Polymer Bulletin 3, 91–96 (1980)

Polymer Bulletin

Propagation Rates in the Anionic Polymerization of α-Methyl-α-Butyl-β-Propiolactam

R.W. Lenz[1,3], E. Bigdeli[1,4] and H. Sekiguchi[2]

[1]Material Research Laboratory, Chemical Engineering Department, University of Massachusetts, Amherst, Mass. 01003, USA
[2]Laboratoire de Chimie Macromoléculaire, Ecole Supérieure de Physique et de Chimie, 10, Rue Vauquelin, 75231 Paris 05, France
[3]Presently Senior Humboldt Awardee, Institut für Makromolekulare Chemie der Universität, 7800 Freiburg i.Br., Federal Republic of Germany
[4]Present address: Department of Chemistry, University of Education, 49 Roosevelt Ave., Teheran, Iran

Prof. Dr. Dr. h. c. mult. G. V. Schulz dedicated on the occasion of his 75th birthday

SUMMARY

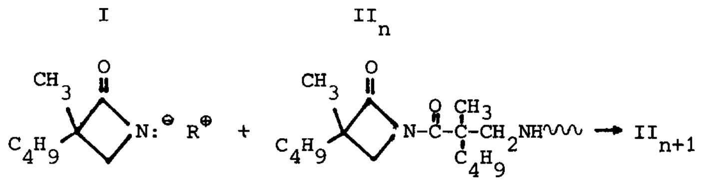
The anionic polymerization of α-methyl-α-butyl-β-propiolactam, MBPL, was studied for the effect of the lactam salt coinitiator on the rate of propagation. It was found that the lithium and tetramethylammonium salts gave essentially identical rate constants but the potassium salt gave a slightly higher value indicating more free ion character for the latter. However, the very small variation in rates observed as a function of the counterion suggests that anion solvation is the most important factor in these reactions, as previously proposed.

INTRODUCTION

Previous investigations in these laboratories have been concerned with the effects of ion pair structure on the propagation rate constant in the anionic polymerization reactions of substituted β-lactones and lactams 1-3). In these earlier investigations, rate studies were made on the effects of cation, solvent and temperarure on specific monomers, and also on the effect of substituents in the monomer on the propagation rate constants for polymerization reactions carried out under different sets of conditions. Unexpected substituent and solvent effects were observed which were interpreted in terms of changes in ion pair structure effecting the propagation rate constant 1,3).

The present investigation was directed at evaluating the effect of changes in the structure of the lactam amide salt used as the coinitiator on the propagation rate constant for one specific lactam monomer, α-methyl-α-butyl-β-propiolactam, MBPL, polymerized in dimethyl sulfoxide solvent. In all previous investigations on this type of monomer, salts of pyrollidone were used as the initiator and N-acetyl pyrollidone was used as the coinitiator, and also salts of α,α-dimethyl-β-propiolactam, DMPL, were used for comparison in the polymerization of MBPL monomer. For the former, the lithium and tetramethylammonium salts were investigated, while for the latter the lithium, potassium and tetramethylammonium salts were all studied. In all cases, N-acetylpyrrolidone was the coinitiator and infrared spectroscopy was used for the rate measurements as previously described 1). The propagation reaction is generally represented by the type of equation shown below:

0170-0839/80/0003/0091/$01.20



RESULTS

All rate plots for the five different combinations of amide anion initiator and counterion gave excellent linear relationships directly from the origin at the beginning of the polymerization reaction. Because of the high ratio of monomer to initiatior and the comparable rate constants for initiation and propagation, the initiation reaction was completed very quickly relative to the propagation reaction, and it was only possible to determine with good accuracy the propagation rate constants in these experiments. The rate constants obtained for each type of initiator are compiled in Table 1, along with the results previously obtained for the propagation rate constants using pyrrolidone salts as the initiator [1,2]. The results in Table 1 indicate that the propagation rate constants obtained in these investigations were independent of the type of lactam anion initiator used, as would be expected. There was, however, some effect of the counterion.

The potassium salt gave slightly higher rate constants than either the lithium or tetramethylammonium salts, and the latter two gave essentially identical results. The result with the potassium counterion is in very good agreement with that from a previous investigation on the same monomer [1]. However, the order of reactivity is opposite to that obtained with the equivalent β-lactone monomer [3]. In the polymerization of α-methyl-α-butyl-β-propiolactone in DMSO, the propagation reaction involving the tetraethylammonium counterion had a rate constant approximetely 10 percent higher than that for the potassium counterion.

The slightly smaller rate constants in Table 1 for the lithium and tetramethylammonium salts indicate that the ion pairs formed with these counterions had less free ion character than with the potassium cation. The comparative results for lithium and potassium counterions would be expected from the previous proposal that in dimethyl sulfoxide a structured solvated ion pair is formed in these polymerization reactions [1,3].

According to this proposal, the ion pair so formed contains both anion and cation solvation by interaction with this dipolar solvent. In that case, therefore, the smaller cation would be expected to be more strongly coordinated by the solvent dipole. As indicated by the data in Table 1, however, the differences among the three different cations are very small, which again is consistent with the previous suggestion that anion solvation plays the more important role in this polymerization reaction [1,3]. Nevertheless, the lower reactivity with the tetramethylammonium counterion is difficult to rationalize on this basis.

Table 1 Comparison of propagation rate constants with different initiators and different salts in the polymerization of α-methyl-α-butyl-β-propiolactam

Lactam	k_p for each salt, $M^{-1}min^{-1}$		
Initiator[a]	$Li^{\oplus}$	$K^{\oplus}$	$(CH_3)_4N^{\oplus}$
MBPL	1.01 ± 0.10	-	1.01 ± 0.12
DMPL	0.95 ± 0.09	1.12 ± 0.04	0.96 ± 0.03
PYR	-	1.2 ± 0.09[b]	0.9 ± 0.2[c]

a) MBPL: α-methyl-α-butyl-β-propiolactam; DMPL: α,α-dimethyl-β-propiolactam; PYR: pyrollidone

b) Reference 1 c) Reference 2

EXPERIMENTAL

POTASSIUM SALT OF α,α-DIMETHYL-β-PROPIOLACTAM

A mixture of 25 ml of dry ethyl ether and 4 ml of carefully dried ethyl alcohol 4) was placed in a 100 ml conical flask and purged with a stream of dry nitrogen. Approximately 0,5 g of potassium chips was added to the mixture under the nitrogen atmosphere with cooling. After the potassium completely reacted, the ether and excess alcohol were removed by distillation under vacuum with constant stirring. To remove the last traces of alcohol, the resulting white solid was pulverized under nitrogen and a small quantity of dry ethyl ether was added and evaporated again under vacuum at 10^{-2} mm Hg. The white residue was suspended in 5 ml of dry ethyl ether and combined with a solution of 1.0 g of the β-lactam in 3 ml of ether. The potassium ethoxide dissolved immediately,after which a white mass of the potassium salt of β-lactam precipitated. The product was filtered, washed with dry ethyl ether and converted into a suspension in the same solvent for use in the polymerization reaction. The yield was 886 mg (64 %); Anal., Calcd: C, 43,76 %; H, 5.87 %; N, 10.20 %; K.28.49; Found: C,42.98 %; H, 5.79 %; N, 10.10 %; K, 28.51.

TETRAMETHYLAMMONIUM SALT OF α,α-DIMETHYL-β-PROPIOLACTAM

The procedure used was a modification of the methods previously described for the synthesis of the tetramethylammonium salts of 2-pyrrolidone 5) and 2-piperidone 6,7). Two solutions were first prepared as follows: 1) 0.46 g of sodium were reacted with 15 ml of carefully dried ethyl alcohol, and 2) 2.2 g of predried tetramethylammonium chloride was dissolved in 15 ml of carefully dried ethyl alcohol. The two solutions were combined and allowed to stand for 30 minutes after which precipitation of sodium chloride was achieved by addition of 70 ml of dry ethyl ether. After standing overnight, the solution was filtered, and ether and ethyl alcohol were removed by distillation in vacuum. The syrup-like residue was dissolved in a small volume of dry ethyl ether and filtered through a sintered glass funnel to eliminate any insoluble residue, such as unreacted tetramethylammonium chloride. A solution of 2 g of the β-lactam in 20 ml of dry ethyl ether was added to the filtrate and precipitation of the salt was completed by gradual addition of the dry ethyl ether. The product was very hygroscopic and had to be filtered under a nitrogen atmosphere, after which it was suspended in dry ethyl ether for use. The yield was 67 %. Anal., Calcd: C, 62.75; H, 11.70; N, 16.25; Found: C, 62.35; H, 11.67; N, 16.13.

LITHIUM SALT OF α,α-DIMETHYL-β-PROPIOLACTAM

A solution of n-butyllithium in hexane was filtered under nitrogen, and a portion of it was reacted with a 10 % ethanol solution in ethyl ether. The resulting ethoxide was titrated to determine the concentration of the original solution, which was 2.2 M. A 5.50 ml portion of this solution corresponding to $1.21 \times 10^{-2} \times 10^{-2}$ m of n-butyllithium was added to a solution of 1.20 g (1.21×10^{-2} m) of α,α-dimethyl-β-propiolactam in 40 ml of dry diethyl ether under nitrogen . After the reaction had proceded for one-half to one hour with stirring, most of the solvent was removed by distillation under reduced pressure of nitrogen; yield 58 %, Anal,. Calcd: C, 57.16 %; H, 7.67 %; N, 13.33 %; Found: C. 56.96 %; H, 8.24 %; N, 12.98 %.

LITHIUM SALT OF α-METHYL-α-BUTYL-β-PROPIOLACTAM

This salt was prepared by the same procedure as described for the lithium salt of α,α-dimethyl-β-propiolactam. The yield was 902 mg. Anal., Calcd: C, 65.29 %; H, 9.59 %; N, 9.52 %; Found: C, 65.14 %; H, 9.90 %; N, 8.98 %.

TETRAMETHYLAMMONIUM SALT OF α-METHYL-α-BUTYL-β-PROPIOLACTAM

This salt was prepared by the same procedure as described for the tetramethylammonium salt of α,α-dimethyl-β-propiolactam. The yield was 1.12 g Anal., Calcd: C, 67.24 %; H, 12.22 %; N, 13.06 %; C, 66.95 %; H, 11.98 %; N, 12.86 %.

POLYMERIZATION REACTIONS

All polymerization reactions were carried out in a 50 ml roundbottom flask equipped with a magnetic stirrer and a three-way stopcock with a serum cap for addition of the monomer from a syringe. The reaction flask was dried by repeated heating under vacuum and purging with dry argon before and after a weighed amount of initiator was added. The reaction vessel was kept under a slow stream of argon at all times. N-acetyl-pyrrolidone as co-initiator (prepared as previously described 1)) was added followed by the monomer. Both were added by injection through the serum cap from a syringe.

RATE MEASUREMENTS

Table 2: Rate constants for propagation in the polymerization of α-methyl-α-butyl-β-propiolactam with salts of the monomer [a)]

Reaction Number [b)]	Initiator Salt	Initial Concentrations M [c)] $[M]_o$	$[I]_o$	$[C]_o$	k_a [b)] min^{-1}	k_p [c)] $M^{-1}min^{-1}$
	Lithium					
1		0.205	0.0152	0.0122	0.0114	0.93
2		0.174	0.0255	0.0188	0.0206	1.11
3		0.195	0.0112	0.0118	0.0114	0.98
	Tetramethylammonium					
4		0.0275	0.0052	0.0065	0.0060	0.92
5		0.0226	0.0084	0.0078	0.0086	1.13
6		0.0182	0.0123	0.0148	0.0146	0.98

a) In DMSO solution at 22-24°C with N-acetylpyrrolidone as coinitiator

b) [M]-monomer, [I]-initiator, [Co]-coinitiator; k_a-apparent rate constant, k_p-true rate constant of propagation

c) see Figure 1

Table 3: Rate constants for propagation in the polymerization of α-methyl-α-butyl-β-propiolactam with salts of α,α-dimethyl-β-propiolactam [a)]

Reaction Number [b)]	Initiator Salt	Initial Concentration M [c)] $[M]_o$	$[I]_o$	$[C]_o$	k_a min	k_p $M^{-1}min^{-1}$
	Lithium					
1		0.174	0.0153	0.0132	0.0125	0.95
2		0.184	0.0098	0.0092	0.0080	0.86
3		0.190	0.0121	0.0096	0.0100	1.04
	Potassium					
4		0.220	0.0142	0.0121	0.0139	1.13
5		0.192	0.0124	0.0113	0.0122	1.08
6		0.167	0.0153	0.0144	0.0161	1.15
	Tetramethylammonium					
7		0.173	0.0162	0.0151	0.0172	0.95
8		0.116	0.0157	0.0112	0.0128	0.99
9		0.186	0.0098	0.0092	0.0086	0.93

a) In DMSO solution at 22-24°C with N-acetylpyrrolidone as coinitiator b) see Table 2 for abbreviations c) see Figure 2

Infrared spectroscopy was used for determination of the propagation rate constants[1]. Samples of the reaction solution were periodically removed from the reactor with a syringe, and the intensities of the monomer and polymer carbonyl peaks were determined on a Perkin-Elmer Model 257 Infrared Spectrometer in a 0.0025 cm. solution cell. Absorption by the reaction solution was balanced against pure DMSO in duplicate cells. The apparent rate constants k_a for propagation was determined from the plot of the intensity of the monomer peak as a function of time and also from the numerical data by regression analysis. The apparent rate constants were then converted into true rate constants, k_p, by dividing by the appropriate initiator concentrations. The results are collected in Tables 2 and 3.

ACKNOWLEDGEMENT

The authors are grateful to the National Science Foundation for the support of this work, The use of the facilities of the NSF-sponsored Materials Research Laboratory at the University of Massachusetts is gratefully achnowledged.

LITERATURE

1. C. D. Eisenbach and R. W. Lenz, Macromolecules, 9, 227, (1976)
2. C. D. Eisenbach, R. W. Lenz, H. Sekiguchi, J. Polymer Sci., Letters, 15, 83 (1977)
3. E. Bigdeli and R. W. Lenz, Macromolecules, 11, 493 (1978)
4. C. S. Marvel and F. D. Hager, Org. Synth., Coll. Vol I, p. 249 (1956)
5. H. Sekiguchi, P. Rapacoulia and B. Coutin, French Patent 2,121,395 (1972); U. S. Patent 3,835,100 (1974); Britisch Patent 1,393,002 (1975); H. Sekiguchi and P. Tsourkas-Rapacoulina, Bull. Soc. Chim. France, 1974, 2585
6. H. Sekiguchi and B. Coutin, in Macromolecular Syntheses 6, in press
7. H. Sekiguchi and B. Coutin, J. Polymer Sci. Polymer Chem. Ed., 11, 1601 (1973)

Received July 21, 1980
Accepted July 25, 1980