Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization of Cyclic Imino Ethers. X. Kinetics, Chain Transfer, and Repolymerization

M. Litt[ab]; A. Levy[ac]; J. Herz[ad]
[a] Central Research Laboratories Allied Chemical Corporation, Morristown, New Jersey [b] Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio [c] Ethicon Corporation, Somerville, New Jersey [d] Central Research Laboratories, Stauffer Chemical Corporation, Tarrytown, New York

To cite this Article Litt, M. , Levy, A. and Herz, J.(1975) 'Polymerization of Cyclic Imino Ethers. X. Kinetics, Chain Transfer, and Repolymerization', Journal of Macromolecular Science, Part A, 9: 5, 703 — 727
To link to this Article: DOI: 10.1080/00222337508065890
URL: http://dx.doi.org/10.1080/00222337508065890

J. MACROMOL. SCI.—CHEM., A9(5), pp. 703-727 (1975)

Polymerization of Cyclic Imino Ethers. X. Kinetics, Chain Transfer, and Repolymerization

M. LITT,* A. LEVY,† and J. HERZ‡

Central Research Laboratories
Allied Chemical Corporation
Morristown, New Jersey 07960

ABSTRACT

The main conclusions in studies on polymerization catalysts and the nature of chain transfer in the polymerization of cyclic imino ethers were that there is extensive chain transfer in the 2-alkyl oxazolines to produce polymer with a reactive end. Toward the end of polymerization, these chain-transferred molecules repolymerize back on the active center producing a multibranched star polymer. A theory for the data was developed.

INTRODUCTION

The polymerization of cyclic imino ethers has been studied by four groups [1-9] over the last few years. While the mechanism has been recognized as a cationic polymerization from the first, it has not been studied in detail until recently. Tomalia and Sheetz [3] investigated the polymerization of methyl oxazoline with BF_3 etherate. In this case the counterion is destroyed. Recently,

---

*Present address: Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.

†Present address: Ethicon Corporation, Somerville, New Jersey 08876.

‡Present address: Central Research Laboratories, Stauffer Chemical Corporation, Tarrytown, New York 10591.

Kagiya and Matsuda [8] studied the polymerization of phenyl oxazoline using a wide variety of catalysts. They found that perchloric acid produced the fastest rate of polymerization. There were no unusual phenomena connected with this study except that the polymerization rate constant in solvents was smaller than in bulk. Saegusa has concentrated on the polymerization of unsubstituted oxazolines [9].

Our studies were, in the main, on alkyl oxazolines and oxazines. Potential catalysts were surveyed, the better ones were looked at more closely, and finally one of the best, perchloric acid, was investigated in detail. The polymerization mechanism is much more complicated in the aliphatic oxazoline series compared to the aromatic oxazoline series. This paper summarizes our studies on catalysts, reaction rates, chain transfer, and repolymerization.

EXPERIMENTAL

Monomers

Monomers were synthesized as described previously [6, 7].

Catalysts

In the initial screening, catalysts were purchased from various supply houses and used as received. HI, HBr, and perchloric acid, obtained as aqueous solutions, and p-toluene sulfonic acid hydrate were used in the form of salts of phenyl oxazine.

Preparation of Mineral Acid Salts of 2-Phenyl Δ2-Oxazine

$HClO_4$ Salt. To a solution of 5.08 g (0.032 mole) of 2-phenyl oxazine in 30 ml of absolute ethanol was added an equivalent amount of mineral acid [perchloric acid 70% solution, 4.6 g (0.032 mole)] dissolved in 30 ml of absolute ethanol. Upon chilling to 0°C, white crystals precipitated. A further crop was obtained by adding ether. After drying under vacuum, a total weight of 6.9 g (83% yield), mp = 118.5 to 119.5°C, was obtained.

Element analysis: Calculated for $C_{10}H_{12}ClNO_5$: C, 45.90; H, 4.62; N, 5.35. Found: C, 46.21; H, 4.37; N, 5.97.

Toluene Sulfonic Acid Salt. In a 250-ml flask was placed 6.44 g (0.040 mole) of 2-phenyl oxazine and 50 ml of absolute ethanol. To this was added 7.48 g (0.0039 mole) of hydrated p-toluene sulfonic acid in 50 ml of absolute alcohol. Upon chilling, 9.0 g (69%) of the expected salt, a white crystalline solid, precipitated. It was filtered and dried under vacuum, mp = 157.5°C.

Analysis for $C_{17}H_{19}NO_4S$: Calculated: C, 61.24; H, 5.74; N, 4.20; S, 9.62. Found: C, 60.93; H, 6.05; N, 4.65; S, 9.7.

Heating for 2 days at 85°C under vacuum turned the compound pale pink, mp = 155.5 to 157.5°C.

HI Salt. A solution of 5.25 g (0.033 mole) in 30 ml of absolute alcohol was mixed with 8.94 g (0.033 mole) of 47% HI in 30 ml of ethanol. After chilling and adding several milliliters of ethyl ether, a yellowish crystalline solid precipitated. It was washed several times with absolute ether and gave a pale yellow product, mp = 97 to 98°C.

2-p-Chlorophenyl Δ2-Oxazolenium Perchlorate (PCOP)

To a solution of 18.16 g (0.10 mole) 2-(p-chlorophenyl) Δ2-oxazoline in 100 ml absolute ethanol was added 14.5 g of 70% $HClO_4$ solution (0.10 mole). The solution was refrigerated overnight (~4°C); the precipitate was filtered out and washed with absolute ether. Yield, 21.4 g (75%). The salt was recrystallized from absolute ethanol, mp = 193.5 to 195°C.

Polymerizations

Screening

Lewis acid initiators were screened as follows. About 5 g of pure monomer, either 2-phenyl oxazine or one of several alkyl oxazolines, was distilled into a dried weighed polymerization tube. To this was added the Lewis acid; the tube was chilled, degassed, and sealed under vacuum. When the initial screening was done on oxazolines, catalyst was added in a ratio of about 1:500 to monomer. For 2-phenyl oxazine, the Lewis acid added was weighed in and was used either at a monomer/initiator ratio of 200 or 500. The sealed tubes were heated in an aluminum block for the times indicated. Where no times are indicated, they were heated for at least 20 hr at 130°C. The results are summarized in Table 1.

Oxygen and halogen acids were tested as the free acid, ester, or as "onium" salts. The procedure described above was used. p-Toluene sulfonic acid was obtained as the hydrate. It was dried under vacuum at 150°C before use.

TABLE 1. Lewis Acids and Inorganic Salts as Polymerization Initiators

Monomer	Initiator	M/I	Time (hr)	Temp (°C)	% Polymer[a]
Phenyl oxazine	$BF_3O(Et)_2$	200	16	160	100
	I_2	200	20	130	100
	$AlCl_3$	500	24	160	15
	$FeCl_3$	500	24	160	15
	$VOCl_2$	200	48	160	0
	$LiClO_4$	500	48	160	0
	$Mg(ClO_4)_2$	200	0.5	160	100
Various oxazolines	SbF_5				+++
	$\phi N_2^+PF_6^-$				80
	$SbCl_5$				+
	$SnCl_4$				+
	PCl_3				+

[a] +++ = good polymerization, + = poor polymerization.

Relative Polymerization Rates

The procedure was the same as in the Screening section above. All monomer to initiator molar ratios (M/I) were 200. Tubes, polymerized in a heated alunimum block, were removed every half hour and inverted. The time to complete polymerization was taken as the time when the viscosity of the polymerizate no longer increased. This is a rough estimate, but the relative order of initiators can be told by this method. The relative rates were reasonably meaningful (±25%).

Measurement of Polymerization Rate

An appropriate amount of the perchloric acid salt of 2-(p-chlorophenyl) oxazoline was weighed into a cleaned, flamed flask. An appropriate amount of 2-heptyl oxazoline was distilled from sodium through a spinning band column into the flask. Where solvent was used, the dried solvent was then distilled into the same flask using a second column. When the initiator had dissolved, known amounts of solution were syringed into cleaned, flamed polymerization tubes. These were then sealed under vacuum after chilling. They were polymerized by setting all the tubes in an oil bath set at a temperature of either 115, 130, or 145°C, and removing tubes at appropriate intervals.

Polymer was isolated by adding the polymerizate to dioxane, making the resulting solution acid with HCl, and then adding water. The polymer precipitated cleanly. The procedure was then repeated. It was filtered into a sintered glass funnel, washed with water, and dried under vacuum at 40°C for 60 hr. Constant weight was achieved after 30 hr drying in a separate experiment.

Runs to Complete Conversion

The perchloric acid salt of 2-(p-chlorophenyl) oxazoline was dissolved in dried, distilled acetonitrile to make up a 0.1-M solution. An appropriate amount of this solution was syringed into a cleaned, flamed polymerization tube and the acetonitrile evaporated away slowly. After drying and weighing, the tube was connected to a distilling column and the monomer, either 2-pentyl or 2-isobutyl oxazoline, was distilled from sodium, using a spinning band column, into the polymerization tube. This was chilled, sealed under vacuum, and reweighed. It was polymerized for an appropriate period of time at 160°C, usually 4 hr for those with a molar ratio of less than 10,000 and 40 hr for those with a higher ratio. Complete polymerization is about 1.5 hr at M/I = 10,000. A check was carried out by polymerizing two samples of 2-isobutyl oxazoline with M/I ≈ 14,500. One was heated for 7.5 hr and one for 67 hr. $\overline{X}_n$ and $[\eta]$ were unchanged within experimental error. $\overline{X}_w$ increased from 3,500 to 5,000. This is discussed later.

Characterization

Element analyses were performed by the analytical staff at Allied Chemical Corp. Reduced viscosities were normally run as a 0.52% solution of the polymer in m-cresol. When other concentrations or solvents were used, it is noted in the text.

Intrinsic viscosities were run in a dilution viscometer in various solvents. These are noted in footnotes to the tables.

Number-average molecular weights were measured in chlorobenzene using high-speed membrane osmometry.

Weight-average molecular weights were measured by light scattering in acetic acid or butanol or both. Zimm plots were made and the values given are for turbidity extrapolated to zero concentration and zero degrees.

RESULTS AND DISCUSSION

This work was done over a period of many years and thus some parts are crude. Related research has been done more elegantly by the present researchers [8, 10, 11]. The areas covered are 1) effects of catalysts, 2) rate of polymerization of 2-heptyl oxazoline with $HClO_4$ as a function of temperature and solvent, and 3) molecular weights of the polymers.

Effect of Catalyst

As is well known, the cyclic imino ethers are highly basic compared to other cationically polymerized monomers. They therefore destroy the Lewis acid catalysts [3]. However, oxygen acids, their esters, as well as iodides and bromides, are stable catalysts for the system. General data summarizing scanning work on yields of polymer covering various oxazolines and oxazines are given in Table 1.

BF_3 etherate and SbF_5 are consumed before polymerization is complete if higher M/I ratios are used. While the times of heating were long to insure maximum polymerization, most reactions were over in 1 to 2 hr. The only unusual point of Table 1 is that anhydrous $Mg(ClO_4)_2$ is an initiator for oxazoline polymerization.

Similarly, the effect of various oxygen and halogen acids, esters, and salts on the viscosity of polymers from phenyl oxazine is given in Table 2.

As can be seen, phenyl oxazine polymerized by a strong acid can achieve high molecular weights, $\eta_{sp}/c = 2.4$. Aliphatic oxazines cannot be prepared with viscosities greater than 1 at 130°C, no matter what catalyst is used [7].

Esters or anhydrides of weak acids, e.g., acetic acid, cannot initiate polymerization; the anion is too reactive and adds to the cationic end of the polymer. The same seems to be true for alkyl chlorides, though these do react very slowly. We have found that the use of chlorinated aliphatic solvents such as $CHCl_3$ or $C_2H_2Cl_4$ in monomer preparation can cause slow polymerization of the monomer when such a solution stands at room temperature for several months.

The effect of catalyst on the relative rates of polymerization and viscosities for 2-phenyl and 2-pentyl oxazine polymers is shown in Table 3.

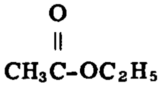
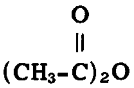
The relative rates at 130°C for methyl tosylate and HI initiators are of the same order of magnitude as those found by Saegusa [10]. The major points are 1) the use of dimethyl sulfate or fuming H_2SO_4 lowers the viscosity by a factor of 2, showing that both ends of the sulfate group grow polymer molecules; and 2) the use of iodide or bromide initiators also lowers the viscosity tremendously, indicating some unknown chain transfer reaction which is greater for the more nucleophilic bromide.

The alkyl substituent allows more rapid polymerization by a factor of 2 to 3 over that of the aromatic substituent. Surprisingly, phenyl oxazoline seems to polymerize at about the same rate as phenyl oxazine.

Rates of Polymerization of 2-(n-Heptyl) Oxazoline

Polymerizations were done in bulk at 129.6°C using 2-(p-chlorophenyl) oxazolinium perchlorate (PCOP) as initiator. A typical polymerization curve is shown in Fig. 1. The observed rate as a function of initiator concentration is shown in Fig. 2. This is about 2.5 to 3 times faster than that found for phenyl oxazoline in nitromethane, a solvent which slowed the polymerization [12]. This corresponds to the relative rates shown in Table 3 for oxazines of about three to one.

TABLE 2. Acids, Esters, and Alkyl Halides as Polymerization Initiators

Monomer(M)	Initiator(I)	M/I	Time (hr)	Temp (°C)	% Polymer	η_{sp}/c[a]
Phenyl oxazine	$H_2SO_4(SO_3)_{0.3}$	200	4	130	100	0.45
	$CH_3C_6H_4SO_3H$	500	12	130	100	0.9
	$CH_3C_6H_4SO_3CH_3$	200	7	130	100	0.9
	$(CH_3)_2SO_4$	2,500	6	160	100	2.4
	 $CH_3\overset{\overset{O}{\|}}{C}\text{-}OC_2H_5$	500	48	160	0	
	 $(CH_3\text{-}\overset{\overset{O}{\|}}{C})_2O$	500	48	160	0	
	CH_3I	50	96	86	100	0.17
	C_3H_7Br	200	7	160	100	0.3
	$BrCH_2CH_2Br$	100	4	160	100	0.23
	$C_6H_5CH_2Cl$	200	40	160	0	
	$(C_6H_5CH_2)_3S^+ClO_4^-$	200	2.5	130	100	0.38

[a] All viscosities run at 1.5% solution in m-cresol at 30°C.

TABLE 3. Relative Polymerization Rates for Different Initiators

Monomer	Initiator	M/I	Time[a]	Temp (°C)	η_{sp}/c[c]
Phenyl oxazine	$HClO_4$[b]	200	3	130	0.8
	$HSO_3C_6H_4CH_3$[b]	200	6	130	0.9
	$CH_3SO_3C_6H_4CH_3$	200	6	130	0.9
	$H_2SO_4.(SO_3)_{0.3}$	200	4	130	0.4
	HI[b]	200	12	130	0.5
	CH_3I	200	8	160	0.45
	C_3H_7Br	200	7	160	0.3
Pentyl oxazine	$HClO_4$[b]	200	1.1	130	0.44
	$CH_3SO_3C_6H_4CH_3$	200	3	130	0.44
	$HSO_3C_6H_4CH_3$[b]	200	3-4	130	0.44
	$H_2SO_4(SO_3)_{0.3}$	200	1.5	130	0.24
	$(CH_3)_2SO_4$	200	1.5	130	0.25
Phenyl oxazoline	$HSO_3C_6H_4CH_3$[b]	200	6-7	130	0.91
	HI[b]	200	12-16	130	0.51

[a] Time in hours to estimated completion of polymerization. No further viscosity change.

[b] Used as the salt of phenyl oxazine.

[c] All viscosities run as 1.5% solution in m-cresol.

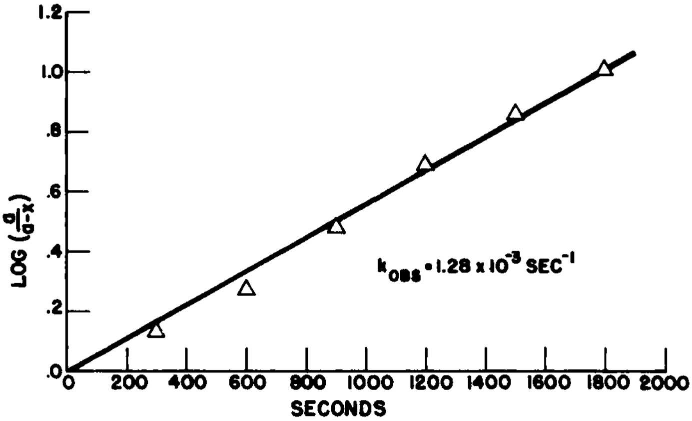


FIG. 1. First-order plot for bulk polymerization of n-heptyl oxazoline at 129.6°C with 2-(p-chlorophenyl oxazolineium perchlorate as initiator.

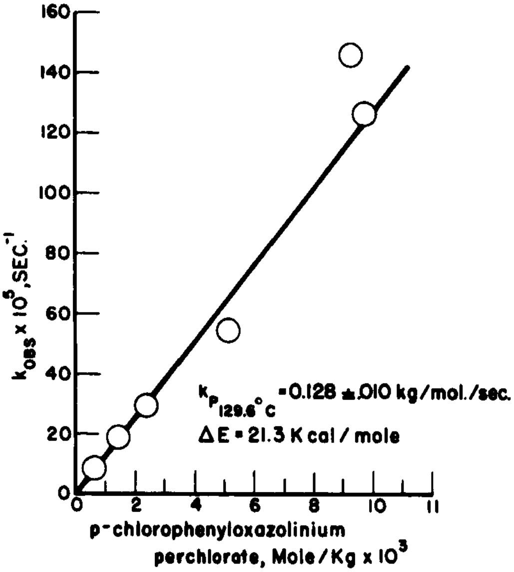


FIG. 2. Determination of rate constant of polymerization for bulk polymerization of 2-(n-heptyl) oxazoline at 129.6°C.

The work at different temperatures was done in a solvent since the polymer crystallized below 130°C. Initially, dimethyl acetamide was chosen as the solvent. However, the rate constant of polymerization (first order in monomer and initiator) was solvent dependent as shown in Fig. 3.

(A wide variety of solvents has been investigated in the polymerization of phenyl oxazoline by Kagiya, Matsuda, and Hirata [12]. All polymerizations were done at 3 $\underline{M}$ concentration of monomer, and the relative rates of polymerization were compared as a function of polarity and nucleophilicity. For high dielectric constant solvents, the higher the nucleophilicity, the lower the rate.)

We found that the rate diminished rapidly by a factor of 2 up to 50% dilution and then seemed to remain constant. This cannot be explained in terms of competitive solvation and reaction of the active cation with a solvated monomer. It can be explained by saying that the monomer solvated cation attacks a free monomer twice as fast as a DMAC solvated cation, and at 50% solvent essentially all the cation is solvated with DMAC. This seems unlikely, though it may be true. Kagiya et al. [12] postulated a similar equilibrium.

We therefore chose to work in butyrolactone as it is a relatively nonnucleophilic, polar solvent. The rate constant at 50% solvent

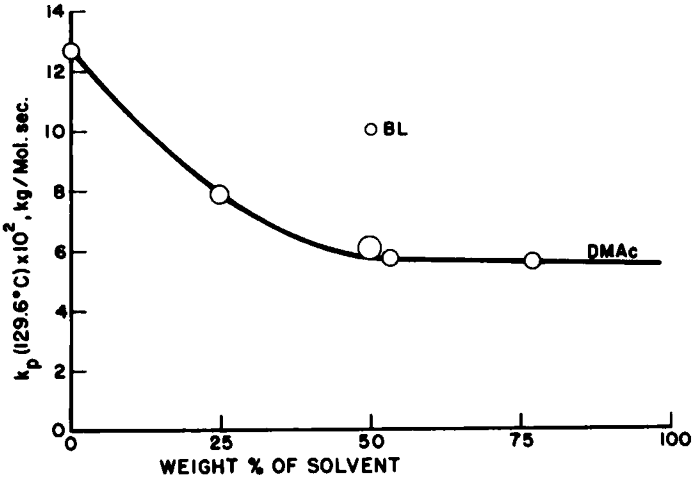


FIG. 3. Rate constant of polymerization as a function of monomer concentration in DMAC and butyrolactone (BL).

TABLE 4. Propagation Rate Constants (k_p) and Activation Parameters in the Polymerization of Heptyl Oxazoline with PCOP (50% Monomer in γ-Butyrolactone)

T (°C)	k_p (kg/mole sec)
115.0	0.0334
129.6	0.100
145.0	0.216
ΔE_p (kcal/mole)	21.3
A_p (kg/mole sec)	3.2×10^{10}

was 0.100 vs 0.127 kg/mole sec in bulk. In DMAC the rate constant dropped by a factor of 2.3 from the bulk. The data for rate constants as a function of temperature are given in Table 4.

The activation energy is about that found for most cyclic imino ether polymerizations [10, 11]. However, our pre-exponential factor is very high when compared to that of phenyl oxazine [11] though lower than that for oxazoline [9]. As our lowest M/I ratio was 500, complete initiation was achieved early in the polymerization and we only observed the polymerization.

Chain Transfer and Repolymerization

Chain transfer has been noted for most oxazolines and oxazines. Some extreme examples were found; benzyl oxazoline ($\eta_{sp}/c = 0.21$ at 130°C and M/I = 1000) [6] and 2-(acetoxymethyl) oxazoline ($\eta_{sp}/c = 0.37$ at M/I = 1300 and $\eta_{sp}/c = 0.34$ at M/I = 500) [13]. For comparison, a normal n-alkyl oxazoline such as pentyl oxazoline will have $\eta_{sp}/c \approx 0.7$ at M/I = 560 [14] and one can easily get reduced viscosities above 1 for 2-(n-alkyl) oxazolines at M/I > 2000. (The mechanism for chain transfer in 2-phenyl oxazoline and oxazine is still a puzzle.) We therefore decided to investigate the mechanism and effect of chain transfer in alkyl oxazolines. Two sets of experiments were run. First, heptyl oxazoline was polymerized at 130°C

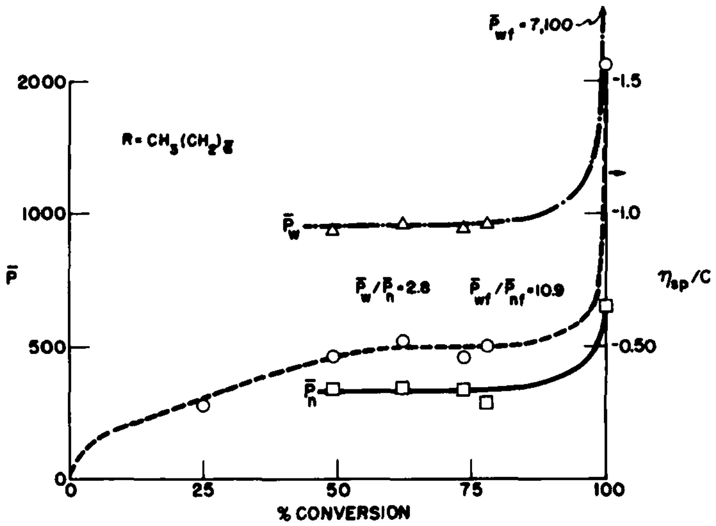


FIG. 4. $\overline{P}_n$, $\overline{P}_w$, and $\{\eta\}$ of polymers of 2-(n-heptyl oxazoline) as a function of conversion.

with M/I = 9810 (I = PCOP). Samples were removed at various times, and conversion, intrinsic viscosity, $\overline{P}_n$, and $\overline{P}_w$ were determined for each sample. The data are given in Fig. 4. From the time the conversion reached 50%, where enough polymer could be isolated for all the determinations, $[\eta]$, $\overline{P}_n$, and $\overline{P}_w$ remain constant at least to 78% conversion. At 100% conversion, 56 hr at 130°C, all three values rise considerably; the greatest rise is in $\overline{P}_w$ which goes from ~1000 to 7100. The constant value of $\overline{P}_n$ at ~300 and the relatively low and constant ratio of $\overline{P}_w$ to $\overline{P}_n$, 2.8, during the polymerization indicates that the major reaction controlling the degree of polymerization is chain transfer, and the chain transfer constant to a 2-(n-alkyl) oxazoline at 130°C is about 1/300.

The upturn in all the values at 100% conversion was puzzling. A series of experiments were therefore run with 2-pentyl oxazoline and 2-isobutyl oxazoline at various M/I concentrations (I = PCOP) from ~500 to ~40,000. All polymerizations were taken to 100% conversion (3.5 hr at 160°C and 0.5 hr at 180°C for 2-pentyl oxazoline except for M/I = 37,000, which was heated for 44 hr

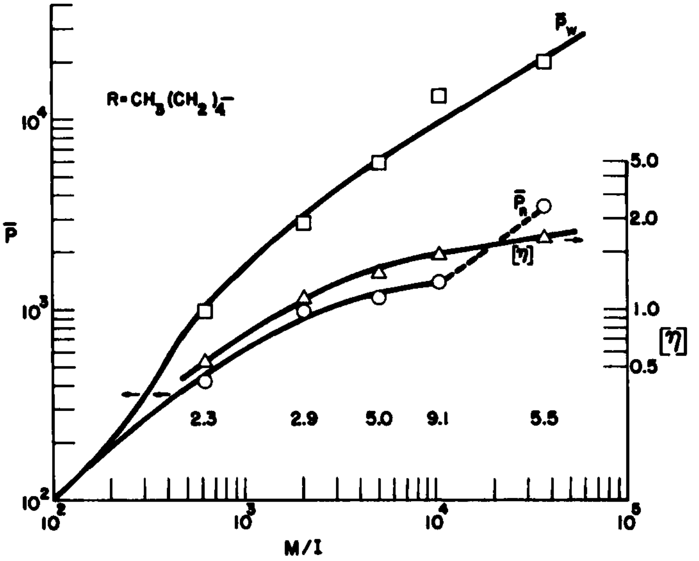


FIG. 5. Polymerization of 2-(n-pentyl oxazoline) to 100% conversion at various M/I ratios. I = PCOP.

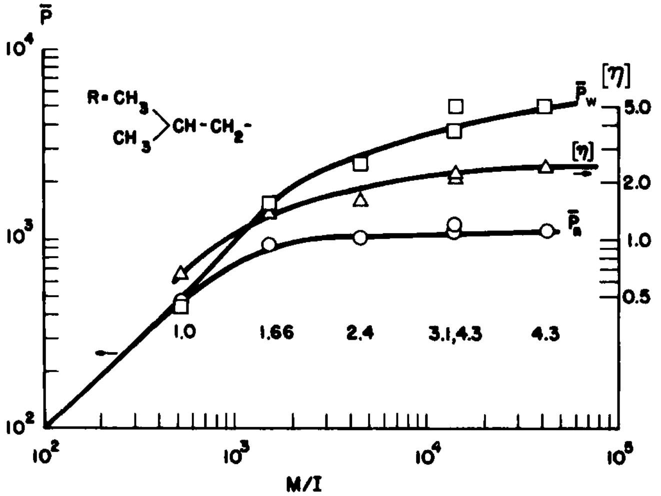


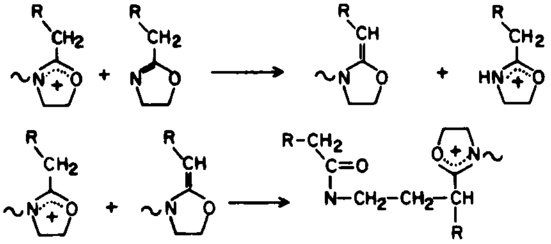
FIG. 6. Polymerization of 2-isobutyl oxazoline to 100% conversion at various M/I ratios. I = (PCOP).

at 160°C, and similar heating times for 2-isobutyl oxazoline). The data are presented in Figs. 5 and 6 and Tables 5 and 6.

In Fig. 5 and Table 5 it can be seen that even at M/I = 500, $\overline{P}_n$ is less than 500 while $\overline{P}_w$ is about 1000, with $\overline{P}_w/\overline{P}_n = 2.3$. The ratio rises rapidly as M/I increases. Heating time and temperature obviously affect $\overline{P}_n$ greatly as shown by the 44-hr heating for M/I = 37,000 and the large $\overline{P}_w/\overline{P}_n$ value for the sample with M/I = 10,535. This last was heated to 180°C, above the melting point of the polymer.

The same effect is shown to a lesser degree by 2-isobutyl oxazoline, Fig. 6. At M/I = 500, $\overline{P}_n = \overline{P}_w = 500$; living monodisperse polymer was obtained. The chain transfer constant is obviously much less than 1/500. As M/I increases, $\overline{P}_n$ becomes constant at about 1000, which means that the chain transfer constant is near 1/800 at 160°C. $\overline{P}_w$, however, increases steadily with increasing M/I as does $[\eta]$ to a lesser degree.

The above data make sense when the following reactions are postulated. The major site of chain transfer must be the carbon α to the 2-carbon of the ring. This is shown by the greater chain transfer on oxazoline polymers with activated α-methylene groups such as 2-benzyl [6] and 2-acetoxymethyl oxazoline [13]. Conversely, shielding the α-methylene group as in 2-isobutyl oxazoline lowers the chain transfer constant considerably. We can visualize the chain transfer reaction as



This was proposed earlier, but supporting evidence was not given [13]. The chain transferred polymer is now an enamine, though hindered, and can attack active sites such as quaternized oxazolines (polymer reactive ends), though apparently more slowly than does

TABLE 5. Molecular Weights and Viscosities as a Function of M/I (PCOP) for 2-Pentyl Oxazoline Polymerized at 160°C

		$\overline{P}_w$					Viscosity parameters			
M/I	t (hr)	a	b	$\langle \overline{r}^2 \rangle^{1/2}$	$\overline{P}_n$ [d]	$\overline{P}_w/\overline{P}_n$	$[\eta]$ [c]	k'	$[\eta]$ [d]	k'
531	4[g]	1,000		274	425	2.3	0.53	0.55	0.34	0.52
2,030	4[g]	2,850		390	993	2.9	1.14	0.50	0.74	0.51
5,056	4[g]	5,850	6,050	570/620	1160	5.0	1.59	0.52	0.98	0.64
10,535	4[g]	12,910	13,130	720/910	1400	9.2	1.93	0.63	1.34	0.60
37,000	44	19,720			3550	5.5	2.36	0.86	1.40	1.10
5,750[e]	26	6,630		628	910	7.3	1.88	0.45		
[f]			1,550	437	930	1.67	1.19	0.17		

[a] Determination in acetic acid/0.5 M NaCl at 546 nm, 25°C.
[b] Determined in n-butanol at 546 nm, 25°C.
[c] Determined in m-cresol, 25°C.
[d] Determined in chlorobenzene, 25°C.
[e] Polymerized at 130°C.
[f] Initial M/I = 10,444, reaction stopped at 79% conversion. True M/I = 8270.
[g] Tubes kept at 160°C for 3½ hr, then raised to 180°C for ½ hr.

TABLE 6. Molecular Weights and Viscosities as a Function of M/I (PCOP) for 2-Isobutyl Oxazoline Polymerized at 160°C

		$\overline{P}_w$					
M/I	t (hr)	a	b	$\langle \overline{r}_Z{}^2 \rangle^{1/2}$	$\overline{P}_n{}^c$	$\overline{P}_w/\overline{P}_n$	$[\eta]^d$
514	6	440		222	472	~1.0	0.66
1,581	6	1490		326	920	1.62	1.39
4,519	7.5	2600	2360	425/344	1030	2.41	1.59
13,940	7.5	3590	3690	484/490	1200	3.03	2.11
14,888	67		4720	/518	1100	3.88	2.20
41,180	25	5010	5260	523/537	1110	4.63	2.33

[a] Determined in acetic acid at 25°C, 546 nm.
[b] Determined in n-butanol at 25°C, 546 nm.
[c] Determined in chlorobenzene at 37°C.
[d] Determined in m-cresol at 25°C.

monomer. Thus polymerization is initially Poisson as shown here for 2-isobutyl oxazoline, Fig. 6, and by Kagiya and Matsuda for 2-phenyl oxazoline [15]. However, with alkyl oxazolines, chain transfer occurs readily, generating many polymer molecules per active center. These chain transferred molecules have a reactive, though hindered, enamine end. At the end of the polymerization, the chain transferred polymer molecules repolymerize on the active center, generating branches near its end. The molecule is probably star-shaped, with some extra branches along the chain.

The extent of repolymerization can be seen qualitatively in Tables 5 and 6. We can compare the last experiment in Table 5, M/I = 10,444 but polymerized only to 79% conversion, with that polymerized to 100% conversion. $\overline{P}_n$ rose by about 50% while $\overline{P}_w$ rose by about 840%. $\overline{P}_w/\overline{P}_n$ rose from 1.67 to 9.2. The individual determinations are accurate only to ~±20%, but the change is remarkable.

The star branching can also be noted in the Huggins constant, k', of the viscosity determinations. It is high, 0.5, even at M/I = 531, and rises steadily as M/I rises. However, for the incompletely polymerized sample, k' is only 0.17, showing a relatively linear molecule. There is probably some repolymerization during the whole polymerization, generating polymer with long branches.

Similarly, Table 6 compares two samples of about the same M/I, ~14,000. Heating for 67 hr as compared to 7.5 hr did not change $\overline{P}_n$ but did raise $\overline{P}_w$ by about 25%. As the polymers were crystalline (T_m = 210°C [6]) and mobility is restricted, this is a significant change. $\overline{P}_w/\overline{P}_n$ rose, showing greater polydispersity. There was almost no change in viscosity at higher M/I values, showing that the average molecular volume in solution was almost independent of $\overline{P}_w$. The effect of steric factors on the repolymerization can be seen by comparing Tables 5 and 6. In spite of the greater chain transfer for the n-pentyl oxazoline, $\overline{P}_n$ is almost the same as for isobutyl oxazoline because of more repolymerization. However, due also to this, $\overline{P}_w$ is much higher at a given M/I for n-pentyl oxazoline.

The extent of repolymerization can be calculated easily from the rise in $\overline{P}_n$ and $\overline{P}_w$ if a chain transfer constant is assumed.

For example, take heptyl oxazoline in Fig. 3. $\overline{P}_n$ rises from ~300 to ~700 at 100% conversion, meaning that about 60% of the polymer molecules have repolymerized. Since there were about 35 chain transfers, the star molecules must contain about 21 chains each.

A similar effect, though much less marked, seems to be present for the phenyl derivatives. One can easily get very high viscosity polymers in this system. Table 7 gives some data on phenyl oxazine; we have similar results on phenyl oxazoline which are being analyzed further at present.

The Huggins constant is ~0.42. This is much higher than that found in truly linear molecules, where it is about 0.2 to 0.25, but lower than that found for pentyl oxazoline at 100% conversion, even at low M/I. Thus there is extensive branching. However, the molecule increases in size as M/I increases. It is obviously a longer molecule than those obtained from the alkyl oxazolines at similar M/I as shown by the higher $[\eta]$, and thus probably has less branching and longer branches.

The problem is: What is the mechanism of chain transfer? One tentative suggestion is that there is very slow cationic attack on the benzene rings, either of monomer or polymer. Another possibility is that the ring-opened ester, present in equilibrium with the salt, can have the elements of acid removed by monomer, leaving either a vinyl amide or a propenyl amide.

TABLE 7. Polymerization of 2-Phenyl Oxazine with Dimethyl Sulfate,[a] Effect on Viscosity

M/I	$\overline{P}_{n\ \mathrm{calc}}$	η_{sp}/c[b]	$[\eta]$[c]	k'[d]
1000	500	0.9		
2500	1000	2.0	1.88	0.42
4700	2350	2.4	2.35	0.43

[a] Polymerized for 18 hr at 160°C.
[b] 0.52% in m-cresol, 25°C.
[c] In m-cresol, 25°C.
[d] Huggins constant.

Theoretical Treatment of Repolymerization

An equation describing the final $\overline{P}_n$ and $\overline{P}_w$ can be derived readily if the following assumptions are made:

1. No repolymerization of polymer chains occurs until essentially all the monomer has been used up.
2. No chain transfer can occur on the dead polymer chains.
3. All active centers have an equal chance to repolymerize all the polymer molecules.
4. With no early repolymerization, $\overline{P}_n/\overline{P}_w \approx 2$.

We can make the following definitions:

$\overline{P}_{n(0)}$ = initial number average degree of polymerization resulting from chain transfer
x = number of chain transfers per active center
= $M/[I\overline{P}_{n(0)}]$
n = number of polymer molecules which have repolymerized on the active center by the end of the reaction

The following equations can be written for the star portion of the polymer. If i molecules have been added to the active end, each of average molecular length $\overline{P}_{n(0)}$, by standard molecular weight theory, with a most probable distribution:

$$\overline{P}_{n(i)} = (i + 1)\overline{P}_{n(0)} \qquad (1)$$

$$\overline{P}_{w(i)} = (i + 2)\overline{P}_{n(0)} \qquad (2)$$

We can sum over all i's. If the assumption is made that all active ends have had the same chance to add, i.e., the distribution of chains in a repolymerized active center is a Poisson distribution, the equations are easily solvable.

$$\overline{P}_{n(n)} = \frac{\sum_{0}^{\infty} (i + 1)P_{n(0)}f(i)}{\sum_{0}^{\infty} f(i)} \qquad (3)$$

where

$$f(i) = \ell^{-n} \frac{n^i}{i!} \tag{4}$$

$$\overline{P}_{n(n)} = \ell^{-n}\overline{P}_{n(0)} \sum_0^\infty \frac{(i + 1)n^i}{i!} = (n + 1)\overline{P}_{n(0)} \tag{5}$$

$$\overline{P}_{w(n)} = \frac{\ell^{-2}\left[\overline{P}_{n(0)}\right]^2 \sum_0^\infty (i + 2)^2 \frac{n^i}{i!}}{\ell^{-2}\,\overline{P}_{n(0)} \sum_0^\infty (i + 1) \frac{n^i}{i!}} \tag{6}$$

Summing by standard methods:

$$\overline{P}_{w(n)} = \frac{n^2 + 5n + 4}{n + 1}\,\overline{P}_{n(0)} = (n + 4)\overline{P}_{n(0)} \tag{7}$$

The molecular weight of the total polymer is the average of the repolymerized star molecules and the single chain transferred molecules. It can be written as

$$\overline{P}_w = \frac{\Sigma[\overline{P}_w(i)]w(i)}{\Sigma\, w(i)} = \frac{\Sigma\, \overline{P}_w(i)\overline{P}_n(i)f(i)}{\Sigma\, \overline{P}_n(i)f(i)} \tag{8}$$

$$\overline{P}_n = \frac{\Sigma\, \overline{P}_n(i)f(i)}{\Sigma\, f(i)} \tag{9}$$

For each active center which has had n chain transfers and an average of x repolymerizations, there is one star molecule. With an average degree of polymerization described by Eqs. (5) and (7), and (x - n) chain transferred single molecules of average molecular weight $\overline{P}_{n(0)}$ and $\overline{P}_{w(0)} \approx 2\,\overline{P}_{n(0)}$.

$$\overline{P}_n = \frac{(n + 1) + (x - n)}{(x - n) + 1}\,\overline{P}_{n(0)} = \frac{x + 1}{x - n + 1}\,\overline{P}_{n(0)} \tag{10}$$

Using Eq. (7) to calculate $\overline{P}_w$, we get

$$\overline{P}_w = \frac{(n^2 + 5n + 4) + 2(x - n)}{n + 1 + x - n} \overline{P}_{n(0)} = \frac{n^2 + 3n + 4 + 2x}{x + 1} \overline{P}_{n(0)} \quad (11)$$

The ratio $\overline{P}_w/\overline{P}_n$ is therefore

$$\frac{\overline{P}_w}{\overline{P}_n} = \frac{(n^2 + 3n + 4 + 2x)(x - n + 1)}{(x + 1)^2} \quad (12)$$

This can correlate the data for isobutyl oxazoline quite well using a chain transfer constant of 1/800. The equations work properly only when M/I is greater than three times the chain transfer constant, as the initial portion of the polymerization, before chain transfer has given an equilibrium distribution of molecular weights, is ignored. The results for 2-isobutyl oxazoline are given in Table 8, while those for 2-pentyl oxazoline are in Table 9.

One value did not fit; that where the sample M/I = 13,500 was heated for 67 hr. Here $\overline{P}_n$ was lower than that sample heated less time, showing that there was some random error.

TABLE 8. Comparison of Experimental and Theoretical Values of $\overline{P}_w/\overline{P}_n$ for Poly(N-isovaleryl Ethyleneimine)

M/I	x^a	n^b	$\overline{P}_w/\overline{P}_n$ Calc	$\overline{P}_w/\overline{P}_n$ Exptl
4,500	5.63	1.26	2.52	2.40
13,500[c]	16.9	5.64	3.30	3.04
40,000	50.0	14.0	4.86	4.62

[a] Calculated using a chain transfer constant of 1/800.
[b] Calculated from Eq. (9), $n = (x + 1)(1 - \overline{P}_{n(0)}/\overline{P}_n)$.
[c] Heated for 7 hr at 160°C.

TABLE 9. Comparison of Experimental and Theoretical Values of $\bar{P}_w/\bar{P}_n$ for Poly(N-hexanoyl Ethyleneimine)

			$\bar{P}_w/\bar{P}_n$	
M/I	x^a	n^b	Calc	Exptl
531	3.2	1.94	2.56	2.3
2,030	12.2	10.2	2.81	2.9
5,056	30.3	25.9	4.48	5.0
10,535	63.2	55.7	7.0	9.2
37,000	222.0	211.6	10.5	5.5

[a] Calculated using a chain transfer constant of 1/167.
[b] Calculated from Eq. (9).

A reasonable fit was found for polymers of n-pentyl oxazoline below M/C = 10,000, using a chain transfer constant of 150 to 200, Table 8. At the higher values of M/I, especially at 40,000, $\bar{P}_n$ determined by osmometry is too inaccurate to get good agreement.

For poly(N-octanoyl ethyleneimine) the agreement for the sample polymerized to 100% conversion is $\bar{P}_w/\bar{P}_{n\,\mathrm{exp}} = 6.22$, $\bar{P}_w/\bar{P}_n$ calc = 6.65 (chain transfer constant of 1/200) = 5.86 (chain transfer constant of 1/300). Overall, the data indicate that some repolymerization occurs with n-alkyl oxazolines before 100% conversion, but most happens at the end.

SUMMARY AND CONCLUSIONS

This paper covers several aspects of the polymerization of oxazolines and oxazines but concentrates on chain transfer. Results on the 2-phenyl derivatives imply that these polymers are branched at high M/I. Work in progress with T. Provder confirms this. Also, the iodide and bromide counterions participate in a chain transfer reaction, which may go through the ring-opened ester.

The 2-alkyl oxazines and oxazolines show clear evidence for extensive chain transfer. The chain transfer constant for n-alkyl oxazolines where $n > 4$ is in the neighborhood of 1/200 to 1/300. (It is larger for 2-methyl oxazoline, i.e., viscosities are lower for this polymer at comparable M/I as compared to other alkyl oxazolines.)

The chain transferred polymer has an end which is basically a substituted enamine ether and as such is quite nucleophilic. It thus can add back to the active center, regenerating another oxazolineium or oxazineium cation. However, as it is more hindered and less nucleophilic than a monomer, it reacts slowly. There is some repolymerization of chain transferred polymer molecules onto growing chains during the polymerization, giving long branches. However, most of the repolymerization occurs during the last few percent of the polymerization and thus tends to generate a star polymer. These may have as many as 100 to 200 branches to the star when M/I = 37,000.

With branching near the methylene carbon α to the ring, chain transfer and repolymerization are both reduced due to steric hinderance. The polymer molecular weight increases and $\bar{P}_w/\bar{P}_n$ decreases. One can easily obtain living polymers in this system.

ACKNOWLEDGMENTS

We wish to thank Allied Chemical Corp., Morristown, New Jersey, for permission to publish this work. We also thank Mr. E. Walsh for the molecular weight and viscosity determinations.

REFERENCES

[1] For Paper VIII of this series, see M. Litt, J. Herz, and E. Turi, in Block Copolymers (S. Aggarwal, ed.), Plenum, New York, 1970, p. 313.
[2] T. Kagiya, S. Narisawa, T. Manabe, and K. Fukui, J. Polym. Sci., Part B, 4, 441 (1966).
[3] D. A. Tomalia and D. P. Sheetz, J. Polym. Sci., Part A-1, 4, 2253 (1966).
[4] W. Seeliger and W. Thier, Angew. Chem., 78, 613 (1966).
[5] M. Litt. T. G. Bassiri, and A. Levy, Belgian Patents, 666,828 and 666,831 (1965).

[6] T. G. Bassiri, A. Levy, and M. Litt, J. Polym. Sci., Part B, 5, 871 (1967).

[7] A. Levy and M. Litt, Ibid., 5, 881 (1967).

[8] T. Kagiya and T. Matsuda, J. Macromol. Sci.—Chem., A5, 1277 (1971); A6, 135 (1972).

[9] T. Saegusa, H. Ikeda, and H. Fujii, Macromolecules, 6, 315 (1973).

[10] T. Saegusa, S. Kobayashi, and Y. Nagura, Ibid., 7, 264, 272 (1974).

[11] T. Kagiya, T. Matsuda, M. Kakato, and R. Hirata, J. Macromol. Sci.—Chem., A6, 1631 (1972).

[12] T. Kagiya, T. Matsuda and R. Hirata, Ibid., A6, 451 (1972).

[13] A. Levy and M. Litt, J. Polym. Sci., Part A-1, 6, 1883 (1968).

[14] A. Levy and M. Litt, Ibid., 6, 63 (1968).

[15] T. Kagiya and T. Matsuda, J. Macromol. Sci.—Chem., A5, 1265 (1971).