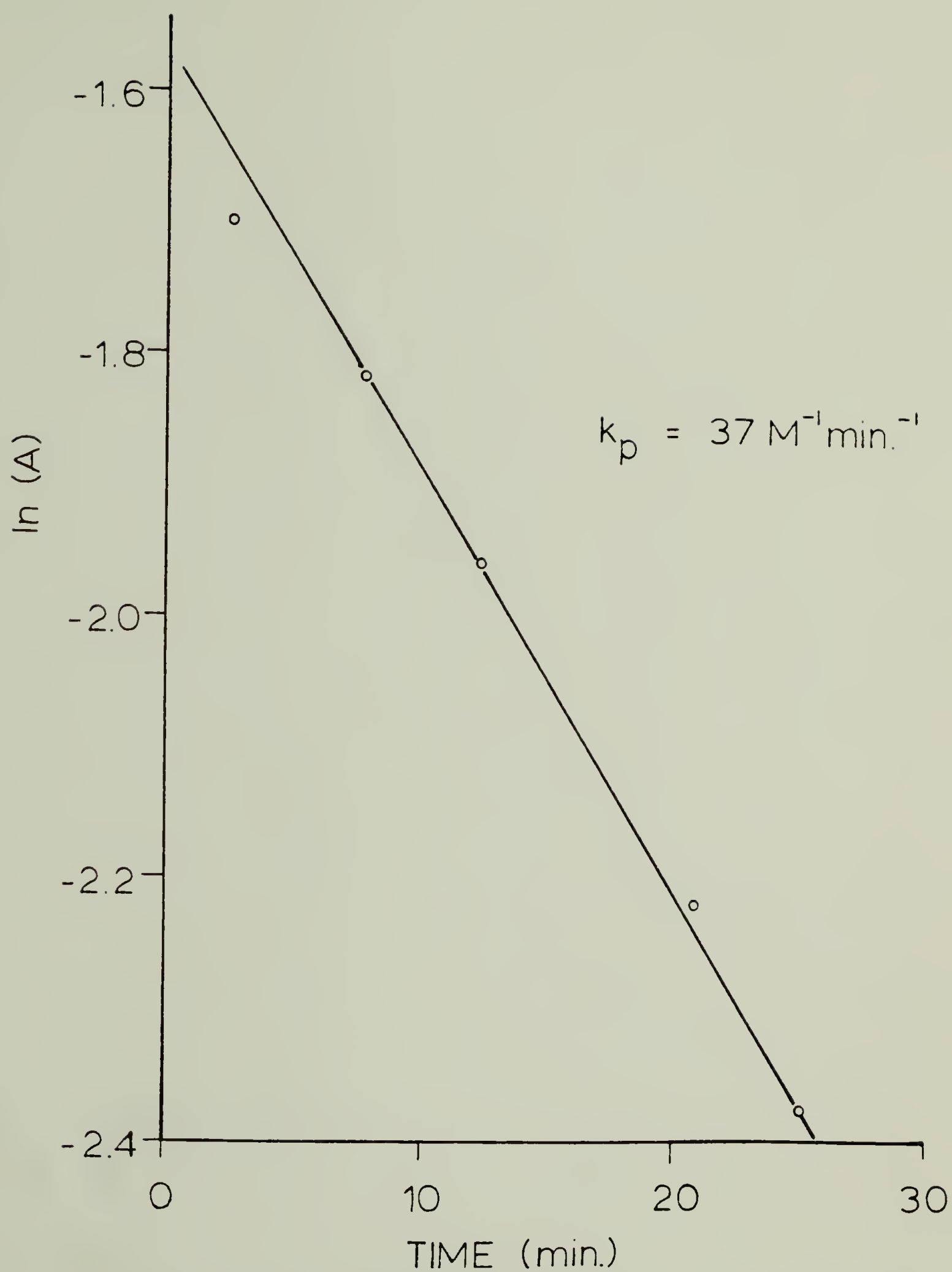


Figure 7. Conversion as a function of time of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in tetrahydrofuran at  $34^\circ\text{C}$  from measurements on quenched samples.



active chains are created throughout the polymerization reaction.

The monomer disappeared by a first order process (see Figure 8). The slope of this line was taken as the apparent rate constant,  $k_a = k_p \{I_o\}$ , and was equal to  $0.066 \text{ min.}^{-1}$  when  $\{M_o\} = 0.214 \text{ M}$ . Bigdeli and Lenz {41} polymerized  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in dimethyl sulfoxide but also added tetraethylammonium benzoate to initiate polymerization. The apparent rate constant was slightly greater than that found in the absence of tetraethylammonium benzoate ( $k_a = 0.076 \text{ min.}^{-1}$  when  $\{I_o\} = 0.066 \text{ M}$  and  $\{M_o\} = 0.153 \text{ M}$ ). The two modes of initiation, therefore, are competitive.

Similar behavior was observed in the polymerization of 1, 2-butylene oxide initiated by potassium t-butoxide in dimethyl sulfoxide {62}. Dilatometry revealed that the monomer disappeared by a first order process prior to phase separation of the polymer. Phase separation occurred later at lower initiator concentrations. The molecular weights of the polymers obtained were substantially lower than those theoretically predicted, and the distributions were broad. The investigators eliminated chain transfer to monomer as a cause of these effects because no double bonds were detected in the polymer. Phase separation of the polymer also was not responsible because there was no single molecular weight at which precipitation occurred. The explanation, they decided, was that formation of potassium dimethyl and butanol occurred by reaction between solvent and initiator. Chain transfer to the butanol formed and to the solvent decreased the molecular weight and broadened the molecular weight distribution. The authors did not consider formation of another initiating species by reaction of the monomer with the solvent.



Figure 8. Conversion as a function of time of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in dimethyl sulfoxide.

Nucleophilic attack on epoxide rings by the sulfoxide oxygen causes ring cleavage to occur, with formation of  $\alpha$ -hydroxyketones and dimethyl sulfide {43}{44}. Both the intermediates and the end products of this reaction can initiate polymerization {42}. Similar behavior of dimethyl sulfoxide towards  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone, as shown in Figure 9, should also be possible, because this monomer is also highly electrophilic because of ring strain.

### 3.4 Polymerization Reactions in N, N-Dimethylformamide

N, N-Dimethylformamide also interacts directly with  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone to initiate polymerization. The apparent rate constant obtained from plots of  $\ln$  (absorbance) as a function of time (see Figure 10) was proportional to the monomer concentration, while the polymer molecular weight was independent of monomer concentration (see Table 5). This result implies that the initiator concentration was proportional to the monomer concentration.

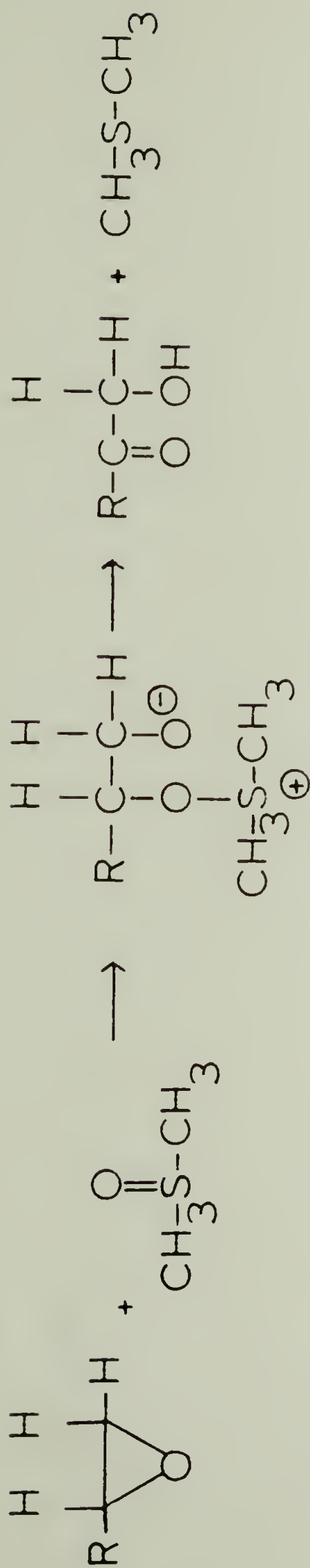
Table 5

Rate Constant and Molecular Weight as a Function of Monomer Concentration in N, N-Dimethylformamide

$\{M_o\}$ (M)	$k_a$ ( $M^{-1} \text{ min.}^{-1}$ )	$\bar{M}_W$	$\bar{M}_N$
0.299	$0.062 \pm 0.008$	68000	64000
0.145	$0.032 \pm 0.004$	70000	51000

N, N-Dimethylformamide can act as a nucleophile under certain conditions. Nucleophilic attack of N, N-dimethylformamide {63} on a

(a)



(b)

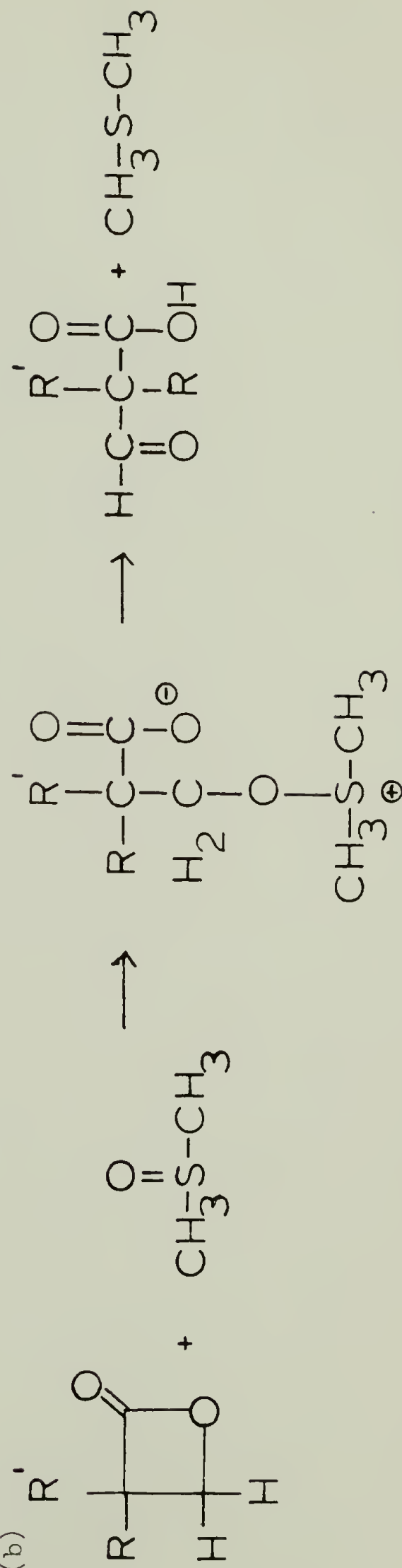


Figure 9. Oxidation of heterocycles by dimethyl sulfoxide. A. Epoxides. From Reference {44}.  
 B.  $\alpha$ ,  $\alpha$ -Disubstituted- $\beta$ -propiolactones.



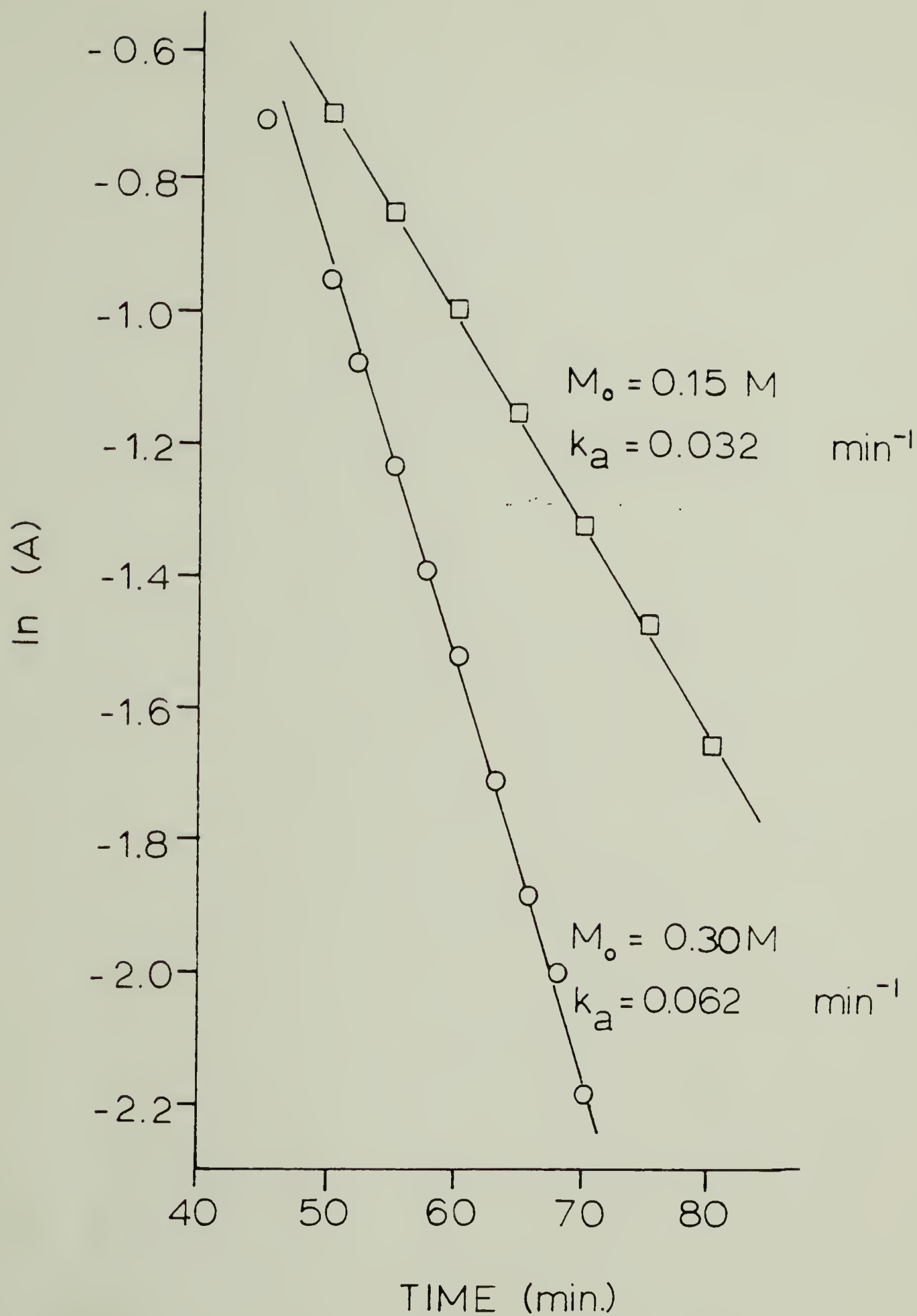


Figure 10. Conversion as a function of time of  $\alpha$ -methyl- $\alpha$ -propyl  $\beta$ -propiolactone in N, N-dimethylformamide.

cyclic anhydride causes ring cleavage to form the corresponding N, N-dimethylamide. When succinic anhydride was heated with N, N-dimethylformamide and a catalytic amount of sulfuric acid, a 90 % yield of N, N-dimethylsuccinamic acid was obtained as shown by the reaction in Figure 11a. Analogously, nucleophilic attack by N, N-dimethylformamide on  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone would form a carboxylic acid, as shown in Figure 11b, and the product should be capable of initiating a polymerization reaction.

The effects of dimethyl sulfoxide and of N, N-dimethylformamide on the polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone initiated by tetraethylammonium benzoate, therefore, are obscured by the reaction between the monomer and the solvent. In order to accurately assess the effects of reaction solvent on polymerization rates, inert solvents must be used.

### 3.5 Anionic Polymerization of $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone in N-Methylpyrrolidone

3.5.1 Beer's Law in N-Methylpyrrolidone. Measurements that were performed to verify Beer's Law for the monomer in N-methylpyrrolidone were complicated by solvent etching of the NaCl IR plates. NaCl can initiate the anionic polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in N-methylpyrrolidone, but this reaction is suppressed in the presence of methanol. In any case, the monomer was found to be inert in N-methylpyrrolidone in the absence of NaCl.

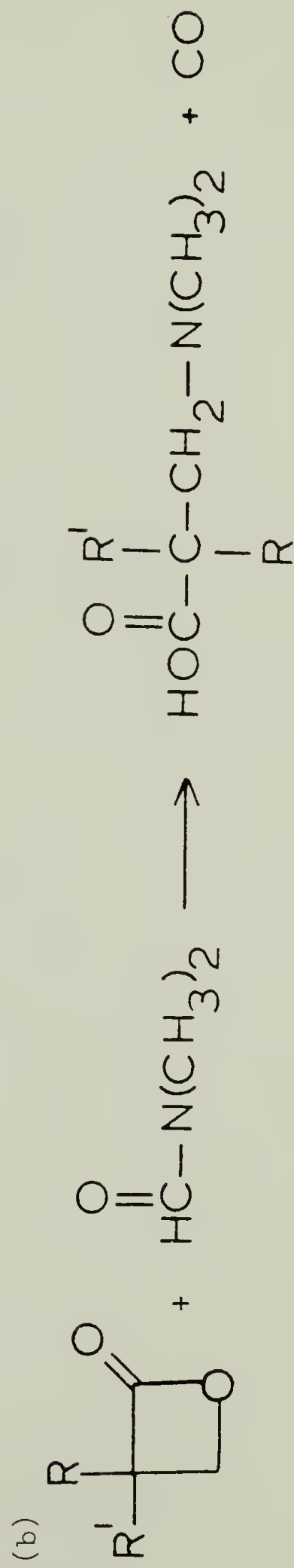
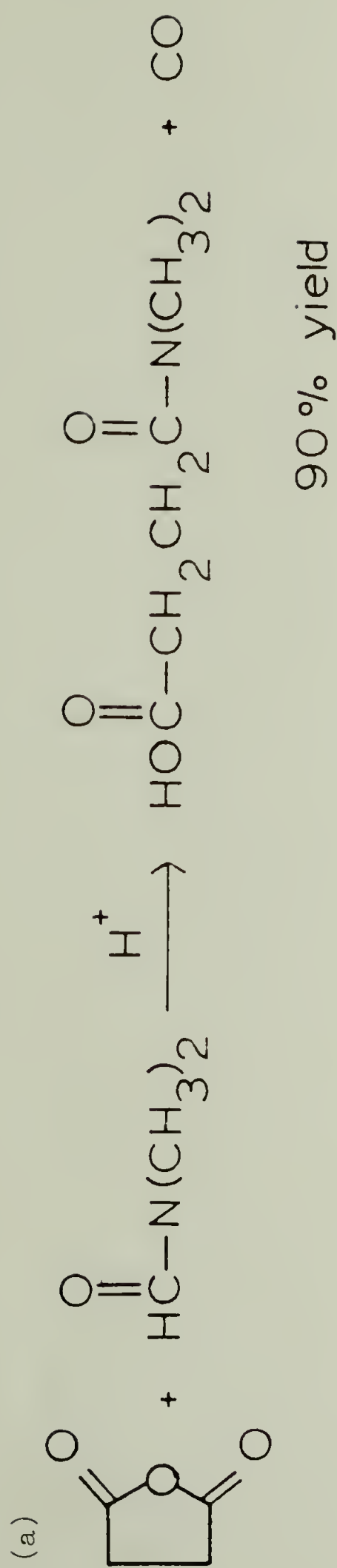


Figure 11. Nucleophilic attack by N, N-dimethylformamide. A. on succinic anhydride. From Reference {63}. B. on  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones.

3.5.2 Rate Measurements in N-Methylpyrrolidone. The polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone initiated by tetraethylammonium benzoate is five times faster in N-methylpyrrolidone than in tetrahydrofuran (see Figure 12). The overall rate constant,  $k_p$ , was  $168 \pm 8 \text{ M}^{-1} \text{ min.}^{-1}$  in N-methylpyrrolidone. The observed molecular weights of the polymers formed agreed with the calculated values and the polymers had narrow molecular weight distributions (see Table 6).

Table 6

Calculated and Experimental Molecular Weights of  
Poly( $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone)  
Prepared in N-Methylpyrrolidone\*

$\{I_o\}$ (M)	$\{M_o\}$ (M)	Polymer- ization Time (min.)	Calculated MW	Observed $\bar{M}_W$ $\bar{M}_N$		$\bar{M}_W / \bar{M}_N$
0.0002081	0.1310	5.00	12980	11000	10000	1.10
0.0002077	0.1449	10.00	26420	22000	20000	1.10
0.0002080	0.1369	15.00	34500	32000	28000	1.11
0.0002079	0.1403	20.00	45000	36000	33000	1.11

\* with tetraethylammonium benzoate at  $34^\circ\text{C}$

### 3.6 Anionic Polymerization of $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone in Acetone

Measurements of absorbance as a function of monomer concentration verified that Beer's Law was obeyed in acetone. The polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was faster in acetone than in tetra-

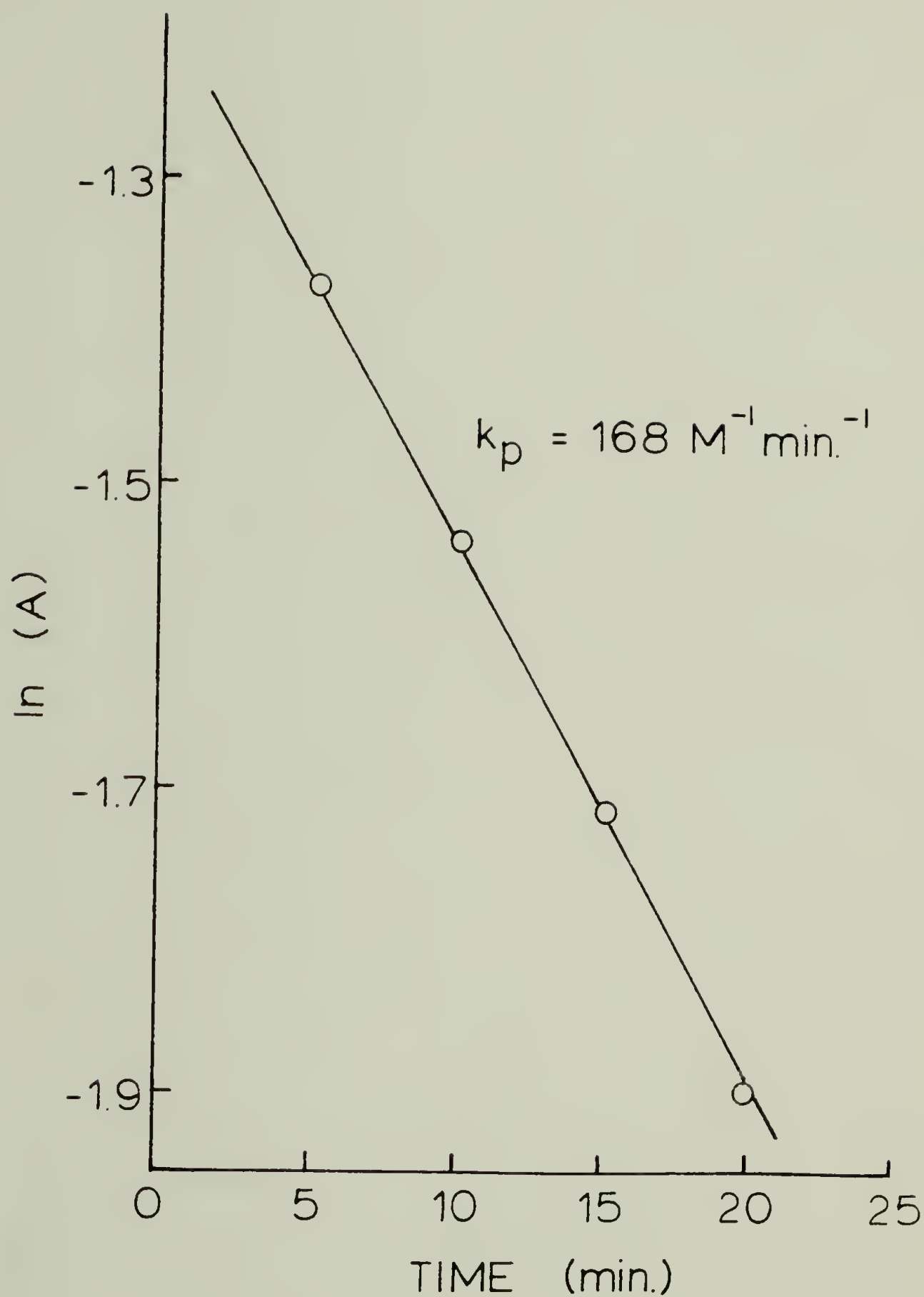


Figure 12. Conversion as a function of time of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in N-methylpyrrolidone at  $34^\circ\text{C}$ .



hydrofuran, but the rate constant was strongly dependent on the monomer concentration (see Figure 13 and Table 7). One possible explanation of this effect is that in acetone, the living chain ends may exist in the form of both free ions and ion pairs {27}. The concentration of free ions may increase upon addition of increasing amounts of the highly polar monomer,  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone. Hence, it is suggested that the monomer can preferentially solvate the active end-group.

Table 7

Dependence of Polymerization Rate Constant  
in Acetone on Concentration of  
 $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone\*

Monomer Concentration	Initiator Concentration	$k_p$ ( $M^{-1}min.^{-1}$ )
0.0902 M	0.000256 M	87.90
0.0931 M	0.000323 M	103.13
0.0983 M	0.000351 M	141.72

\* with tetraethylammonium benzoate at 34°C

### 3.7 Reactions in Halogenated Solvents

The polymerization reactions of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone were attempted in both methylene chloride and chloroform but no polymerization occurred in either case.

Reutov and coworkers {64}, and Klabunde and Burton {65} found that

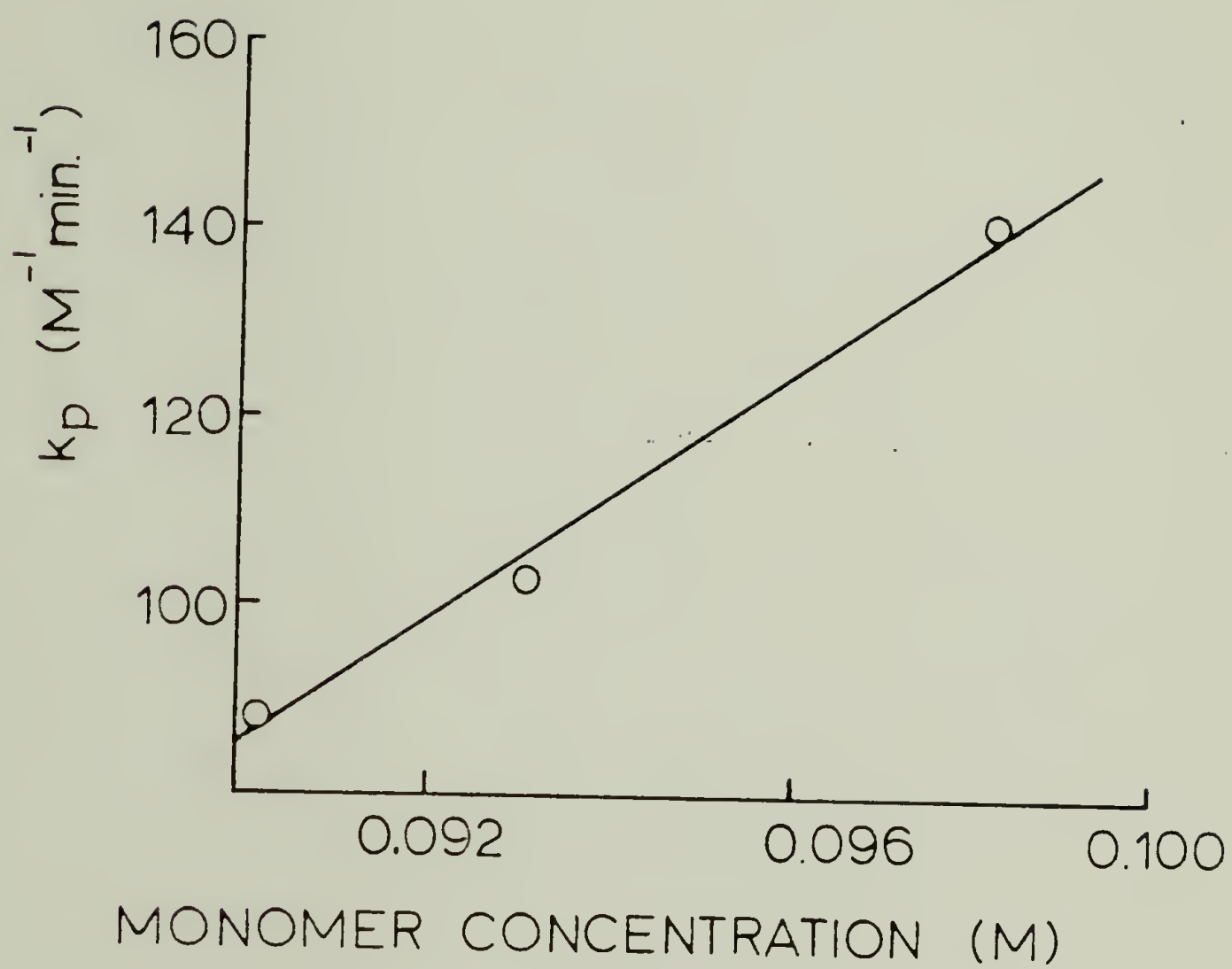


Figure 13. Polymerization rate constant as a function of monomer concentration in acetone at  $34^{\circ}\text{C}$ .

the  $pK_a$  of chloroform was 15. Its acidity is similar to water ( $pK_a = 14$ ) and slightly greater than methanol ( $pK_a = 16$ ) {64}. The polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in chloroform, therefore, may be terminated by hydrogen ion donation from the solvent.

Slomkowski {66} reported that methylene chloride was an unsuitable solvent for the tetramethylammonium acetate initiated polymerization of  $\beta$ -propiolactone. The concentration of active species decreased with time and a precipitate formed. Using NMR spectroscopy, it was determined that the following reaction occurred:



Similar reactions may occur with tetraethylammonium benzoate in both methylene chloride and chloroform, and these reactions would result in termination of polymerization.

### 3.8 Correlation of Rate Constant and Solvent Parameters Describing Anion Solvation

Bigdeli and Lenz {41} polymerized  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in tetrahydrofuran and in dimethyl sulfoxide and found that the polymerization rate was less in dimethyl sulfoxide, which is a more polar solvent. They believed that anion solvation occurred to a greater extent in dimethyl sulfoxide (AN = 19.3) than in tetrahydrofuran (AN = 8.0). If anion solvation occurs, the carboxylate anion end group would have to be desolvated before propagation could occur, and this requirement should increase the activation energy of propagation and decrease the

propagation rate. The occurrence of side reactions between monomer and solvent were not considered by those authors.

Measurements of the polymerization rates in tetrahydrofuran, acetone and N-methylpyrrolidone do not support their conclusions (see Table 8). The polymerization rate was greatest in the solvent with the highest acceptor number, N-methylpyrrolidone (AN = 13.3) and least in the solvent with the lowest acceptor number, tetrahydrofuran (AN = 8.0). Acceptor numbers do not accurately describe solvation effects in anionic polymerization.

Table 8

Correlation of Polymerization Rate Constants  
and Solvent Properties\*\*

Solvent	$k_p$ ( $M^{-1} \text{ min.}^{-1}$ )	$\epsilon$	Z	$E_T$	DN	AN	$\pi^*$
THF <sup>a</sup>	$37.0 \pm 0.7$	7.6	58.8	37.4	20.0	8.0	0.576
Acetone	$110 \pm 3^b$	20.7	65.7	42.2	17.0	12.5	0.683
NMP <sup>c</sup>	$168 \pm 8$	33.0		42.2	27.3	13.3	0.921

\*\* with tetraethylammonium benzoate at 34°C

<sup>a</sup>THF = tetrahydrofuran

<sup>b</sup>average value

<sup>c</sup>NMP = N-methylpyrrolidone

### 3.9 Correlation of Rate Constant and Solvent Parameters Describing Cation Solvation

The apparent rate constant  $k_p$  is a composite rate constant and

$$k_p = (1 - f) k_p^+ + f k_p^- \quad (3.2)$$

where  $f$  is the fraction of free ions,  $k_p^+$  is the propagation rate constant of ion pairs, and  $k_p^-$  is the propagation rate constant of free ions.

Polymerization rates are enhanced in dipolar aprotic solvents primarily because of increased dissociation of ion pairs into free ions. While  $k_p^+$  also increases as the character of the ion pairs changes, the effect is small.

Dissociation is enhanced in solvents that can stabilize the resulting ions. It has been reported previously that anions are not solvated to any great extent in dipolar aprotic solvents {67}, therefore, the degree of dissociation of an ion pair is determined by the extent of cation solvation. When the cation is stabilized by specific or non-specific interactions with the solvent, dissociation increases, and the nucleophilicity of the anion and the polymerization rate increases.

3.9.1 Solvent Donor Number and Cation Solvation. Solvents that can readily donate electrons favor cation solvation. The donor number is a measure of a solvent's ability to donate electrons to  $\text{SbCl}_5$  as a standard for comparison {10}. Use of the solvent donor number to describe the extent of cation solvation assumes that similar solute-solvent interactions occur in both the reference and reactions systems. If so,



the following equation applies:

$$\ln K_{\text{Diss}} = \frac{m (\text{DN})}{RT} + c' \quad . \quad (2.6)$$

The polymerization rate should be greatest in the solvents with the highest donor numbers, because the degree of dissociation would be greatest in these.

The experimental data, however, do not support this conclusion. Tetrahydrofuran (DN = 20.0) should be a better polymerization solvent than acetone (DN = 17.0) but polymerization rates are substantially greater in acetone (see Table 8). Solvent donor numbers, therefore, do not adequately describe the extent of dissociation of quaternary ammonium salts. There are several possible reasons for this effect as described in the following sections.

3.9.1.1 Steric Interactions. Antimony pentachloride has a trigonal bipyramid structure {68} while quaternary ammonium ions such as the tetraethylammonium ion are tetrahedral {69}. Steric interactions between solvent molecules and the ligands on each cation will differ, and the donor ability of the solvent molecule towards the cation will be affected.

3.9.1.2 Specific versus Nonspecific Interactions. Antimony pentachloride can expand its electron shell to accommodate additional ligands, and so it can be solvated by accepting additional electron pairs from solvent molecules. The cation in a quaternary ammonium ion has a fixed electronic valence, so it is solvated by ion-dipole interactions. This is a different solvation mechanism than in the reference system. An important

assumption in the derivation of Equation 2.6 was that, in order for the free energy of interaction in one system to be linearly related to the free energy of interaction in another, similar interactions must occur in the two systems. A linear relationship between  $\ln K_{\text{Diss}}$  and DN may not exist when two different types of solute-solvent interactions are involved.

3.9.1.3 Entropic and Enthalpic Effects. Gutmann {11} has shown that the solvation entropy of antimony pentachloride is constant, and so differences in the free energy of solvation can be described by the heat of solvation (the donor number). However, donor numbers are determined in dilute solution where differences in solvation entropy will not be apparent. Each solvent molecule acts as an isolated unit, with no other solvent molecules in the vicinity to modify its behavior. In the bulk solvent, dipole-dipole interactions between solvent molecules create a localized solvent structure. The extent of order varies from solvent to solvent. When an ion is placed in solution, the ion disrupts the intermolecular order and imposes a different solvent structure in its vicinity. The loss of entropy of the solvent depends on the extent of solvent order prior to ion solvation, which cannot be assessed in dilute solution. Reorganization of the solvent structure also requires energy. The free energy of solvation measured in dilute solution differs from that measured in the bulk solvent. Equation 2.6 may still be valid for bulk solvents, but the value of the donor number and the constant  $c'$  will change in that case.

3.9.2 Dielectric Constant and Cation Solvation. Solvation of tetraethylammonium ions occurs by ion-solvent dipole interactions {14}.

The extent of ion solvation is related to the magnitude of the dipole moment of the solvent molecules in the vicinity of the ion. The dipole moment is related to the molecular polarizability {70} as follows:

$$\vec{\mu} = \alpha \vec{E}$$

where  $\vec{\mu}$  is the dipole moment,  $\alpha$  is the polarizability, and  $\vec{E}$  is the strength of the electric field imposed by the ion. The polarizability can be related to the dielectric constant {71}. Thus, solvation of ions by ion-solvent dipole interactions, which increase as solvent polarizability increases, is greatest in solvents of high dielectric constant. This conclusion is supported by measurements of the rate of polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone initiated by tetraethylammonium benzoate (see Figure 14 and Table 8). The extent of solvation of the tetraethylammonium ion is related to the dielectric constant in other solvent systems, including propylene carbonate, N, N-dimethylformamide, acetonitrile {19}, hexamethylphosphoramide {24}, N, N-dimethylacetamide, and nitromethane {26}.

In the case of dimethyl sulfoxide, the extent of ion solvation is less than expected from its high dielectric constant {19}{23}{24}{26}. Dimethyl sulfoxide is believed to possess some intermolecular order due to dipole-dipole interactions between solvent molecules {15}{16}{17}. In structured solvents, the degree of dissociation is sometimes less than expected {3}. The energy gained by solvation is offset by the energy required to disrupt the solvent structure and rearrange the solvent

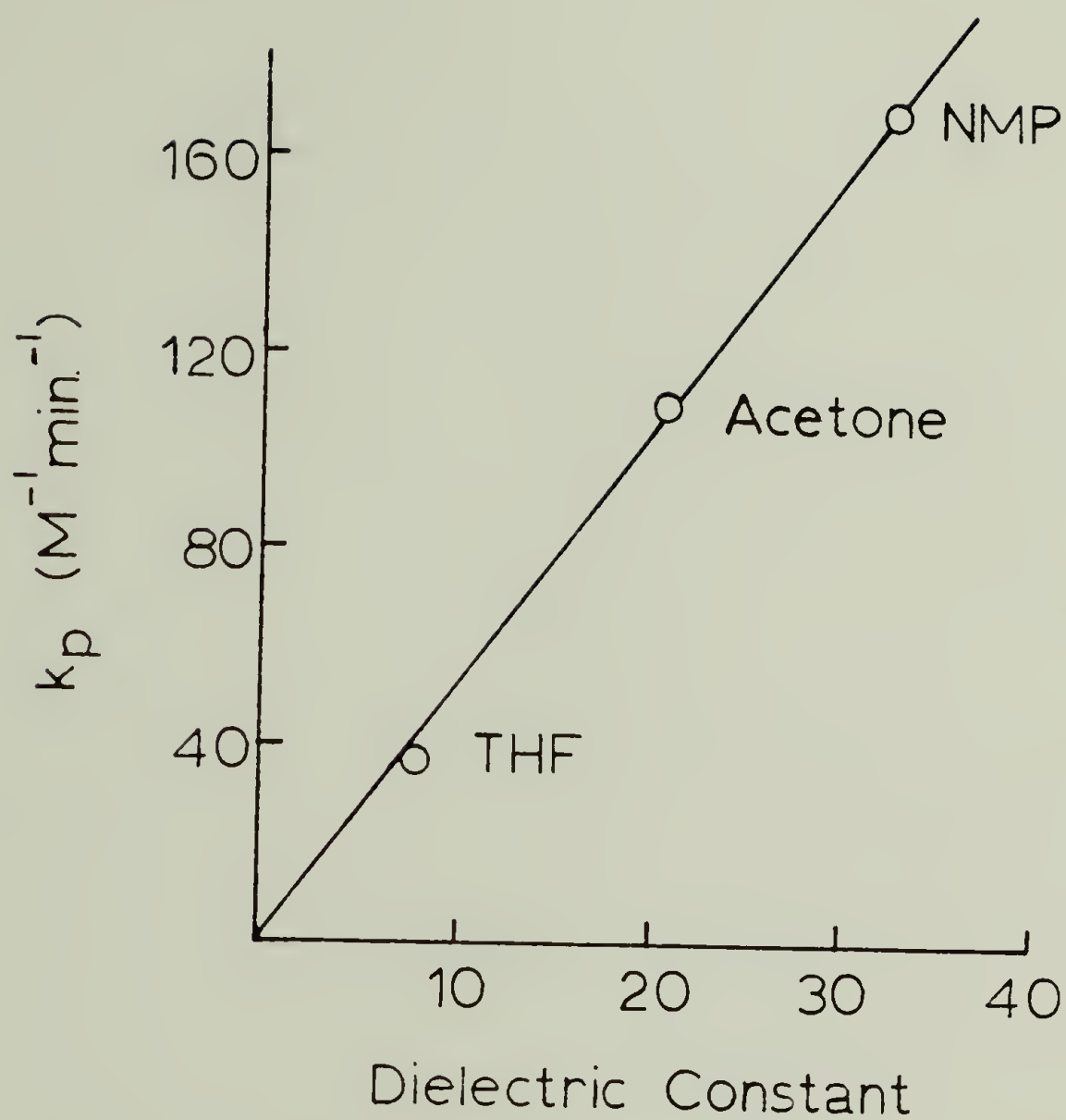


Figure 14. Polymerization rate constant as a function of solvent dielectric constant at 34°C.

THF = Tetrahydrofuran  
NMP = N-Methylpyrrolidone

molecules around an ion. Free ions disrupt the solvent structure to a greater extent than ion pairs, so the proportion of free ions may be less than expected.



## CHAPTER IV

### ANIONIC POLYMERIZATION OF $\alpha$ -ETHYL- $\alpha$ -n-BUTYL- $\beta$ -PROPIOLACTONE

#### 4.1 Polymerization of $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in Dimethyl Sulfoxide

Hvilsted and coworkers {46} polymerized  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in dimethyl sulfoxide with tetraethylammonium benzoate. The conversion was measured by pumping the polymerizing solution through flow-through IR cells and taking periodic readings. Plots of conversion as a function of time showed that the polymerization rate decreased abruptly after about fifteen minutes. Gelation of the polymerization solution also occurred. The molecular weights of the polymers were low and the distributions were multimodal. The authors did not explain this behavior.

4.1.1 Monomer Stability in Dimethyl Sulfoxide. Multimodal molecular weight distributions suggest the presence of two or more propagating species. Dimethyl sulfoxide can initiate the polymerization of some  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones {42}, however, when  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone is placed in dimethyl sulfoxide, the monomer carbonyl absorbance remains unchanged. Polymerization does not occur.

Hall {39} has reported that, as the size of the alkyl substituent

of  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones increased, the anionic polymerization rate decreased, due to steric hindrance to the approach of the incoming carboxylate ion. Apparently, the bulky ethyl and butyl groups interfere with nucleophilic attack by the sulfoxide oxygen to the extent that no discernible reaction occurs with dimethyl sulfoxide.

4.1.2 Monomer Stability in the Presence of NaCl. NaCl can initiate the polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in N-methylpyrrolidone. Likewise,  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone slowly polymerizes in the presence of NaCl in dimethyl sulfoxide (see Figure 15 and Table 9). This reaction is suppressed in the presence of methanol. When experiments were performed in flow-through IR cells made from this compound, NaCl from the cells was apparently dissolved into the polymerizing system. As a result, two competing initiation processes occurred in the same vessel, each with its own characteristic rate constant. The dual initiation contributed to lowering of the molecular weight and broadening of the distribution.

Table 9

Polymerization Rate of  
 $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone  
 Initiated by NaCl

$\{M_o\}$	Initial $k_a$ (min. <sup>-1</sup> )	Final $k_a$ (min. <sup>-1</sup> )
0.0544 M	0.0108	0.0022
0.0327 M	0.0031	0.0016
0.0316 M	0.0019	

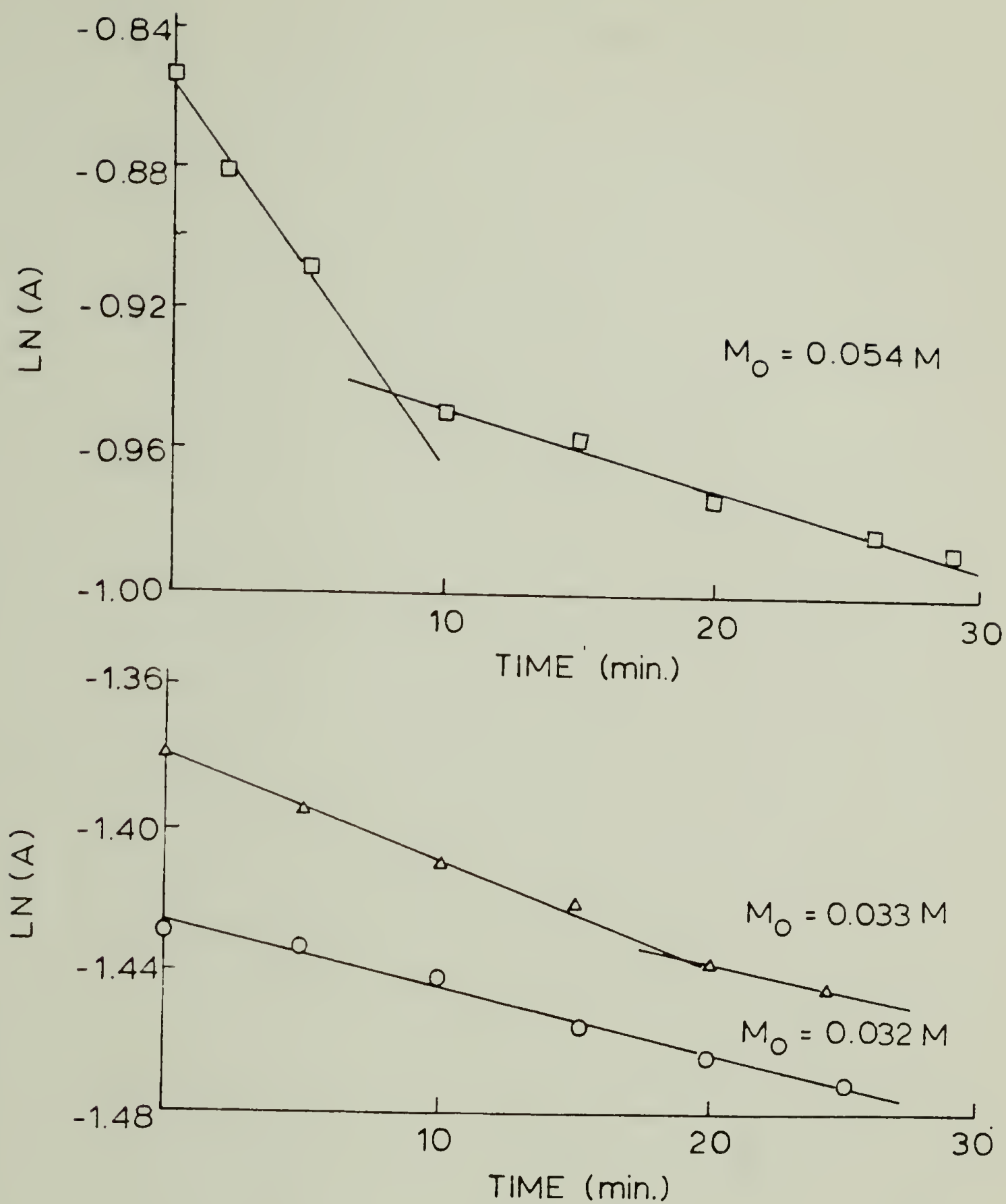


Figure 15. Conversion as a function of time of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone initiated by NaCl in dimethyl sulfoxide.

4.1.3 Effect of Gelation on the Polymerization Kinetics of  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone. Hvilsted and coworkers noted that gelation occurred during the course of polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone. They also noted that the polymerization rate decreased abruptly but they did not determine whether this was caused by gelation of the polymerizing solution.

Kinetic measurements prior to gelation established a rate constant of  $11 \pm 1 \text{ M}^{-1}\text{min.}^{-1}$ . When the polymer concentration was increased, the abrupt decrease in polymerization rate occurred sooner (see Figure 16 and Table 10). This result implies that gelation is responsible for the abrupt decrease in polymerization rate. For a polymer capable of crystallization out of solution to form a gel, a critical polymer molecular weight and polymer concentration are associated with gelation {72}.

Table 10

Dependence of Gelation Time on Initiator Concentration<sup>\*</sup>

$\{M_o\}$	$\{I_o\}$	$k_p$ ( $\text{M}^{-1} \text{ min.}^{-1}$ )	Approximate time of gelation (min.)
0.0714 M	0.000421 M	$11 \pm 1$	15 <sup>a</sup>
0.0541 M	0.000592 M	$12 \pm 1$	10 <sup>a</sup>
0.06 M	0.00056 M		13 <sup>b</sup>

\* tetraethylammonium benzoate at 34°C

<sup>a</sup>from kinetic measurements      <sup>b</sup>from viscosity measurements

As the polymer concentration increases, the critical molecular weight

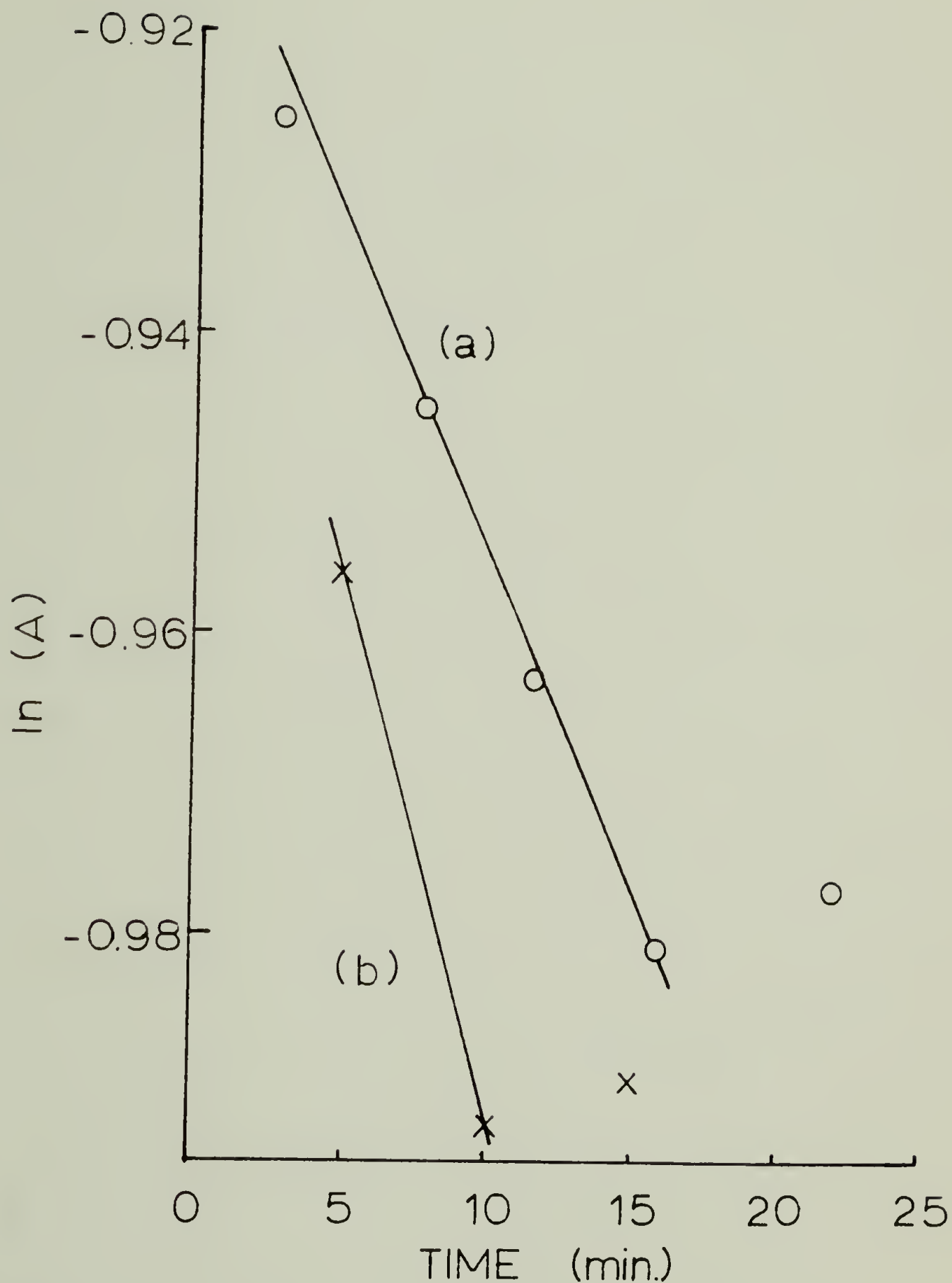


Figure 16. Conversion as a function of time of  $\alpha$ -ethyl- $\alpha$ -*n*-butyl- $\beta$ -propiolactone initiated by tetraethylammonium benzoate in dimethyl sulfoxide at 34°C.  
 A.  $\{I_0\} = 0.000421$  M B.  $\{I_0\} = 0.000592$  M



required for gelation decreases, as does the time required to reach the critical point.

Solution viscosity measurements on the polymerizing system showed that a dramatic increase in viscosity accompanied the decrease in polymerization rate (see Figure 17a and Table 10). Such dependence of viscosity on molecular weight is not expected in the absence of gelation (see Figure 17b). It can be concluded, therefore, that gelation was responsible for the abrupt decrease in polymerization rate.

Thermally reversible gelation is associated with crystallization of segments of the polymer chain {47-57}. Polymers of  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones are crystalline despite the asymmetry of the substituents resulting from polymerization of a racemic monomer mixture. Poly( $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone) is an atactic polymer whose crystallinity is limited by the low degree of stereoregularity of the polymer {73}. Likewise, crystallization of short tactic sequences of poly( $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone) during polymerization could account for gel formation.

4.1.4 Effect of Gelation on the Molecular Weight Distribution of  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone. The molecular weight distributions of polymer samples quenched prior to gelation are somewhat broad but single-valued. Distributions of samples quenched after gelation are bimodal (see Figure 18 and Table 11). It appears, therefore, that at gelation, a portion of the growing chains becomes inaccessible to further growth, while the rest continue to grow. As a result, the molecular weight of the inactive polymer chains remains unchanged with time,

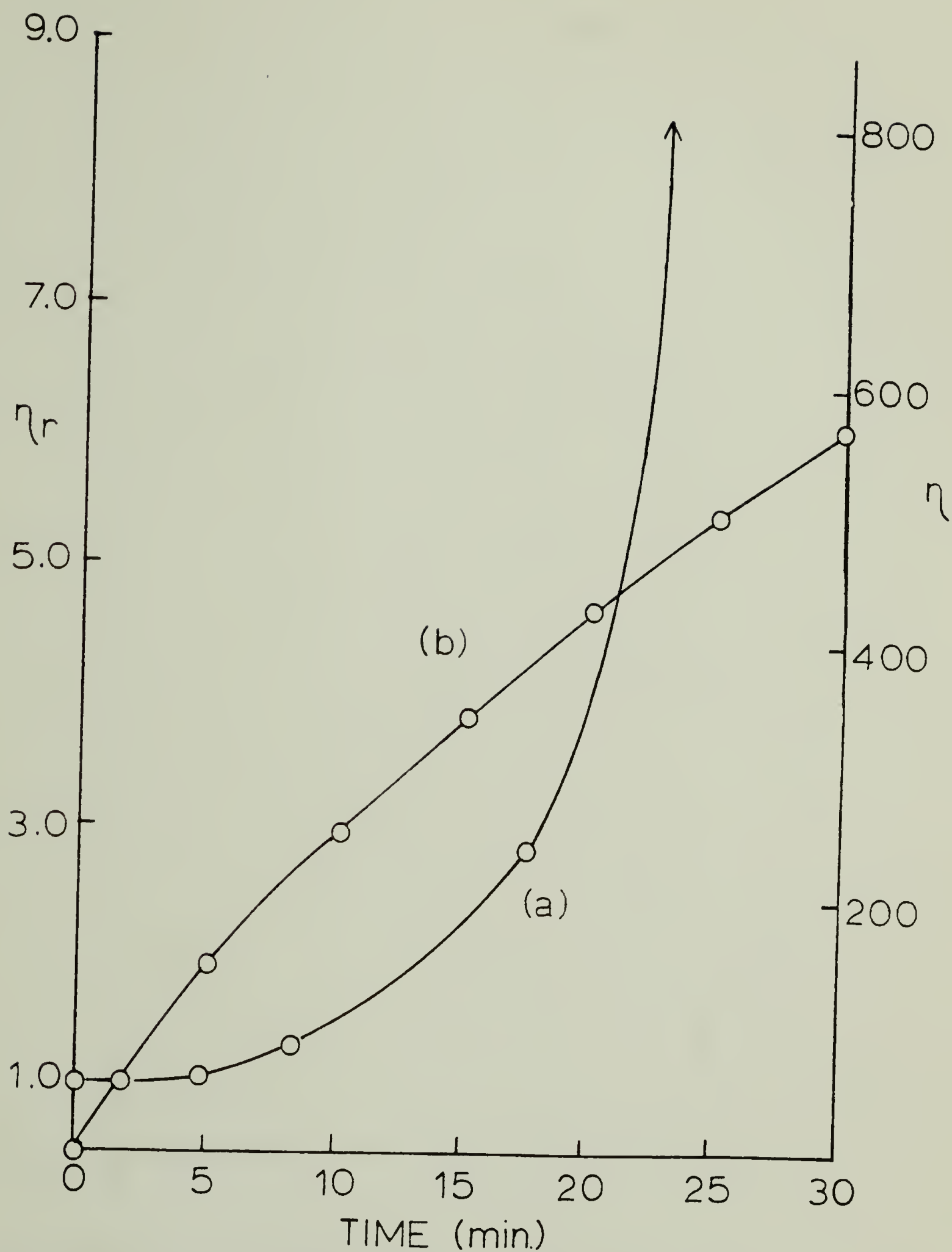


Figure 17. Solution viscosity as a function of conversion.  
 A. Polymerizing solution of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in dimethyl sulfoxide.  
 B. Polymer in the absence of gelation, where  $\{\eta\} = M^{0.8}$ .

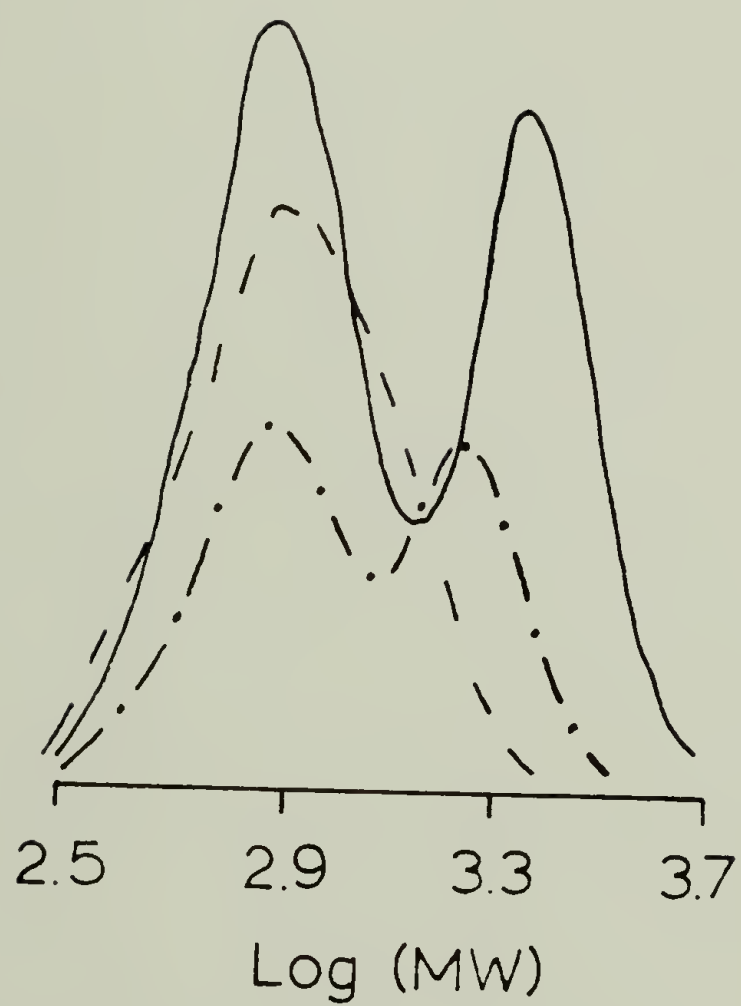


Figure 18. Molecular weight distributions of poly( $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone) prepared in dimethyl sulfoxide. Polymerization times are:  
dashed line: 12 min.  
dotted/dashed line: 25.9 min.  
solid line: 35.3 min.

while the molecular weight of the active polymer chains continues to increase. This situation creates a bimodal distribution whose breadth increases with time.

The fraction of growing polymer chains that continue propagating after gelation can be estimated from the relative areas of the high and low molecular weight polymers in each distribution. About 40 % of the chains continue to propagate (see Table 11 and Appendix V).

Table 11

Molecular Weight as a Function  
of Polymerization Time\*

$\{I_o\}$	Polymerization time (min.)	$\bar{M}_n$ of inactive	$\bar{M}_n$ of active	Fraction of active chains
0.000282 M	25.88	800	2400	0.4099 $\{I_o\}$
0.000283 M	35.33	800	3600	0.3588 $\{I_o\}$

\* initiated by tetraethylammonium benzoate at 34°C

The change in molecular weight with time gives an estimate of the rate constant of propagation after gelation, which was calculated as  $k_p = 13 \text{ M}^{-1} \text{ min.}^{-1}$ . This calculation has a large error associated with it because only two data points were available. The value of  $k_p$  determined spectroscopically prior to gelation is  $11 \text{ M}^{-1} \text{ min.}^{-1}$ . Apparently, the propagation rate of those polymer chains that continue to grow remains unchanged by gelation. The decrease in overall polymerization rate upon gelation, therefore, is due to a sudden decrease in the number of chains capable of growth.

## 4.2 Polymerization of $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-Methylpyrrolidone

When polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was initiated by tetraethylammonium benzoate in N-methylpyrrolidone, gelation did not occur, although the polymer precipitated almost immediately after initiation. Despite the system's heterogeneity, propagation continued with a rate constant of  $57 \pm 3 \text{ M}^{-1} \text{ min.}^{-1}$  (see Figure 19). The molecular weight distributions of these polymers were composed of a single broad peak, as might be expected from a heterogeneous system {74}. That is, all of the polymer chain ends continued to propagate, as shown by the molecular weight distribution curves. It was not possible to determine whether precipitation altered the rate of propagation because precipitation occurred immediately after initiation.

4.2.1 Comparison of N-Methylpyrrolidone and Dimethyl Sulfoxide as Reaction Solvents. N-Methylpyrrolidone ( $\epsilon = 33$ ) is a better reaction solvent than dimethyl sulfoxide ( $\epsilon = 46.4$ ) for the polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone despite its lower dielectric constant (see Table 12). This result supports the conclusion discussed in section 3.9.2 that the counterion, tetraethylammonium ion, is less solvated in dimethyl sulfoxide than expected from its high dielectric constant because of solvent-solvent interactions that compete with the solvent-cation interactions necessary for cation solvation.

4.2.2 Comparison of the Reactivities of  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone and  $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone. The polymerization rate of



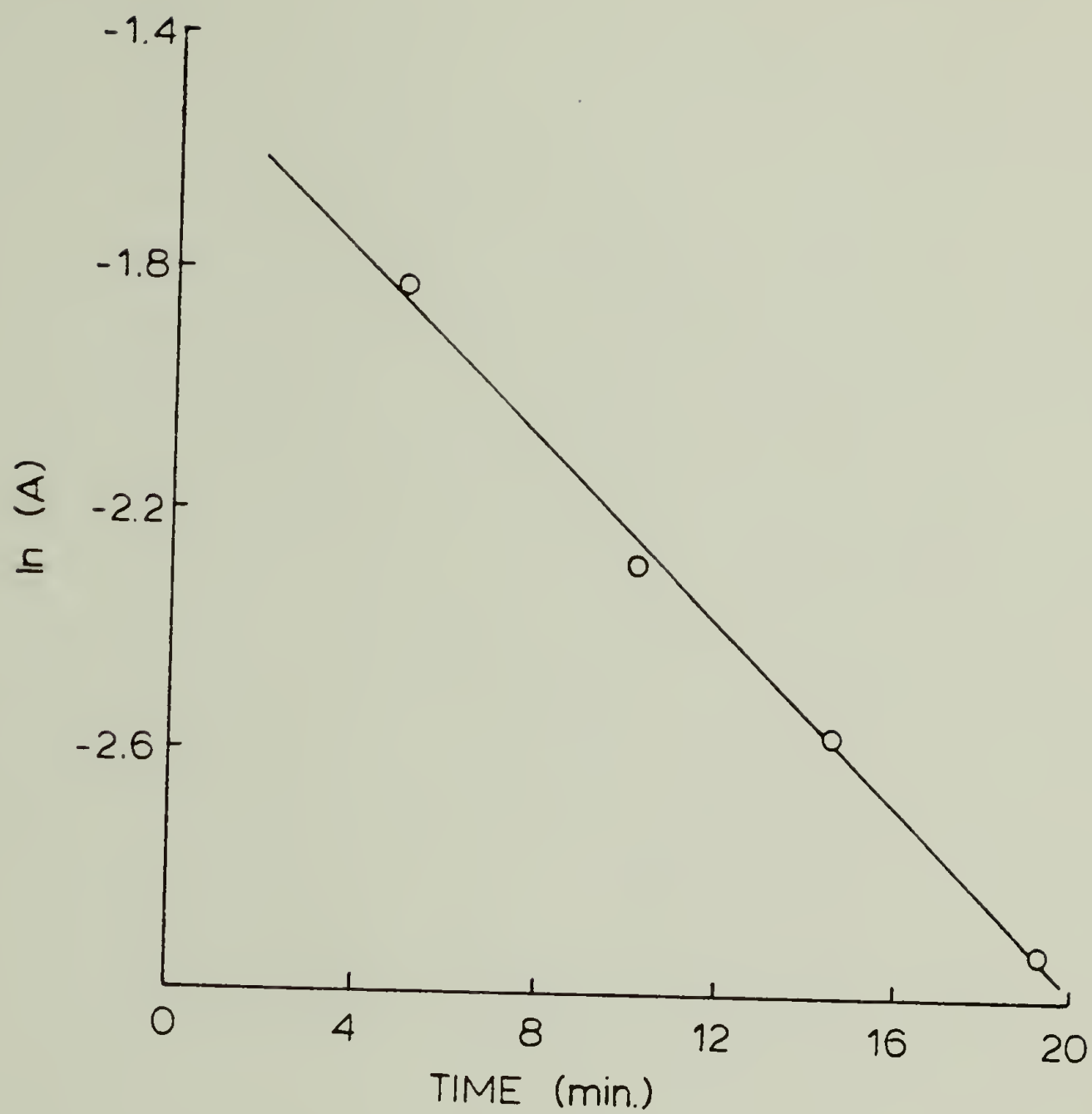


Figure 19. Conversion as a function of time of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-methylpyrrolidone at 34°C.  $k_p = 57 \text{ M}^{-1} \text{ min.}^{-1}$ .

Table 12

Comparison of Propagation Rate Constants  
of  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone  
in N-Methylpyrrolidone and Dimethyl Sulfoxide\*

Solvent	$k_p$ ( $M^{-1} \text{ min.}^{-1}$ )	$\epsilon$
N-Methylpyrrolidone	$57 \pm 3$	33.0
Dimethyl Sulfoxide	$11 \pm 1$	46.4

\*  
initiated by tetraethylammonium benzoate at  
34°C

$\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in N-methylpyrrolidone is greater than that of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone (see Table 13). There are two possible explanations for this behavior. Either precipitation during

Table 13

Comparison of Propagation Rate Constants of  
 $\alpha$ -Methyl- $\alpha$ -propyl- and  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactones  
in N-Methylpyrrolidone\*

Monomer	$k_p$ ( $M^{-1} \text{ min.}^{-1}$ )
$\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone	$168 \pm 6$
$\alpha$ -Ethyl- $\alpha$ - <u>n</u> -butyl- $\beta$ -propiolactone	$57 \pm 3$

\*  
initiated by tetraethylammonium benzoate at 34°C

polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone may substantially decrease the rate of propagation or  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone may be less reactive than  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone towards nucleophilic attack because of its bulkier substituents. The same

order of reactivity is shown when dimethyl sulfoxide is the nucleophile; that is,  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone is unreactive towards dimethyl sulfoxide while  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone is easily polymerized. Further experiments are needed to clarify which explanation is appropriate.

## CHAPTER V

### CONCLUSIONS AND POSSIBLE EXTENSIONS

#### 5.1 Recapitulation

The anionic polymerization rates of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone and  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone were determined with infrared spectroscopy to determine the effects of solvent polarity on polymerization rate.

5.1.1 Solvent Effects in the Anionic Polymerization of  $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone. Evidence for the living nature of the anionic polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in tetrahydrofuran included resumption of polymerization at the same rate after consumption of monomer and subsequent addition of additional monomer, the narrowness of the polymer molecular weight distributions, and the agreement of polymer molecular weights with calculated values. When  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was placed in dimethyl sulfoxide, however, nucleophilic attack on the monomer by the sulfoxide oxygen caused ring cleavage and subsequent polymerization of the monomer. This reaction obscured the study of solvent effects since it competed with polymerization initiated by tetraethylammonium benzoate. Similar behavior was observed in N, N-dimethylformamide.

When  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was polymerized by tetraethylammonium benzoate in other inert dipolar aprotic solvents, living

polymerization systems were obtained. Although the extent of cation solvation was the rate-determining factor, the polymerization rate was not predicted by solvent donor number, but by solvent dielectric constant. Solvation of the tetraethylammonium ion occurs by dipole-cation interactions, because the tetraethylammonium ion cannot expand its electronic valence to accept electrons from a donor molecule. The extent of these interactions is related to the molecular polarizability, which is described by the dielectric constant. The donor number does not describe the degree of counterion solvation because of steric differences between the tetraethylammonium ion and  $\text{SbCl}_5$ , the reference electron acceptor, differences in the nature of the solvent-solute interaction in these two systems, and the presence of solvent-solvent interactions in the bulk solvent which are not present in the dilute reference system.

5.1.2 Polymerization of  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone. Unlike  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone,  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was unreactive towards dimethyl sulfoxide, so dimethyl sulfoxide was a suitable anionic polymerization solvent for this system. When  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was polymerized with tetraethylammonium benzoate in dimethyl sulfoxide, the polymerization rate decreased abruptly at low conversions due to gelation of the growing polymer. The decrease in overall polymerization rate upon gelation was due to a sudden decrease in the number of polymer chains capable of growth. The polymerization rate of the active chains was unaffected by gelation. Bimodal molecular weight distributions arose because two types of chain



ends were present after gelation.

Anionic polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone by tetraethylammonium benzoate in N-methylpyrrolidone continued despite precipitation of the growing polymer at low conversions. Polymer molecular weights were single-valued since all of the active chain ends continued to grow upon precipitation.

The polymerization rate of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-methylpyrrolidone was substantially less than that of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone. Either increased substituent size or decreased polymer solubility was the cause.

N-methylpyrrolidone was a better polymerization solvent than dimethyl sulfoxide despite its lower dielectric constant. Solute-solvent interactions in dimethyl sulfoxide compete with cation-solvent interactions, resulting in decreased counterion solvation.

## 5.2 Suggestions for Future Work

Measurement of reaction kinetics in the presence of an excess of the tetraethylammonium ion during the polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in acetone, N-methylpyrrolidone, and tetrahydrofuran, as well as conductance measurements, would establish  $f$ , the fraction of free ions,  $k_p^-$ , and  $k_p^+$ . The effects of reaction solvent on polymerization rate could then be assessed with greater accuracy.

Study of solvation effects in the polymerization of  $\alpha$ ,  $\alpha$ -disubstituted- $\beta$ -propiolactones could be extended to include cationic initiation. Cationic polymerization of  $\beta$ -propiolactone has been initiated by Lewis acids such as  $\text{SnCl}_4$  {75}{76},  $(\text{C}_2\text{H}_5)_2\text{OH}^+\text{SbF}_6^-$  {36} and tritylium salts

{77}. Extensive chain transfer to monomer (see Figure 20) resulted in low molecular weight polymer, however, this reaction would be impossible for an  $\alpha, \alpha$ -disubstituted monomer.

In preliminary experiments,  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone was polymerized by triphenylmethyl antimony hexachloride in methylene chloride at 35°C. cursory attempts were made to eliminate moisture. The intrinsic viscosity of the polymer in chloroform was 0.36 dl/g. Gel permeation chromatography revealed that the polymer had a bimodal molecular weight distribution, which may result from a rate of polymerization greater than the rate of dissociation of ion pairs {78}. Variation of solvent polarity should vary the position of the equilibrium between ion pairs and free ions, and the proportion of high and low molecular weight polymer. Conductance measurements performed on polymerizing solutions will yield the fraction of free ions, and together with gel permeation chromatography, reveal whether competitive rates of propagation and of ion pair dissociation are responsible for the behavior of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone in cationic polymerization.

There are several unanswered questions concerning the anionic polymerization of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone. When tetraethylammonium benzoate is the initiator, polymerization in N-methylpyrrolidone proceeds at a faster rate than in dimethyl sulfoxide, although dimethyl sulfoxide has a higher dielectric constant. Conductance measurements would establish unequivocally whether the degree of dissociation of the tetraethylammonium counterion is less in dimethyl sulfoxide, as the chemical literature suggests.

The presence of localized structure in dimethyl sulfoxide may be



responsible for decreased solvation of the tetraethylammonium ion. In order to clarify the behavior of dimethyl sulfoxide at lower temperatures, the rate of consumption of monomer could be determined above 60°C in dimethyl sulfoxide, where the solvent structure is no longer present {15}{16}{17}, and compared to measurements performed in N-methylpyrrolidone at that same temperature.

The effect of polymer solubility on polymerization rate requires further investigation. It was unclear whether polymer precipitation or substituent size was the causative factor in decreased polymerization rates of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone compared to that of  $\alpha$ -methyl  $\alpha$ -propyl- $\beta$ -propiolactone in N-methylpyrrolidone. Under the experimental conditions, precipitation occurred so soon after initiation that the polymerization rate of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was determined exclusively after precipitation. By decreasing the initiator concentration, and hence the polymerization rate, the rates of polymerization both before and after precipitation could be measured. FTIR would impart greater accuracy to the measurement.

## CHAPTER VI

### EXPERIMENTAL METHODS

#### 6.1 Monomer Synthesis {79}

6.1.1 3-Bromo-2-methyl-2-propylpropanol. 1 mole of 2-methyl-2-propyl-1,3-propanediol was dissolved in 330 ml. of glacial acetic acid and 5 ml. of HBr (48 % aqueous) were added. The solution was refluxed for 20 minutes. 1.1 moles of HBr (270 ml. of 30-32 % in acetic acid) were added dropwise to the refluxing solution. The mixture was refluxed overnight. The excess acetic acid was removed by distillation. A mixture of 350 ml. of ethanol and 3 ml. of HBr (48 % aqueous) was added to the residue. The ethanol-ethyl acetate azeotrope was removed by distillation. The ethanol-HBr mixture was added and then distilled seven more times, until gas chromatographic analysis indicated that no ethyl acetate was present. The residue was purified by vacuum distillation ( $64^{\circ}\text{C}$  at 0.1 mm. pressure). (see Figures 21 and 22 and Table 14).

6.1.2 3-Bromo-2-methyl-2-propylpropanoic acid. Concentrated nitric acid was weighed out in a ratio of 4.6 ml. per gram of bromoalcohol. The acid was heated to  $70^{\circ}\text{C}$ . Two ml. of ethanol were added to start oxidation. The bromoalcohol was added dropwise at a rate that permitted control of the reaction temperature. Upon completion of addition, the temperature was raised to  $100^{\circ}\text{C}$  and held for 1 hour. Nitrogen was passed over the system to remove the by-product, gaseous  $\text{NO}_2$ . When



the reaction was complete, no further  $\text{NO}_2$  evolved. The mixture was cooled to room temperature. Ice water was added to the mixture and the bromoacid extracted with two batches of methylene chloride. The methylene chloride solution was washed with distilled water and dried with  $\text{MgSO}_4$ . The bromoacid was purified by vacuum distillation ( $104^\circ\text{C}$  at 0.35 mm.). (see Figures 23 and 24 and Table 14).

6.1.3  $\alpha$ -Methyl- $\alpha$ -propyl- $\beta$ -propiolactone. 1 mole of the bromoacid was dissolved in 385 ml. of methylene chloride. A 10 % (by weight) aqueous solution of  $\text{Na}_2\text{CO}_3$  was prepared. 675 ml. were placed in a round bottom flask and stirred vigorously while the methylene chloride solution was added all at once. The mixture was stirred vigorously for 15 minutes. The two layers were separated. Residual lactone was extracted from the aqueous layer with additional methylene chloride. The methylene chloride solutions were dried with  $\text{MgSO}_4$ . The  $\text{MgSO}_4$  and methylene chloride were removed. The lactone was dried over  $\text{CaH}_2$  overnight under an argon atmosphere, then fractionally distilled at  $55^\circ\text{C}$  at 0.4 mm. pressure. It was stored in the refrigerator under an inert atmosphere. (see Figures 25 and 26 and Table 14).

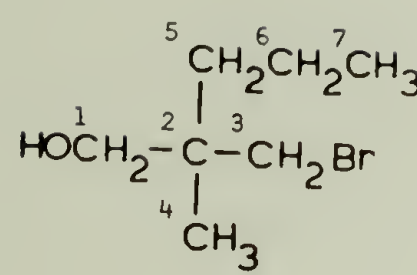
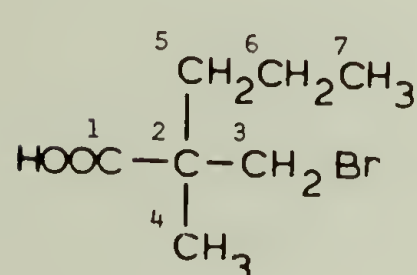
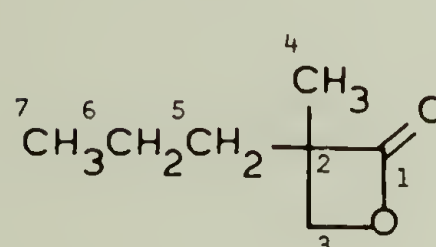
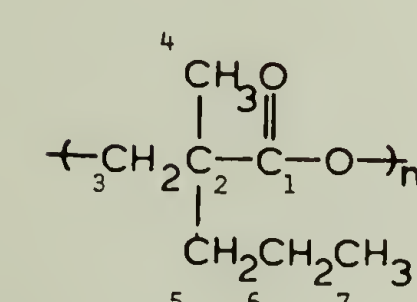
## 6.2 Reagent Purification

All reagents were purified and dried immediately prior to use and were stored only for brief periods of time under inert atmospheres.

6.2.1 Monomer Purification.  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone was further purified with a Waters preparative high pressure liquid chromato-

Table 14

<sup>13</sup>C NMR Chemical Shifts  
Relevant to the Synthesis of  
α-Methyl-α-propyl-β-propiolactone

Compound	Chemical Shifts (Hz.)*						
	1	2	3	4	5	6	7
	1352.0	837.7	781.2	403.4	752.6	333.2	296.5
	3629.3	949.1	796.1	423.8	789.7	357.6	286.8
	3501.1	1147.0	1428.7	383.1	729.2	358.5	283.2
	3486.3	927.8	1379.2	397.9	763.7	352.2	289.6

\* relative to TMS in CDCl<sub>3</sub>

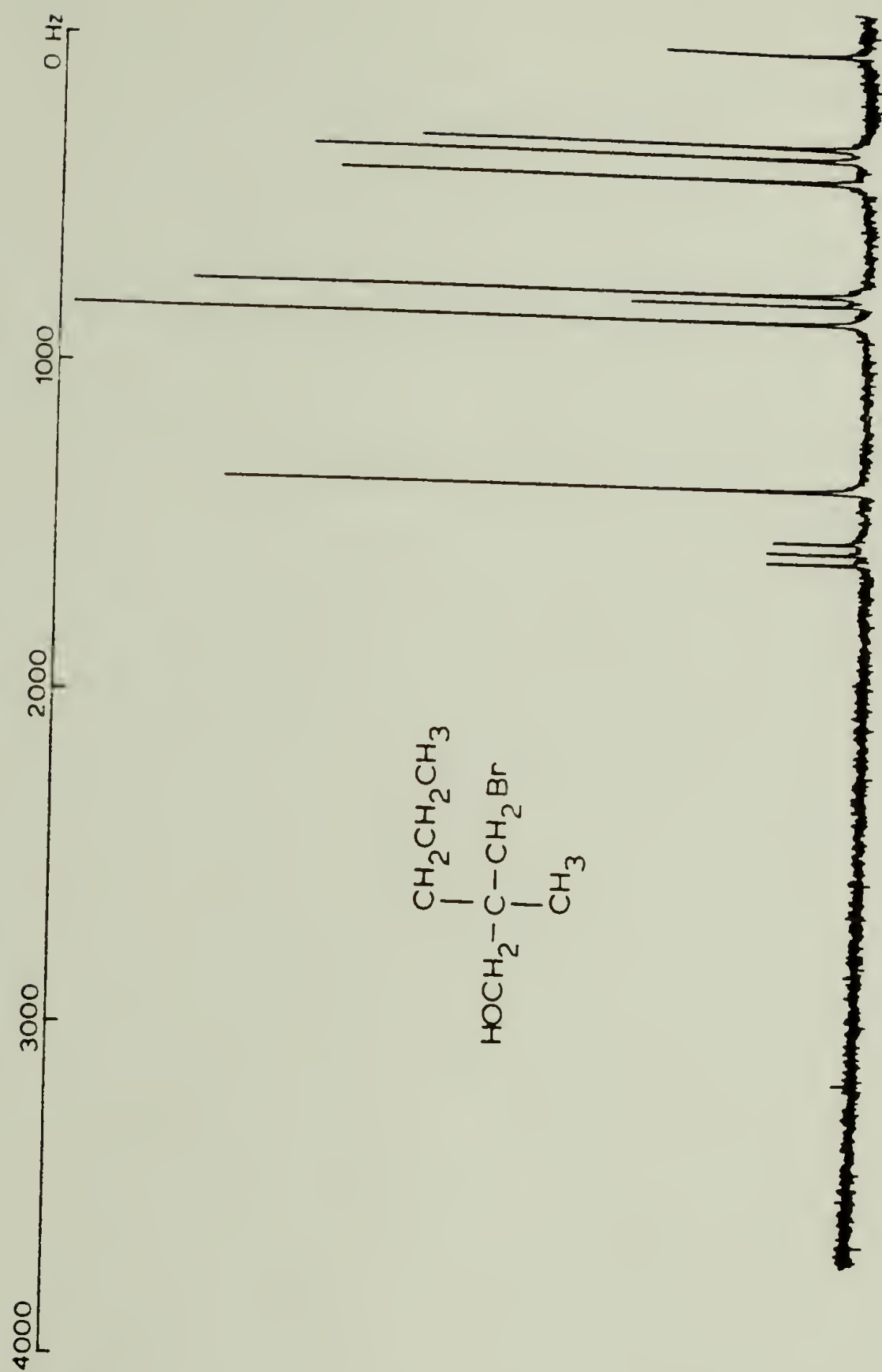


Figure 21.  $^{13}\text{C}$  NMR spectrum of 3-bromo-2-methyl-2-propylpropanol.

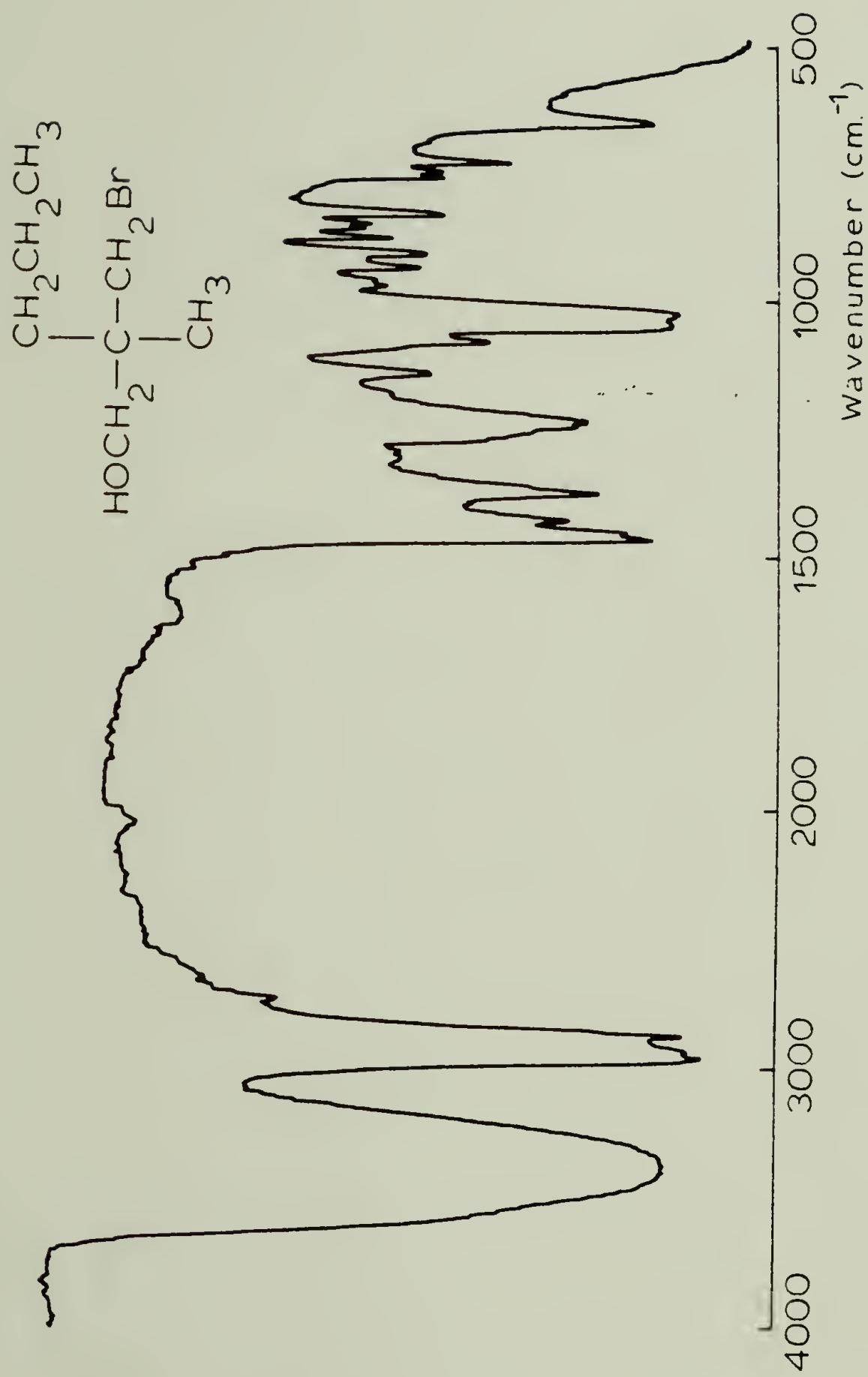


Figure 22. Infrared spectrum of 3-bromo-2-methyl-2-propylpropanol

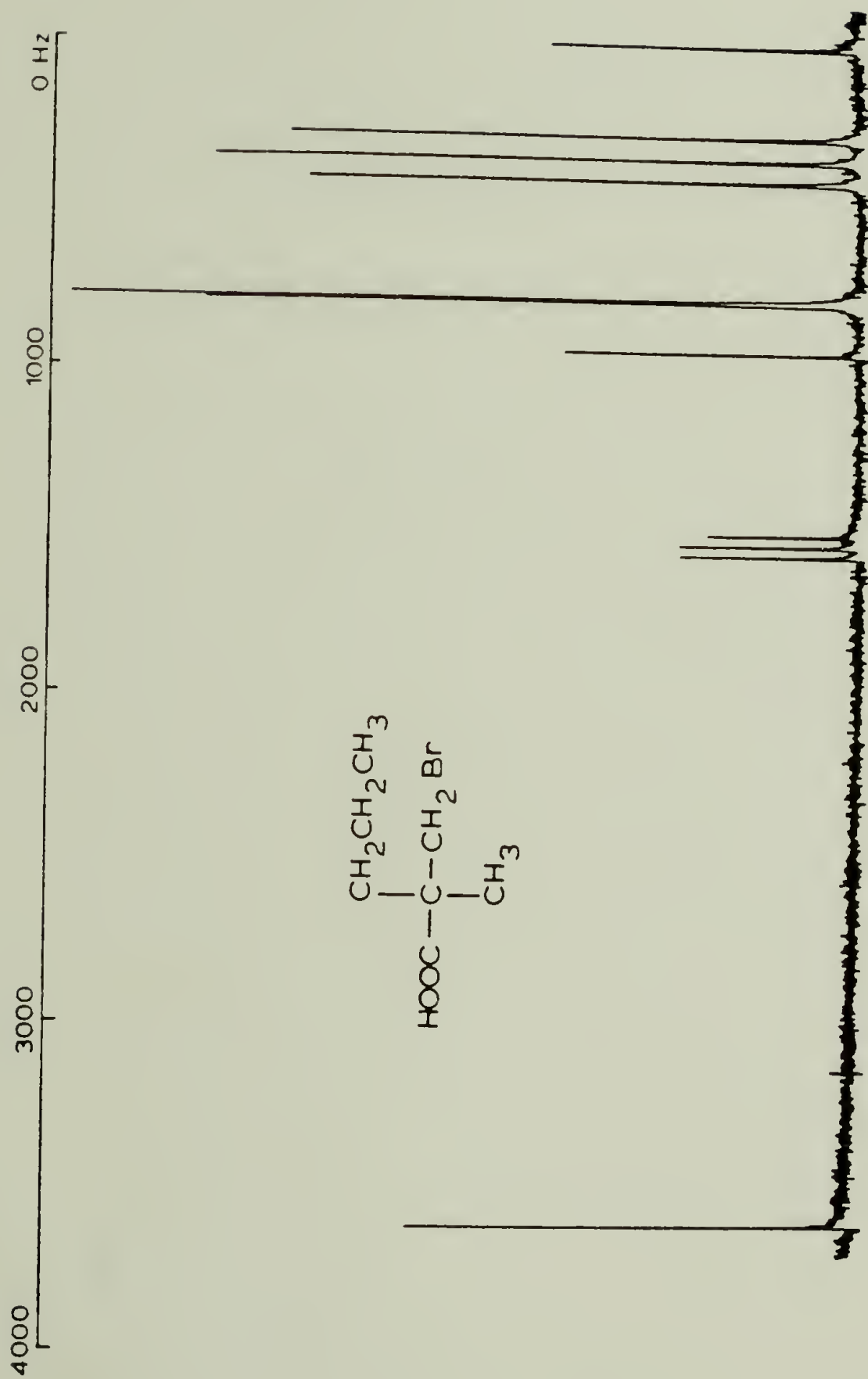


Figure 23.  $^{13}\text{C}$  NMR spectrum of 3-bromo-2-methyl-2-propylpropanoic acid.



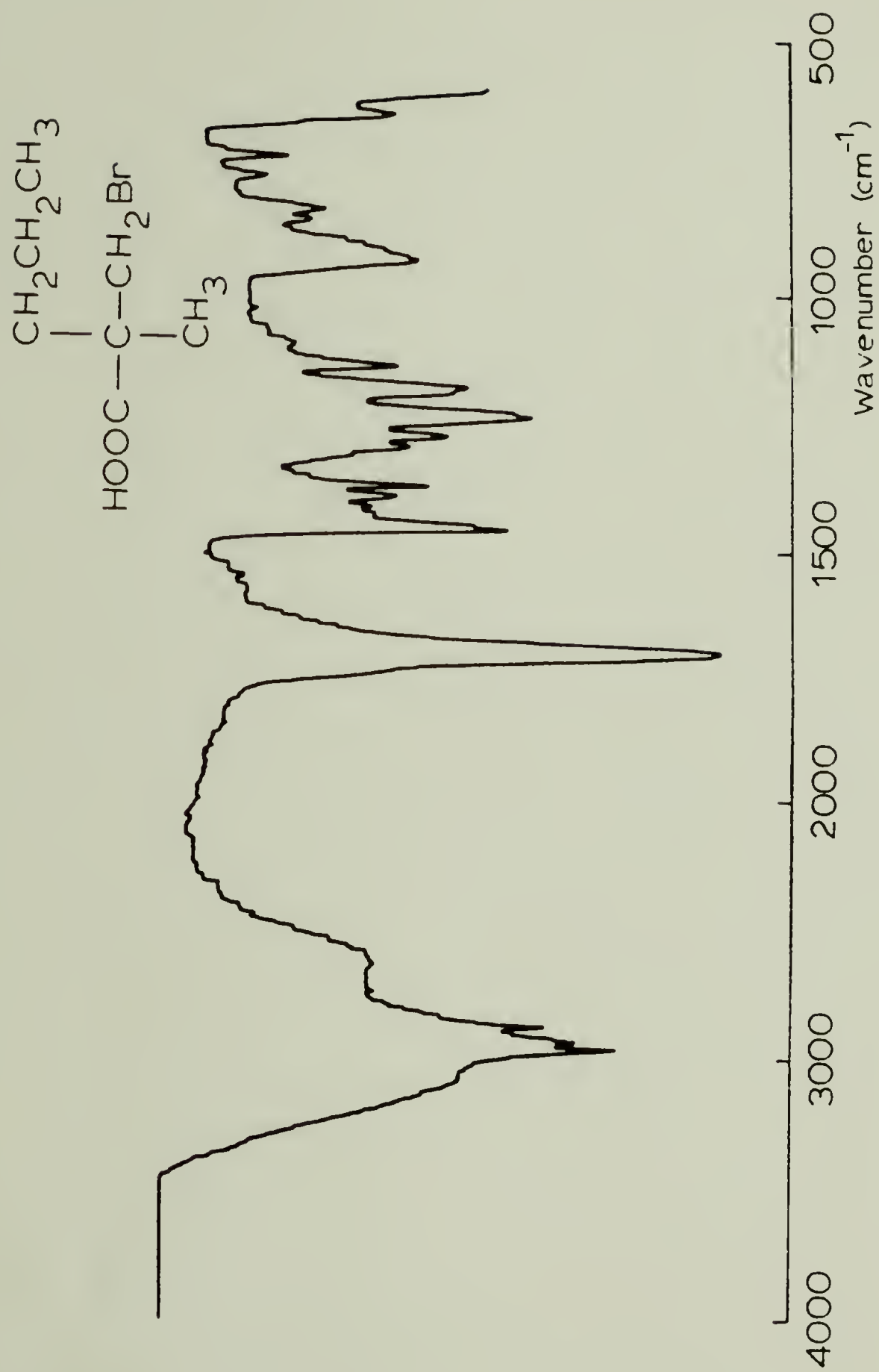


Figure 24. Infrared spectrum of 3-bromo-2-methyl-2-propylpropanoic acid.

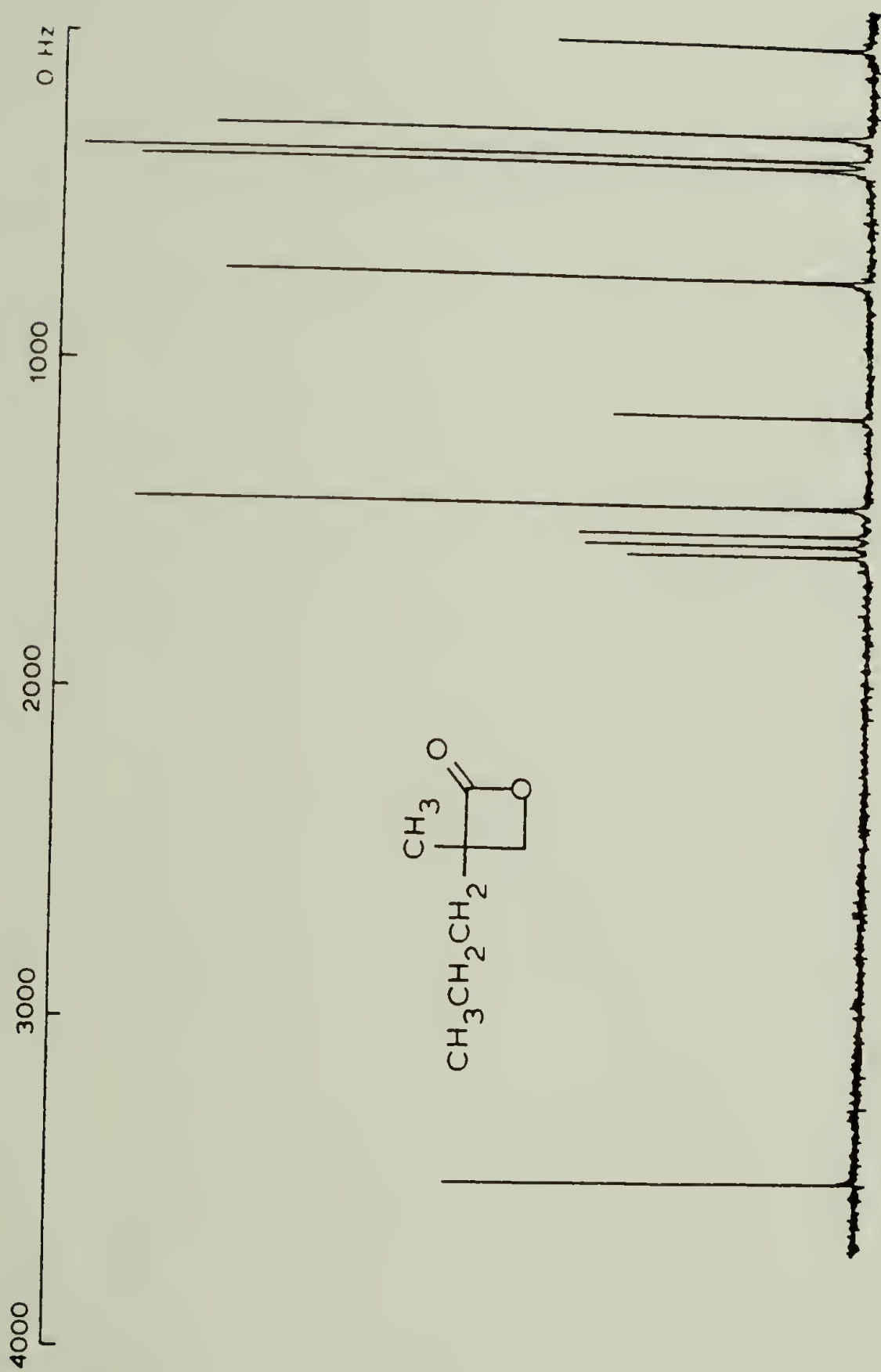


Figure 25.  $^{13}\text{C}$  NMR spectrum of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone.

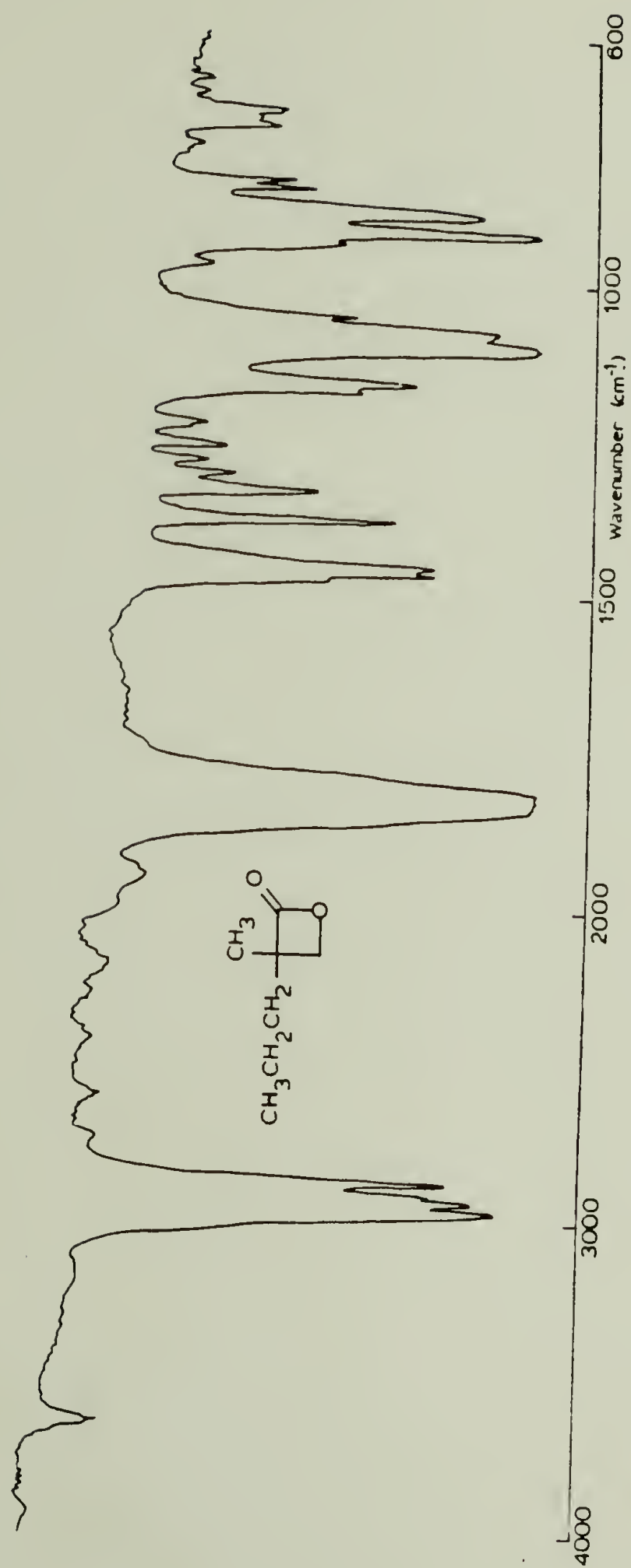


Figure 26. Infrared spectrum of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone.

graph with methylene chloride as solvent, while  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone could be purified by vacuum distillation. Both monomers were dried by stirring over  $\text{CaH}_2$  overnight under an inert atmosphere, followed by fractional distillation under reduced pressure.

6.2.2 Purification of Tetrahydrofuran. Tetrahydrofuran was stirred vigorously over  $\text{CaH}_2$  for several days under an inert atmosphere and then fractionally distilled.

6.2.3 Purification of Dimethyl Sulfoxide. Dimethyl sulfoxide was stirred vigorously over a drying agent, under an inert atmosphere and then fractionally distilled under reduced pressure. Several different drying agents were used, including  $\text{CaH}_2$ , activated 4 A molecular sieves, and  $\text{BaO}$ .

6.2.4 Purification of N, N-Dimethylformamide. N, N-Dimethylformamide was dried with activated 3 A molecular sieves overnight, then with  $\text{P}_2\text{O}_5$ , and fractionally distilled under reduced pressure. Other drying agents included  $\text{BaO}$  and  $\text{CaH}_2$ . Polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone purified in this manner, so other methods of purification were attempted.

First, the purified N, N-dimethylformamide was placed under vacuum for several days and then dry argon was bubbled through the solvent to remove any gaseous or low-boiling impurities. The polymerization rate of monomer in N, N-dimethylformamide was unaffected.

Second, crude N, N-dimethylformamide was shaken with 10 %  $\text{KOH}$  and extracted with several batches of methylene chloride. The organic layer was dried with  $\text{MgSO}_4$  overnight, and the  $\text{MgSO}_4$  and the methylene chloride

were removed. The N, N-dimethylformamide was dried overnight with activated 4 A molecular sieves. The sieves were removed and the N, N-dimethylformamide was dried with  $\text{CaH}_2$  overnight under an inert atmosphere. It was fractionally distilled under reduced pressure. Polymerization of  $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone still occurred in N, N-dimethylformamide purified in this manner.

6.2.5 Purification of Acetone. Acetone was stirred vigorously over  $\text{B}_2\text{O}_3$  overnight under an inert atmosphere and then fractionally distilled. The process was repeated and the middle fraction was retained for immediate use.

6.2.6 Purification of N-Methylpyrrolidone. N-Methylpyrrolidone was treated with 10 % KOH. Several batches of methylene chloride were used to extract the N-methylpyrrolidone from the mixture. The organic layer was dried with  $\text{MgSO}_4$  overnight. The  $\text{MgSO}_4$  and the methylene chloride were removed. The N-methylpyrrolidone was dried overnight with activated 4 A molecular sieves. The sieves were removed and the N-methylpyrrolidone was dried with  $\text{CaH}_2$  overnight under an inert atmosphere. It was fractionally distilled under reduced pressure.

6.2.7 Purification of Chlorinated Solvents. Chlorinated solvents were stirred vigorously over  $\text{CaH}_2$  under an inert atmosphere, and then fractionally distilled.

6.2.8 Purification of Tetraethylammonium Benzoate. Benzene was dried overnight with  $\text{CaH}_2$  and fractionally distilled. Tetraethylammonium benzoate was placed in the freshly distilled benzene and heated. The



initiator is sparingly soluble in benzene even at elevated temperatures so an excess of benzene was necessary. The benzene-water azeotrope was removed by distillation and the initiator allowed to recrystallize slowly at room temperature under an argon atmosphere. The excess benzene was removed by suction filtration. The initiator was placed in a drying pistol at 56°C overnight. It was stored in a nitrogen-filled glove box.

### 6.3 Polymerization Procedure

The polymerization vessels were dried with a Bunsen burner flame while under vacuum, then filled with argon. Manipulations of the initiator were performed in a nitrogen-filled glove box. Liquid reagents were transferred with double-tipped needles whenever possible, otherwise gas-tight syringes were used. A stock initiator solution was prepared and a weighed amount injected into each polymerization vessel. The vessels were placed in a constant temperature bath at 34°C and the reaction mixture allowed to equilibrate. A weighed amount of monomer was added and allowed to polymerize a given length of time, after which polymerization was quenched with a known amount of methanol (see Table 14 and Figure 27).

### 6.4 Determination of Polymerization Rate Constants

6.4.1 From Quenched Samples. A small sample from each quenched polymerization solution was injected into a solution IR cell with NaCl plates. A reference cell containing the initiator solution and methanol was prepared. The absorbance of the monomer carbonyl group was measured on a Varian 283 IR spectrophotometer. Each absorbance was normalized

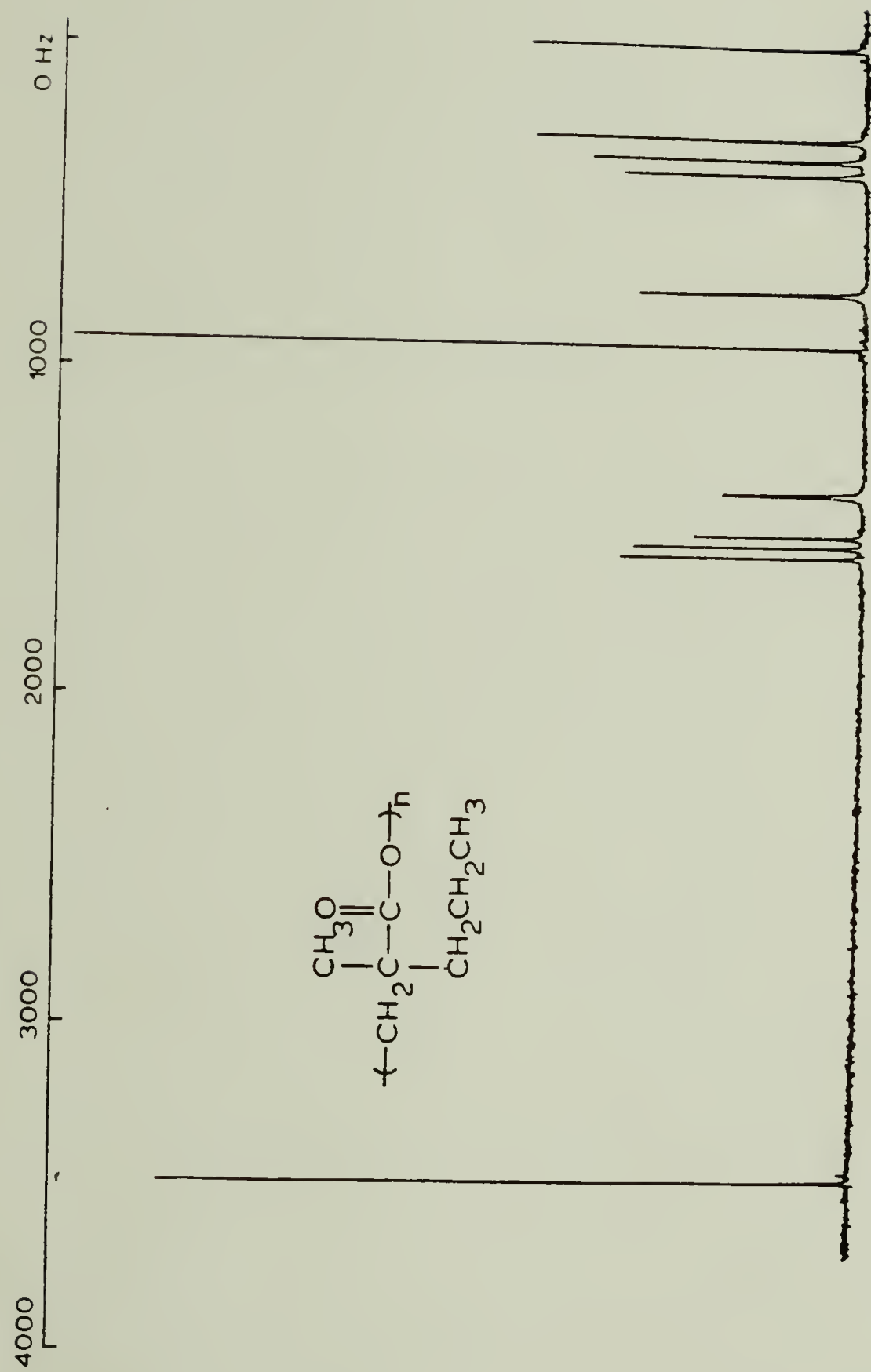


Figure 27.  $^{13}\text{C}$  NMR spectrum of poly( $\alpha$ -methyl- $\alpha$ -propyl- $\beta$ -propiolactone)

to a given initial monomer concentration.

6.4.2 From Polymerization Solutions of  $\alpha$ -Ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-Methylpyrrolidone. Because polymer precipitated during polymerization, spectroscopic measurements of the as-polymerized solutions of  $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone in N-methylpyrrolidone would be inaccurate. The polymer was dissolved by adding a known amount of chloroform to each solution, and the carbonyl absorbance of the unreacted monomer was then determined.

6.4.3 From Polymerizations Initiated by Dimethyl Sulfoxide, N, N-Dimethylformamide, or NaCl. A portion of the polymerizing solution was placed in an IR cell and the monomer carbonyl absorbance of this sample measured periodically until all of the monomer had been consumed.

### 6.5 Molecular Weight Distributions

Molecular weight distributions were determined with a Waters 201 high performance gel permeation chromatograph. All molecular weights were reported relative to polystyrene standards. The chromatography solvent was tetrahydrofuran, except for samples of poly( $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone) prepared in N-methylpyrrolidone. These samples were insoluble in tetrahydrofuran and their molecular weight distributions were determined in chloroform.

### 6.6 Estimation of the Fraction of Growing Chains Capable of Propagation after Gelation

Estimation of the fraction of growing chains capable of propagation

after gelation of poly( $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone) in dimethyl sulfoxide was accomplished by comparing the areas of the chromatograms of the inactive and active materials. Areas were measured with a planimeter.

6.7 Determination of the Gel Point of  
Poly( $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone)  
in Dimethyl Sulfoxide

An Ostwald viscometer with an ASTM size of 100 was fitted with a rubber septum and heated under vacuum. It was filled with argon and a weighed amount of an initiator solution was placed in the viscometer, along with a magnetic stirbar. The viscometer was placed in a constant temperature bath at 34°C and the reaction mixture was allowed to equilibrate. A weighed amount of monomer was added and the solution stirred vigorously. Viscosity measurements were performed throughout the course of polymerization until the fluid no longer flowed through the capillary. The polymerization time was noted as each viscosity measurement began.

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A P P E N D I X    I

ERROR ANALYSIS



The error in  $c$ , the initiator concentration, is as follows:

$$\begin{aligned}
 (\Delta c) = & \left[ \frac{1000 \rho_{sv} \rho_m w_{sol} \Delta w_i}{w_{sv} 251.3712 (\rho_m w_{sol} + \rho_{sol} w_m)} \right]^2 \\
 & + \left[ \frac{w_i 1000 \rho_{sv} \rho_m}{w_{sv} 251.3712} \left( \frac{(\rho_m w_{sol} + \rho_{sol} w_m) - \rho_m w_{sol}}{(\rho_m w_{sol} + \rho_{sol} w_m)} \right) \right]^2 \Delta w_{sol}^2 \\
 & + \left[ \frac{w_i 1000 \rho_{sv} \rho_m w_{sol} \Delta w_{sv}}{(\rho_m w_{sol} + \rho_{sol} w_m) w_{sv} 251.3712} \right]^2 \\
 & + \left[ \frac{\rho_{sol} w_i 1000 \rho_{sv} \rho_m w_{sol} \Delta w_m}{w_{sv} 251.3712 (\rho_m w_{sol} + \rho_{sol} w_m)^2} \right]^2 \\
 & + \left[ \frac{\rho_m w_{sol} w_i 1000}{w_{sv} 251.3712} \left( \frac{(\rho_m w_{sol} + \rho_{sv} w_m) - \rho_{sv} w_m}{(\rho_m w_{sol} + \rho_{sol} w_m)^2} \right) \Delta \rho_{sv} \right]^2
 \end{aligned}$$

where  $w_i$  = weight initiator

$w_{sc}$  = weight solvent in initiator solution

$w_{sol}$  = weight initiator solution used

$w_m$  = weight monomer

$\rho_{sv}$  = density of solvent

$\rho_{sol}$  = density of initiator solution

$\rho_m$  = density of monomer

$\Delta w_i$  = uncertainty in weight of initiator

$\Delta w_{sv}$  = uncertainty in weight of solvent

$\Delta w_{sol}$  = uncertainty in weight of initiator solution

$\Delta w_m$  = uncertainty in weight of monomer

and  $\Delta \rho_{sv}$  = uncertainty in density of initiator solution.

Then, since  $\Delta w_i = \Delta w_{sol} = \Delta w_m = 2 \times 10^{-4}$ , and  $\Delta \rho_{sv} = 0.016$  and, for example,

$$\rho_{sv} \approx \rho_{sol} = 0.7899$$

$$\rho_m = 0.9552$$

$$w_{sol} = 3.3485$$

$$w_i = 0.0027$$

$$w_{sv} = 32.73$$

$$\text{and } w_m = 0.0496,$$

then  $\Delta c = 0.0000144$  and  $c = 0.00026 \pm 0.00001$  M.

The error in  $k_p$ , the propagation rate constant, is as follows:

$$(\Delta k_p)^2 = \left[ \frac{\Delta \text{slope}}{c} \right]^2 + \left[ \frac{\text{slope } \Delta c}{c} \right]^2$$

where slope = slope of plot of  $\ln$  (absorbance) as a function of time

$c$  = initiator concentration

$\Delta c$  = uncertainty in initiator concentration

$\Delta \text{slope}$  = uncertainty in slope.

Then, if  $c = 0.000256$

$$\text{slope} = 0.022503$$

$$\Delta c = 0.0000144$$

$$\Delta \text{slope} = 0.006396$$

$$\Delta k_p = 5.5 \text{ and } k_p = 87.9 \pm 5.5 \text{ M}^{-1} \text{min.}^{-1}$$

A P P E N D I X    I I

HEAT CONDUCTION CALCULATIONS

It takes approximately twelve seconds to take a sample from a polymerization vessel and transport it to the IR spectrophotometer, where a measurement of conversion as a function of time will be made. Ideally, the reaction solution should be kept at a constant temperature, but as soon as the solution is removed from the polymerization vessel, it is exposed to lower temperatures. Is the twelve seconds needed to perform the manipulations before measurements are made sufficient to allow substantial temperature changes?

Fourier's law of heat conduction in solids gives an approximate answer {61}. The assumptions in applying this equation are:

1. The sides of the object are perfectly insulated
2. The temperature is constant on any crosssection.

Then

$$\alpha^2 u_{xx} = u_t \quad 0 < x < l, \quad t > 0$$

where  $u$  = temperature

$$\alpha^2 = \text{thermal diffusivity} = \frac{\text{thermal conductivity}}{\text{specific heat} \times \text{density}}$$

$l$  = length of object

$t$  = time

This equation can be solved for inhomogeneous boundary conditions as follows:

$$u(x, t) = (T_2 - T_1) \frac{x}{l} + T_1 + \sum_{n=1}^{\infty} b_n e^{-n^2 \pi^2 \alpha^2 t / l^2} \sin \frac{n \pi x}{l}$$

where  $T_1$  and  $T_2$  are the temperatures at the boundaries and

$$b_n = \frac{2}{l} \int_0^l \left( f(x) - (T_2 - T_1) \frac{x}{l} - T_1 \right) \sin \frac{n\pi x}{l} dx .$$

In this case, a solution at  $34^\circ\text{C}$  at  $t = 0$  is placed in an IR cell of  $l = 0.1$  mm at  $20^\circ\text{C}$  so

$$f(x) = 34^\circ\text{C}$$

$$T_1 = 20^\circ\text{C}$$

$$T_2 = 20^\circ\text{C}$$

$$\text{and } b_n = \frac{2}{l} \int_0^l 14 \sin \frac{n\pi x}{l} dx .$$

The following computer program was used to calculate the temperature at varying points in the IR cell:

A = thermal diffusivity  
 Z = A / B x B  
 X = distance from cell wall  
 R = integer  
 C = time dependent portion of temperature expression  
 Q = Nth expression in infinite time  
 D = sum  
 S = fractional position, for example 0.2 l, 0.3 l  
 U = temperature at given time and position

```

PROGRAM HEAT (OUTPUT, TAPE 6 = OUTPUT)
TIME = 0.0
P = 3.141592654
DO 50 I = 1, 21
  B = 10.00 ** (-4.0)
  A = 1.119 * 10.0 ** (-9.0)
  Z = (A / B) / B
  WRITE (6, 10) TIME
10  FORMAT (/, "TIME =", F4.2, "  seconds" : /)
  X = 0.0
  WRITE (6, 15)
15  FORMAT (1x, "  X", 10X, "Temperature")
  DO 40 J = 1, 11
    R = 0.0

```



```

      D = 0.0
      DO 20 N = 1, 8000
      R = R + 1.0
      C = R*R*P*P*Z*TIME
      IF (C.GT.500.0) GO TO 25
      Q = (28.0/(R*P))*(1.0 - cos (R*P))*Sin(R*P*X/B)*EXP(-C)
20    D = D + Q
25    S = X/B
      U = 20.0 + D
      WRITE (6, 30) S, U
30    FORMAT (F3.1, 11X, F10.2)
      U = 0.0
40    X = X + 0.1*B
50    TIME = TIME + 0.50
      STOP
      END

```

Figure 28 illustrates typical data. The solution reaches room temperature in the time scale of the experiment, which can greatly affect the results.

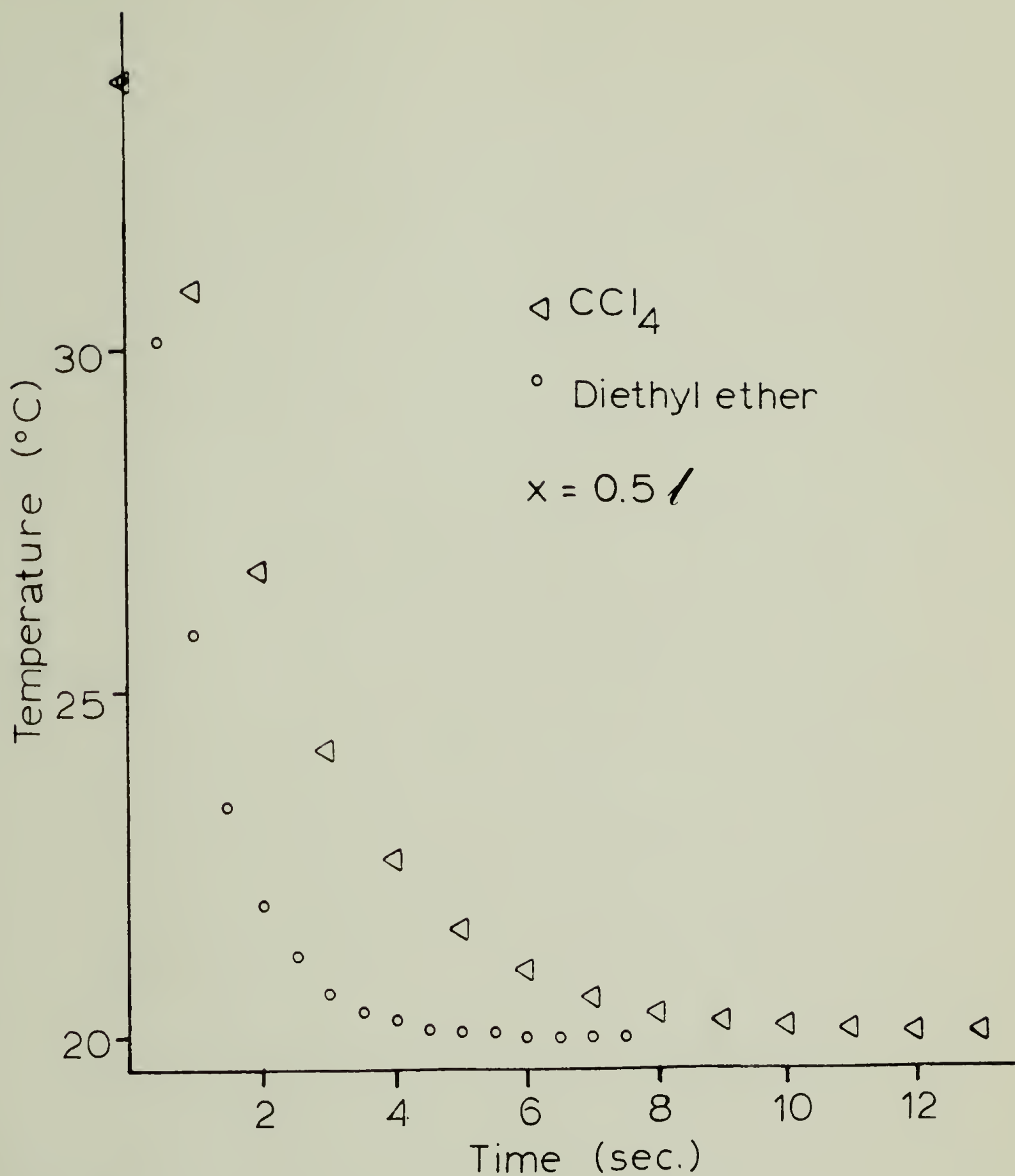


Figure 28. Temperature of a solution initially at  $34^{\circ}\text{C}$  in infrared cells at  $20^{\circ}\text{C}$  as a function of time.  
 circles: in diethyl ether  
 triangles: in chloroform

A P P E N D I X   I I I

KINETIC ANALYSIS

A. Kinetic Analysis in the Absence of Gelation.

$$\ln \{M\} = \ln \{M_o\} - k_p \{I_o\} t$$

where  $\{M\}$  is the monomer concentration,  $t$  is the time,  $k_p$  is the propagation rate constant,  $\{I_o\}$  is the initial initiator concentration and  $\{M_o\}$  is the initial monomer concentration. What if  $\{M_o\}$  is slightly different?

$$\ln \{M'\} = \ln \{M_o'\} - k_p \{I_o\} t.$$

Then  $\ln \{M\}$  and  $\ln \{M'\}$  differ only by  $\ln \{M_o\} - \ln \{M_o'\}$ . In the spectroscopic measurements,  $\ln \{M'\}$  was measured, but the measurement is needed in the  $\{M\}$  reference frame.

$$\ln \{M\} = \ln \{M'\} + \ln \frac{\{M_o\}}{\{M_o'\}}$$

$$\text{and } \ln A = \ln A' + \ln \frac{\{M_o\}}{\{M_o'\}}$$

Actually, in making measurements on quenched samples with different initial monomer concentrations, points are measured on a family of curves with the same slope but different intercepts (see Figure 29a). To make a single kinetic curve, the data must be shifted by an amount equal to the difference in intercepts, or in other words, normalized to a given initial monomer concentration. In this thesis, all measurements of absorbance were shifted by  $\ln (\{M_o\} / \{M_o'\})$  where  $\{M_o\}$  was an arbitrarily chosen initial monomer concentration and  $\{M_o'\}$  was the experimental monomer concentration.

B. Kinetic Analysis in Systems that Gel. Gelation causes a decrease in the slope of plots of  $\ln$  (absorbance) as a function of time, and complicates the kinetic analysis (see Figure 29b). Gelation time is described by the following equation:

$$t_{\text{gel}} = \frac{\ln \left( \{M_o\} - \frac{\{I_o\} \bar{M}_n}{M^*} \right) - \ln \{M_o\}}{-k_p \{I_o\}}$$

where  $\bar{M}_n$  is the number average molecular weight when gelation occurs and  $M^*$  is the molecular weight of one monomer unit. The gelation time depends on the initial monomer concentration. Furthermore, both the gelation time and the rate of propagation after gelation are sensitive to small differences in initiator concentration, which can arise from differences in monomer concentration, and which were neglected in the absence of gelation. Each absorbance measurement produces one point on a family of curves such as in Figure 29b. In order to produce one curve suitable for kinetic analysis, data concerning the differences in initial monomer concentration, the time of gelation and the fraction of chains that continue to propagate must be obtained.



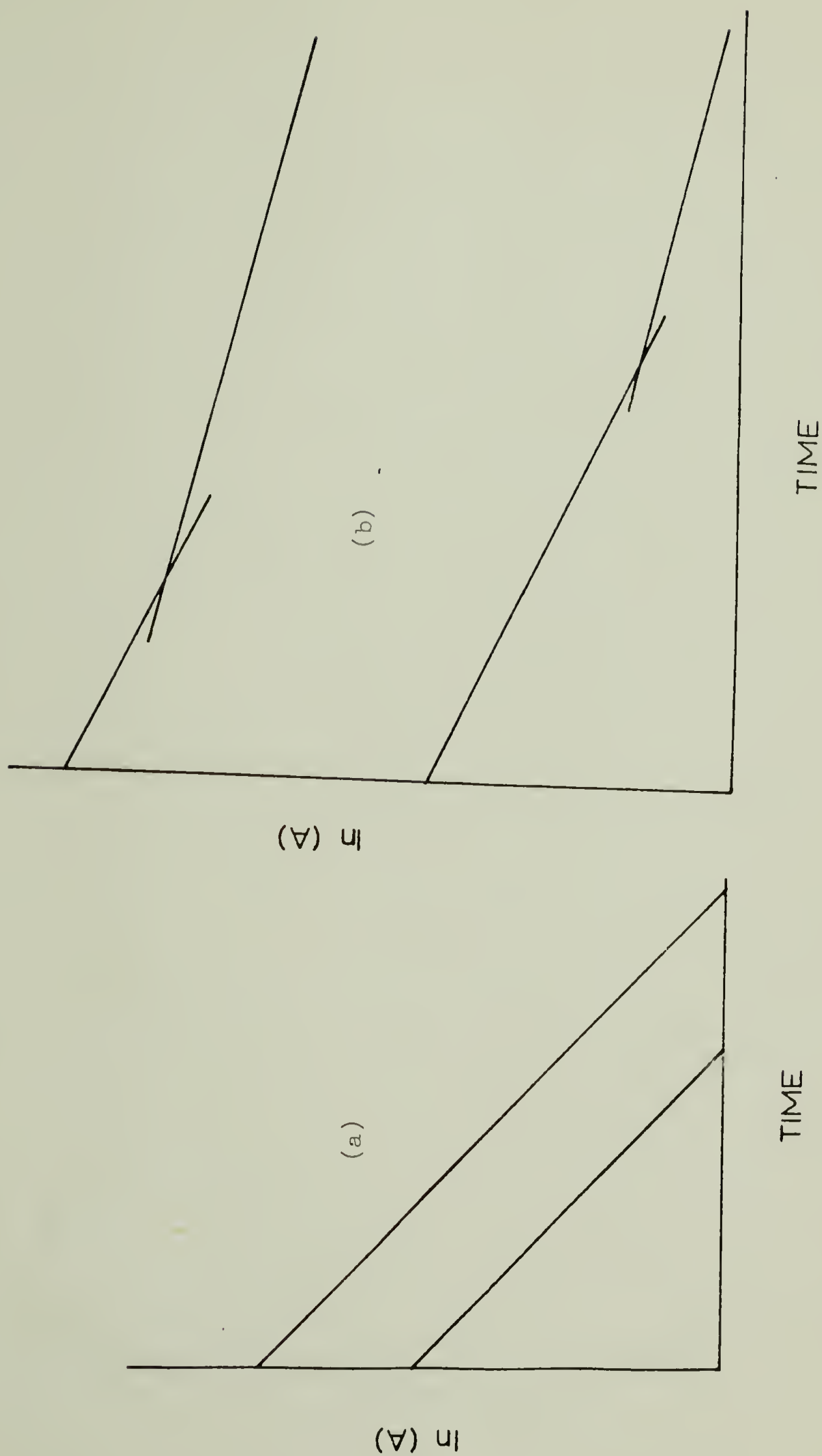


Figure 29. Family of curves defined by conversion measurements.  
 A. In the absence of gelation B. In the presence of gelation.

A P P E N D I X I V

COMPUTER PROGRAM FOR KINETIC ANALYSIS

```

PROGRAM KINETIC (TAPE 10,TAPE 20,TAPE 30)
DIMENSION TIME(10),CONCMX(10),C(10),W(200)
WRITE (20,5)
5 FORMAT(1X,"INITIATOR",-8X,"INITIAL",-8X,"FINAL",-10X,"TIME",-6X,
1"LN(A)/ 1X,"CONCENTRATION",-2X,"MONOMER CONC",-3X,"MONOMER",
2" CONC,"//,
C VARIABLE NAMES
C M= # OF VESSELS
C OT= INITIAL INITIATOR CONCENTRATION
C RHOS= DENSITY OF SOLVENT
C WTSOL= AMOUNT OF SOLVENT IN EACH VESSEL IN GRAMS
C WTMON= AMOUNT MONOMER IN EACH VESSEL IN GRAMS
C WTMETH= AMOUNT METHANOL IN EACH VESSEL IN GRAMS
C TIME= POLYMERIZATION TIME IN MINUTES
C PEAK= PEAK LENGTH IN CM
      READ (10,10)N, OL, RHOS
10 FORMAT (1X, 10,F8.6,F6.4)
      DO 12 J= 1,N
12 W(T)=1.0
      DO 41 I=1,N
      READ (10,20)WTSOL,WTMON,WTMETH,TIME(I),PEAK
20 FORMAT (1X,F6.4,F6.4,F6.4,F6.3,F5.2)
      XMLSOL= WTSOL/RHOS
      XMLMON= WTMON/0.9482
      XMLMET= WTMETH/0.7914
C CALCULATE INITIATOR CONC, AFTER MONOMER ADDITION
      XI= (OI*XMLSOL)/(XMLSOL + XMLMON)
C CALCULATE MONOMER CONC, PRIOR TO QUENCHING
      CONCMO= WTMON*1000.0/((XMLSOL+XMLMON)*156.2259)
C CALCULATE MONOMER CONC, AFTER QUENCHING
      CONCMX(I) = CONCMO*(XMLSOL + XMLMON)/(XMLMET+XMLMON+XMLSOL)

```

```

C CALCULATE TRANSMITTANCE AND ABSORBANCE
T=1.0-FFOR/20.0
Z=1./T
A=ALOG10(Z)
R=ALOG(A)
C NORMALIZE ABSORBANCE
C(I)=R+ALOG(CONCMX(I))-ALOG(CONCMX(1))
WRITE(20,30) YI, CONCMO, CONCMX(1), TIME(I), C(I)
30 FORMAT(1X, F8.6, 10X, F6.4, 9X, F6.3, 4X, F6.3)
WRITE(30,40) TIME(I), C(I)
40 FORMAT(1X, F6.3, 1X, F6.3)
41 CONTINUE
CALL LISW, TIME, C, NA1, AZ, SA1, SA7, STD)
WRITE(20,60) NA, AZ, SAZ, A1, SA1, STD)
60 FORMAT(/, "NO. OF POINTS", I3, /, "INTERCEPT", E14.4, "EX", "STD DEV",
1, E14.4, /, "SLOPE", E14.4, "EX", "STD DEV", E12.4, /, "QUANTILE",
1, " STD DEV", E14.4)
STOP
END

```





A P P E N D I X    V

KINETICS FROM MOLECULAR WEIGHT DISTRIBUTION DATA

In this experiment, two overlapping peaks were present molecular weight distributions of samples of gelled poly( $\alpha$ -ethyl- $\alpha$ -n-butyl- $\beta$ -propiolactone). Because of the overlap, the molecular weight averages cannot easily be determined, and some simplifying assumptions are required.

In living polymerizations, the molecular weight distributions of the resulting polymers are Poisson distributions {80}. To facilitate calculations, a Poisson distribution can be approximated by a Gaussian distribution when the mean is much greater than one {81}. In a Gaussian distribution, the mean corresponds to the position of the peak maximum. The peak is symmetric about the mean {82}. The number average molecular weight can be approximated by the mean of the peak {83}, and the error in this approximation is small when the molecular weight distribution is narrow. The time of gelation is as follows:

$$t_{gel} = \frac{\ln \left( \{M_o\} - \frac{\{I_o\} \bar{M}_{ngel}}{M^*} \right) - \ln \{M_o\}}{-k_p \{I_o\}}$$

where  $\{M_o\}$  is the initial monomer concentration,  $\{I_o\}$  is the initial initiator concentration,  $\bar{M}_{ngel}$  is the molecular weight at gelation,  $M^*$  is the molecular weight of one monomer unit and  $k_p$  is the propagation rate constant before gelation. The concentration of remaining monomer at gelation is as follows:

$$\ln \{M_{gel}\} = \ln \{M_o\} - k_p \{I_o\}t \quad .$$

The molecular weight of the material that continues to grow after gelation is described by the following equation:

$$\bar{M}_n = \bar{M}_{ngel} + \frac{M^*}{\{I_o'\}} (\{M_{gel}\} - e^{-(\ln \{M_{gel}\} - k'_p \{I_o'\}(t - t_{gel}))})$$

where  $k'_p$  is the rate constant of propagation after gelation and  $\{I_o'\}$  is the effective initiator concentration after gelation, and is equal to the fraction of chains that continue to grow.  $\{I_o'\}$  can be determined by measuring the gray areas in Figure 30 (Area (a) and Area (b)).

Because Gaussian curves are symmetric about the mean, the total area under curve A is equal to twice Area (a). Then,

$$\{I_o'\} = \frac{\text{Area (b)}}{\text{Area (a)} + \text{Area (b)}} \{I_o\}$$

By knowing  $\{I_o'\}$ , the above equation can be solved for  $k'_p$ .

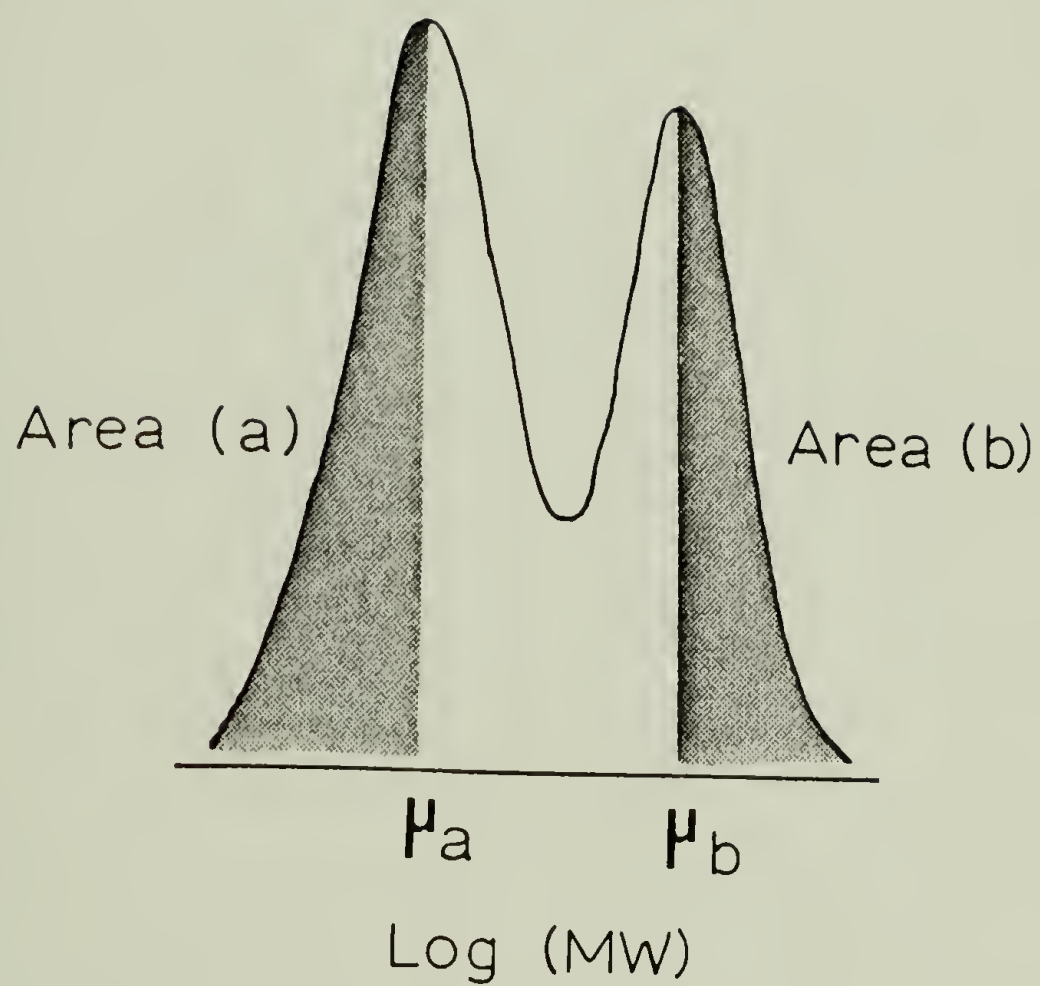


Figure 30. Portion of molecular weight distribution used to determine the fraction of active chain ends present after gelation (in gray).  $\mu$  = mean.



