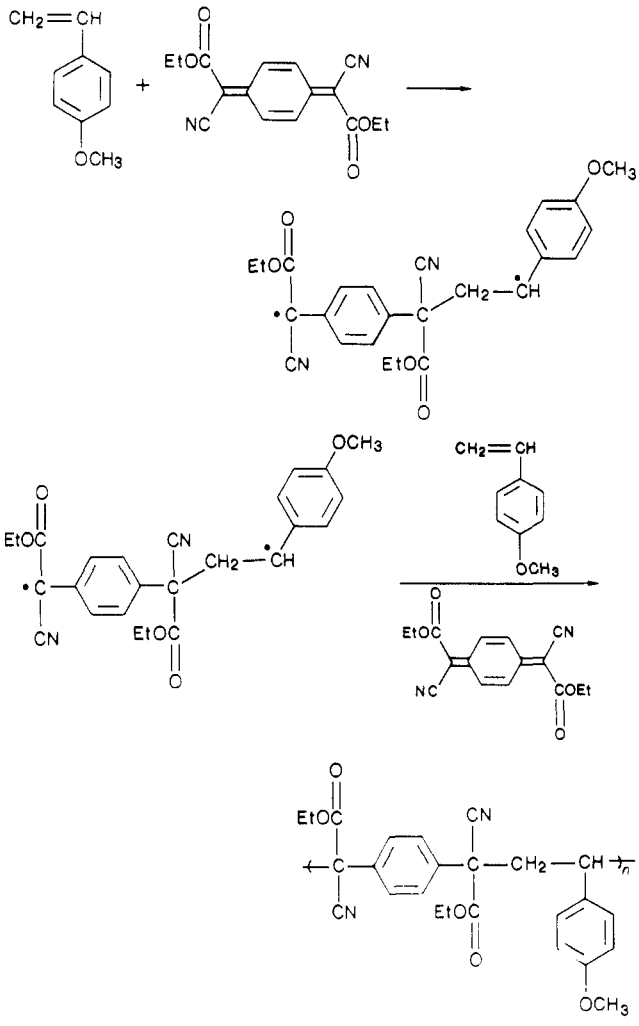
Scheme IV



dimer diradical formation under ambient conditions. Subsequent incorporation of the dimeric DEDCQ diradical in the growing chain results in DEDCQ chain enrichment. If spontaneous DEDCQ homopolymerizations are initiated by a monomeric diradical under ambient conditions, no such chain enrichment will occur.

Finally as we would expect, DEDCQ–*p*-MeOSt copolymerizations proceed faster than those between the olefinic analogue of DEDCQ, diethyl dicyanofumarate, and *p*-MeOSt due to the reactivity of the quinodimethane nucleus.[11]

Molecular Weights. As with the spontaneous homopolymerizations of DEDCQ the spontaneous copolymerizations produced high molecular weight copolymer at low conversion and the molecular weight remained constant thereafter. It is reasonable to expect that at any instant in time the growing chain has at its end a highly stabilized DEDCQ radical (addition of DEDCQ to a styrene radical is very fast). Therefore, propagation by radical combination would again require coupling between two sterically congested centers. For these reasons we conclude that the copolymers also propagate by chain addition.

Acknowledgment. We are indebted to the National Science Foundation, Division of Materials Research, Grant DMR-8400970 for generous support of this work.

Registry No. (DEDCQ)(*p*-MeOSt) (alternating copolymer), 114379-07-6; (DEDCQ)(St) (copolymer), 114379-08-7; (*p*-MeOSt)(dimethyldicyanofumarate) (copolymer), 637-69-4; DEDCQ (homopolymer), 114379-06-5; DEDCQ, 114379-00-9.

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Thermal Polymerization of a 2-(Carboxyalkyl)-2-oxazoline

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ABSTRACT: A 2-(carboxyalkyl)-2-oxazoline was synthesized by the addition of 3-mercaptopropionic acid (MPA) to 2-isopropenyl-2-oxazoline (IPO). Thermal polymerization of 3-[(2-[2-oxazolin-2-yl]propyl)thio]-propionic acid yielded a branched polymer with (1-oxa-2,8-dioxo-5-thia-9-aza-7-methyl-1,9-nonanediyl)ethylene as the repeat unit as identified by ^1H and ^{13}C NMR and IR. Vapor pressure osmometry (VPO) showed number-average molecular weight to be in the range 1050–3370. Hydrolysis of the polymer and analysis of the products by high-performance liquid chromatography (HPLC) and NMR spectroscopy identified the branch site structure as [(1,7-dioxo-8-oxa-4-thia-2-methyl-1-octanyl)imino]ethylene. Various end groups (carboxyl, methacrylamido, acryloyl, and (2-hydroxyethyl)amino) were identified by NMR. The mechanism proposed for the polymerization describes the reactions that result in branching and termination.

Introduction

We recently reported the thermal polymerization of 2-(mercaptoalkyl)-2-oxazolines that proceeds by ring-opening nucleophilic attack of sulfur on the CH_2–O (5-position) of the oxazoline ring.[1] This paper involves an extension of this work to the polymerization of a 2-(carboxyalkyl)-2-oxazoline. We report the synthesis of 3-[(2-[2-oxazolin-2-yl]propyl)thio]propionic acid (III) by the

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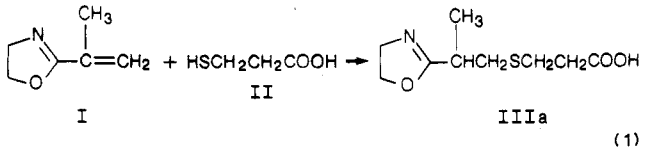
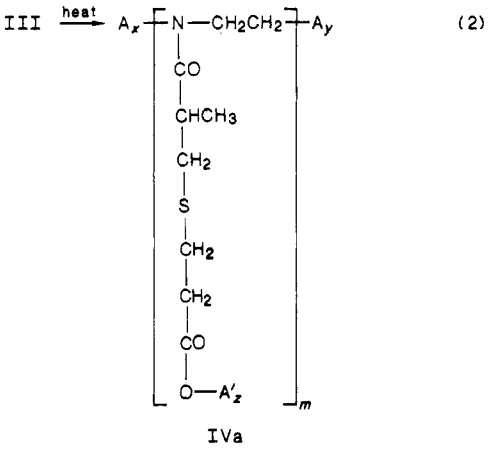
addition of 3-mercaptopropionic acid (MPA) (II) to 2-isopropenyl-2-oxazoline (IPO) (I) (eq 1) and its subsequent



(1)

thermal polymerization to a branched polymer (IV) with (1-oxa-2,8-dioxo-5-thia-9-aza-7-methyl-1,9-nonanediyl)-ethylene as the repeat unit (A and A′) and [(1,7-dioxo-8-oxa-4-thia-2-methyl-1-octanyl)imino]ethylene as the branch site structure (eq 2), where A =



(2)

$-OCOCH_2CH_2SCH_2CH(CH_3)CONHCH_2CH_2-$, and A′ = $-CH_2CH_2NHCOCH(CH_3)CH_2SCH_2CH_2COO-$. A and A′ have the same structure, but their directions in the polymer structure are opposite of each other. Structure IIIa will be referred to as IPOMPA adduct whereas IVa with $m = 0$ and $m \geq 1$ will be referred to as IPOMPA unbranched and branched polymers, respectively.

Experimental Section

Materials. 2-Isopropenyl-2-oxazoline (IPO) (Dow Chemical), 2-mercaptopropionic acid (MPA) (Aldrich), and solvents (DMF, CH_3CN) were dried over 3-Å molecular sieves and then distilled under reduced nitrogen atmosphere. The middle fractions were collected and stored in the refrigerator prior to use. Reagent-grade (Aldrich) 2-aminoethanol and 2-[(2-aminoethyl)amino]ethanol were used as received.

Synthesis of IPOMPA Adduct. Equimolar amounts of IPO and MPA were each separately dissolved in CH_3CN at about 30% concentration inside a drybox under nitrogen. The MPA solution was placed in a round-bottom flask and cooled with ice water and the IPO solution added from an addition funnel with stirring over a period of about 1 h. The reaction mixture was gradually warmed to room temperature, stirring continued for 2 h, and then the mixture cooled overnight in the refrigerator to yield the white crystalline IPOMPA adduct. The adduct was suction filtered, washed twice with cold CH_3CN followed by ether, and then dried in a vacuum desiccator for 2 h. The IPOMPA adduct (85% yield, mp 87 °C) was stored in the refrigerator and used in bulk and solution polymerizations.

Polymerization. For bulk polymerization, the IPOMPA adduct was placed in a polymerization tube, sealed under vacuum (ca. 1 Torr), and then reacted at the desired temperature, 3,5-Di-*tert*-butyl-4-hydroxyanisole (BHA) was added at a concentration of 0.25 mol % as a radical inhibitor in most bulk polymerization experiments. To achieve uniform mixing of the adduct with BHA, the mixture was dissolved in CH_2Cl_2 and solvent evaporated at 30 °C in a rotary evaporator; the resulting solid was used in polymerization experiments.

Acetonitrile and DMF were used as solvents in solution polymerizations and sample preparations were carried out in a drybox under nitrogen. The IPOMPA adduct was dissolved in the solvent at 30% concentration, placed in a polymerization tube, sealed under vacuum (ca. 1 Torr), and then reacted at the desired temperature.

Polymers from solution polymerizations were isolated and purified by cooling the reaction mixture to room temperature and then pouring into a 15-fold excess of diethyl ether at room temperature to precipitate the product. The ether was separated by decantation and the polymer washed with ether, filtered, and then dried overnight in a vacuum oven (ca. 1 Torr) at 50 °C. The reaction mixture from bulk polymerization was dissolved in hot methanol and then purified in the same manner. All polymerization reactions proceeded with near quantitative conversions (>98%) of adduct to polymer.

Hydrolysis of IPOMPA-Branched Polymer. The polymer (1.0 g) and 6 N aqueous HCl (10.0 mL) were placed in a tube, sealed under vacuum, and heated at 100 °C for 24 h. Excess acid and water were evaporated at 60 °C from the reaction mixture by using a rotary evaporator to yield a light yellow viscous liquid. The liquid was extracted with three 5-mL portions of CH_2Cl_2, the combined CH_2Cl_2 extracts were dried over anhydrous $MgSO_4$, and solvent was evaporated to yield a white solid. This solid was identified as 2-methyl-4-thia-1,7-heptanedioic acid by NMR and elemental analysis.

The remaining aqueous solution after CH_2Cl_2 extraction was made alkaline to pH 11 by the addition of 10% NaOH. Benzoyl chloride (1 mL) was added with cooling and vigorous stirring over a period of 15 min. A solid, precipitated when the reaction mixture was brought to pH 8 by adding 3 N HCl, was filtered, washed, dried, and then analyzed and fractionated by high-performance liquid chromatography (HPLC).

High-Performance Liquid Chromatography. Analytical HPLC of the benzoylated hydrolysis products was performed at ambient temperature with a Waters system consisting of a μ-Porasil column, M-6000 solvent delivery unit, U6K universal injector, and 450 variable-wavelength UV monitor with 8-μL flow-through cell. The mobile phase was CH_2Cl_2–CH_3OH (100:1) at a flow rate of 1 mL/min maintained by a pressure of 500–1000 psi. All solvents (HPLC grade, Fisher) were filtered (Millipore) prior to use. The recorder chart paper speed was 0.5 in./min. Sample size was in the range 1–10 mg of material injected in volumes of 1–25 μL of mobile phase. The UV detector was set at 254 nm at 0.1 AUFS (absorbance units for full scale) for detection of the aromatic moiety.

The benzoylated hydrolysis products were fractionated by preparative HPLC with a Waters Prep LC System 500 using a Prep Pack-500 silica column with CH_2Cl_2–CH_3OH (100:1) as the mobile phase. A solution of the products, 0.4 g in 10 mL of mobile phase, was injected into the column and eluted at a flow rate of 50 mL/min. Fractions of 125 mL were collected, and every fraction was analyzed for purity by analytical HPLC. With the elution of the first component the polarity of the mobile phase was increased by increasing the methanol content from 1 to 5 parts. Pure fractions (fractions containing one component as determined by analytical HPLC) of the same component were combined, solvent evaporated with a rotary evaporator under reduced pressure, and dried in a vacuum desiccator overnight.

Benzoylation of 2-Aminoethanol and 2-[(2-Aminoethyl)-amino]ethanol. The di- and tribenzoate derivatives of 2-aminoethanol and 2-[(2-aminoethyl)amino]ethanol, respectively, were prepared by adding benzoyl chloride (0.05 mol) dropwise into a stirred and cooled solution of amine (0.01 mol) in 10% sodium hydroxide (10 mL). The reaction mixture was acidified with 3 N HCl to pH 8 and the resulting white precipitate filtered, washed with water, and recrystallized from ethanol–water.

^1H NMR ($PhCOOCH_2CH_2HNCOPh$): 3.81 (NCH_2, m, 2 H), 4.50 (OCH_2, t, 2 H), 6.9 (NH, br s, 1 H), 7.3–7.6 (aromatic CH, complex m, 6 H), 7.80 (aromatic CH, d, 2 H), and 8.03 ppm (aromatic CH, d, 2 H).

^1H NMR ($PhCOOCH_2CH_2N(COPh)CH_2CH_2NHCOPh$): 3.9 ($NCH_2$, br d, 6 H), 4.45 ($OCH_2$, br s, 2 H), and 7.2–8.1 ppm (NH and aromatic CH, complex m, 16 H).

Spectroscopic Analysis. IR spectra of the polymers were recorded on a Beckman 4260 infrared spectrometer using thin-film samples on NaCl plates. Polymer was deposited as a thin film on a NaCl plate from methanol and the solvent evaporated in a vacuum oven at 45 °C overnight. ^1H (200.1 MHz) and ^{13}C (50.3

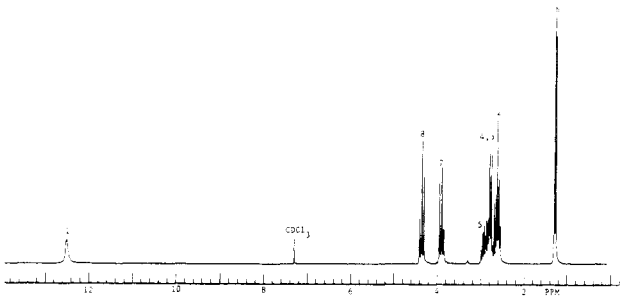


Figure 1. 200.1-MHz ^1H NMR spectrum of IPOMPA adduct in $CDCl_3$ at 25 °C.

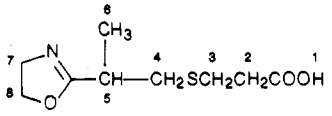
MHz) NMR spectra were recorded on an IBM WP 200SY FTNMR spectrometer using a 5-mm $^{13}C/^1H$ dual probe. ^1H and ^{13}C NMR of the IPOMPA adduct and hydrolysis products were obtained at 25 °C by using 2–10% (w/v) solutions in $CDCl_3$. ^1H NMR of the polymers were obtained at 25 and 100 °C with 6% (w/v) solutions in Me_2SO-d_6 (99.96% deuteriated). ^{13}C NMR spectra of the polymers were obtained at 25 °C by using 5–15% (w/v) solutions in Me_2SO-d_6. Me_4Si was used as an internal standard for both ^1H and ^{13}C NMR. The acquisition parameters for ^1H NMR were 30° pulse angle, 8-s total delay between pulses, and 128–256 total acquisitions. The acquisition parameters for ^{13}C NMR were 30° pulse angle, 2.5-s total delay between pulses, and 10 000–25 000 total acquisitions. Data were acquired and Fourier transformed in 16K.

Vapor Pressure Osmometry (VPO). The number-average molecule weights of polymer samples were determined in DMF (HPLC grade) solution at 105 °C using a Knauer (UIC) vapor pressure osmometer. The VPO instrument was calibrated with benzil (MW 210.13). Four concentrations in the 2–8% (w/w) range were used for analysis.

Results and Discussion

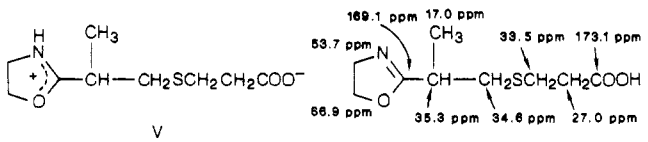
Synthesis of IPOMPA Adduct. The reaction of 2-isopropenyl-2-oxazoline (IPO) and 3-mercaptopropionic acid (MPA) in CH_3CN at room temperature is fast and yields the IPOMPA adduct in quantitative yield. The reaction was monitored with ^1H NMR by following the decay of the methyl (singlet, 1.98 ppm) and olefinic (singlets, 5.37 and 5.75 ppm) signals of IPO. Reaction between IPO and MPA was complete in 2 h as indicated by complete disappearance of ^1H NMR signals due to IPO. The adduct, a crystalline white solid, is soluble in H_2O, CH_3OH, CH_2Cl_2, CH_3CN, DMF, and Me_2SO.

The ^1H NMR spectrum (Figure 1) of IPOMPA adduct is consistent with structure III with signal assignments shown in IIIb. The ^1H NMR spectrum showed no indi-



IIIb

cation of proton transfer from COOH to N to form the zwitterion V. ^{13}C NMR supported structure III for IPOMPA adduct, and the signals are assigned as shown in IIIc.



V

IIIc

Elemental analysis (Found: C, 49.40; H, 7.10; N, 6.39; S, 15.17) was in good agreement with that calculated for structure III (Theory: C, 49.74; H, 6.97; N, 6.45; S, 14.75).

Table I
Molecular Weight and Degree of Branching in Polymerization

polymerization temp, °C	$\bar{M}_n$ by VPO	% branching by ^1H NMR
Solution Polymerization (CH_3CN)[b]		
70	2850	18
90	2000	25
70[c]	2230	
Bulk Polymerization[c]		
70	3370	23
100	3200	18
130	1870	23
160	1160	34
200	1050	
Solution Polymerization (DMF)[b]		
70	2010	13
100	2230	4
130	1950	4
160	2070	3

[a] Reaction time was 65 h for all polymerizations. [b] 30% adduct concentration. [c] 0.25 mol % BHA present.

Solution Polymerization. Solution polymerization of IPOMPA adduct in acetonitrile was carried out at 70 and 90 °C. The polymer, which precipitated from solution during reaction, is a solid material soluble in DMF, Me_2SO, and hot CH_3OH. The molecular weights of isolated polymers were determined by vapor pressure osmometry (VPO), and the results are shown in Table I. The molecular weight of polymer synthesized at 70 °C was slightly higher than that obtained at 90 °C. Polymer molecular weight was lowered somewhat by the addition of the radical inhibitor 3,5-di-*tert*-butyl-4-hydroxyanisole (BHA).

Solution polymerization of IPOMPA adduct was carried out in DMF at the 70–160 °C temperature range. The polymers ranged from colorless solids obtained at polymerization temperatures below 100 °C to light yellow solids at 130 °C and higher. The polymer molecular weight showed no significant change in the temperature range studied (Table I).

Bulk Polymerization. Bulk polymerization of IPOMPA adduct was studied in the 70–200 °C temperature range. The polymers obtained were only partially soluble in solvents such as DMF, CH_3OH, and Me_2SO which were good solvents for the solution-polymerized products. The insoluble portion, presumably cross-linked, swelled in these solvents. Addition of 0.25 mol % BHA to IPOMPA adduct yield completely soluble polymers. The products ranged from colorless solids obtained at polymerization temperatures below 130 °C to yellow solids at temperatures of 160 °C and higher. Solution polymerization always yielded soluble polymers, and the presence of BHA did not have a significant effect on polymer molecular weight. Table I shows the effect of temperature on molecular weight in bulk polymerization of IPOMPA adduct. Molecular weight decreased with increasing temperature with the most significant decrease observed for temperatures of 130 °C and higher. The amount of BHA did not affect polymer molecule weight in the range 0.25–10.0 mol%.

Characterization of IPOMPA Polymer. The IPOMPA polymer was characterized by elemental analysis, IR, and NMR. Elemental analysis (Found: C, 49.39; H, 6.92; N, 6.32; S, 14.68) of polymer prepared in bulk was in good agreement with that calculated for structure IV (Theory: C, 49.74; H, 6.97; N, 6.45; S, 14.75). (Note: the elemental composition of the branch site structure is the same as that of the repeat unit). Figure 2 shows the ^1H NMR spectrum recorded at 100 °C of the polymer prepared in bulk at 130

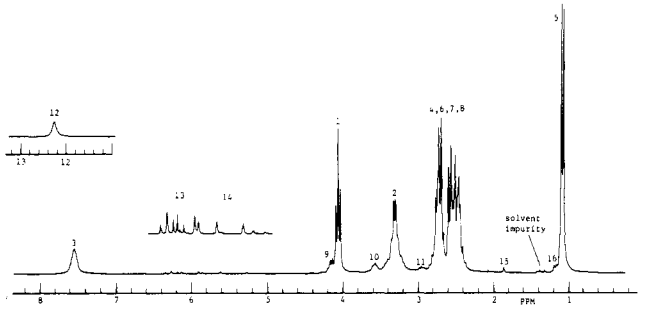


Figure 2. 200.1-MHz ^1H NMR spectrum of IPOMPA polymer (bulk, 130 °C) in Me_2SO-d_6 at 100 °C (10–12 ppm region recorded at 25 °C).

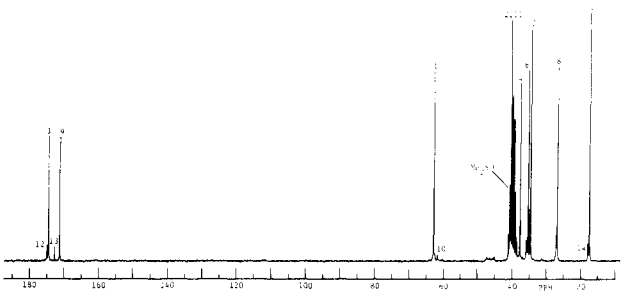
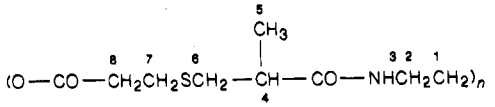


Figure 3. 50.3-MHz ^{13}C NMR spectrum of IPOMPA polymer (bulk, 100 °C) in Me_2SO-d_6 at 100 °C.

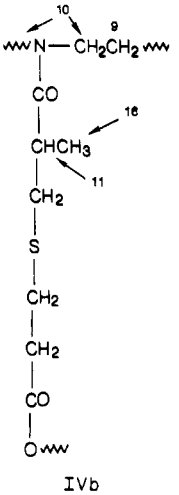
°C. The main signals were assigned to the repeat unit (A and A′ in structure IV) as shown in VI based on chemical



VI

shift values,[2] splitting patterns, signal areas, and deuterium exchange experiments.

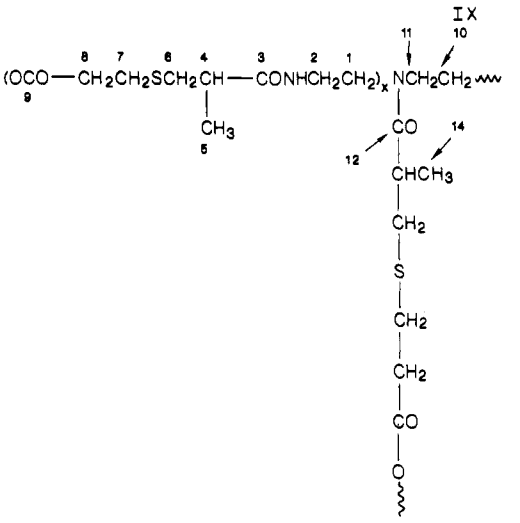
Apart from major signals due to the protons of the repeat unit VI, several other signals were observed at 2.95, 3.58, and 4.15 ppm as shoulders to main signals suggesting significant variations from the linear structure. Branching can occur if the nitrogen of IPOMPA adduct competes with the carboxyl group for nucleophilic attack on the oxazoline ring of another adduct molecule (see the Polymerization Mechanism section for details). The structure of the polymer at the branch point is shown in IVb where



IVb

~~ represents the polymer repeat unit. The signals at 4.17, 3.58, 2.95, and 1.10 ppm (signals 9, 10, 11, and 16, respectively) were assigned to OCH_2, CH_2NCH_2, COCH, and CH_3 protons, respectively, of the branch site. The OCH_2 signal (signal 1 in Figure 2) area is sensitive to the number of branches in the polymer chain. For each branch site in a branched polymer molecule, there is a decrease of one OCH_2 group compared to the corresponding linear, unbranched polymer chain. Therefore, the ratio of signal areas for OCH_2 and CH_3 protons was used to calculate the degree of branching for the various polymer samples (Table I). The percent branching is defined as the number of branch units multiplied by 100% and divided by the total number of repeat units. Both bulk polymerization and solution polymerization in acetonitrile produced highly branched IPOMPA polymer; the polymer contained one branch per five repeat units on the average. The percent branching is much lower for the polymer obtained by solution polymerization in DMF.

Figure 3 shows the ^{13}C NMR spectrum of IPOMPA polymer (bulk polymerization at 100 °C) with various signals assigned as shown in IVc. ^{13}C NMR strongly



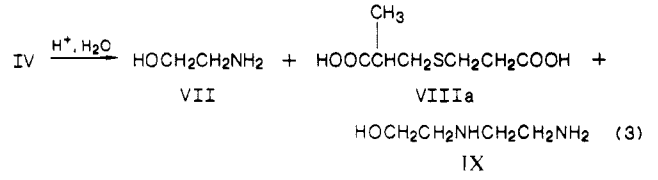
IVc

supported the branched structure for IPOMPA polymer. Four signals were observed in the carbonyl region. Signals 3 and 9 were assigned to the amide and ester carbonyl regions, respectively, of the repeat unit, and signal 12 was assigned to the branch site amide carbonyl carbon. (The fourth carbonyl signal—signal 13—is assigned to COOH end groups—see Polymer End Groups section below.) The degree of branching was determined (by an inverse gated decoupling experiment) to be 20% which is in good agreement with the 18% value calculated from ^1H NMR for this polymer sample.

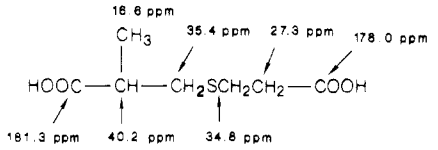
The infrared spectrum of IPOMPA polymer showed major absorption bands at 3300, 3080 (N–H), 2970, 2935 (C–H), 1737 (ester CO), 1650 (amide CO), 1565 (amide II), 1243 (C–N), and 1185 (S–CH_2) cm^{-1} in agreement with structure IV.

Hydrolysis of IPOMPA-Branched Polymer. Further support for the structure of IPOMPA polymer was obtained by hydrolysis of the polymer followed by isolation and characterization of the hydrolysis products according to the procedures summarized in Figure 4. Hydrolysis of structure IV would yield 2-aminoethanol (VII) and 2-methyl-4-thia-1,7-heptanedioic acid (VIII) from the repeat unit and 2-[(2-aminoethyl)amino]ethanol (IX) from branch sites with no homosequences of branch sites (i.e., $m = 1$ in eq 2).

The product isolated from the CH_2Cl_2 extract of the hydrolysate was identified as 2-methyl-4-thia-1,7-hep-



tanedioic acid by ^1H and ^{13}C NMR and elemental analysis. The elemental analysis (Found: C, 43.59; H, 6.30; S, 17.08) was in excellent agreement with that calculated for VIII (Theory: C, 43.73; H, 6.30; S, 16.78). The ^1H NMR showed a doublet at 1.29 ppm (CH_3), broad singlet at 11.60 ppm (COOH), and complex multiplet at 2.74 ppm (CH, SCH_2, CH_2CO) as expected for VIII. ^{13}C NMR also supported structure VIII with the various signals assigned as shown in VIIIb.



VIIIb

Figure 5 shows the analytical HPLC of the benzoylated products of the residual aqueous solution. There are two major fractions—eluting at approximately 5.5 and 12.7 min. Preparative HPLC was carried out to isolate these two fractions. Comparison of the ^1H NMR spectra with those of authentic samples showed the two fractions eluting at 5.5 and 12.7 min to be the benzoyl derivatives of 2-aminoethanol and 2-[(2-aminoethyl)amino]ethanol, respectively. These results verify the branch structure IV for the IPOMPA polymer and indicate the absence of block or homosequences of branch sites. If the polymer contained blocks of branch sites, the hydrolysis should have yielded products of the type $HO-(CH_2CH_2NH)_mCH_2CH_2NH_2$ with $m > 1$. The benzoate derivatives of such products would have retention times longer than that of the benzoate derivative of IX. HPLC showed no compounds with longer retention times than 12.7 min. Furthermore, the degree of branching calculated from HPLC peak areas was 15%—a value close to that obtained from NMR. This number would be much lower if there was a significant amount of block branch sites. (The small peaks at 4.5–5 and 8 min in the HPLC are attributed to incompletely benzoylated derivatives of VII–IX; the peak at 4.1 min is due to an impurity present in the benzoyl chloride.)

The polymers obtained by solution polymerization in acetonitrile showed about the same amount of branching as those obtained by bulk polymerization. This is attributed to the similarity of the two polymerizations. The polymerization in acetonitrile resembled a bulk polymerization since polymer precipitates from solution early in the reaction. Polymerization in DMF was a homogeneous reaction at all conversions. Negligible (3–4%) degrees of branching were observed for polymerization in DMF except for the polymerization at 70 °C which showed 13% branching. Figures 6 and 7 show the ^1H and ^{13}C NMR of the IPOMPA polymer prepared in DMF at 140 °C. The spectra are consistent with unbranched structure VI. For example, signals 10–12 and 14 indicative of the branch sites (Figure 3) are missing from the ^{13}C NMR spectrum (Figure 7) of the polymer obtained by solution polymerization in DMF at 130 °C.

Polymer End Groups. Examination of the ^1H NMR of the IPOMPA polymer prepared in bulk at 130 °C (Figure 2) identified the polymer end groups as carboxyl

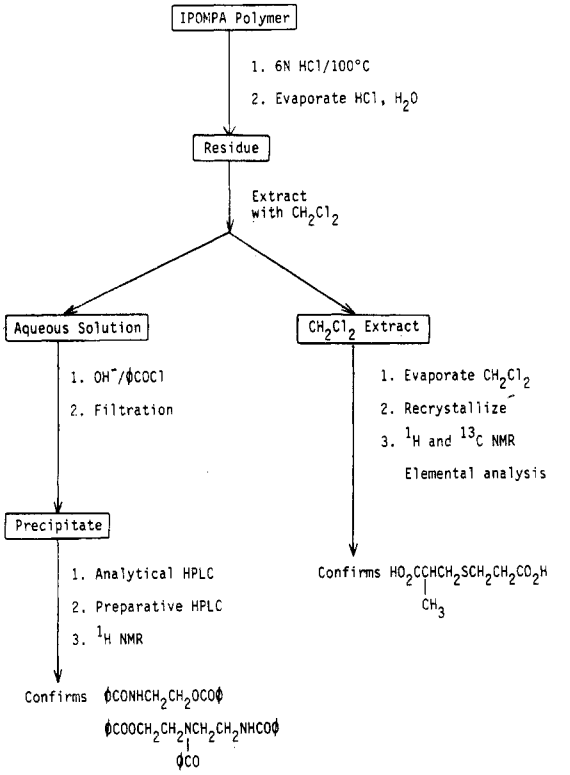


Figure 4. Acidic hydrolysis of IPOMPA polymer followed by separation and identification of products.

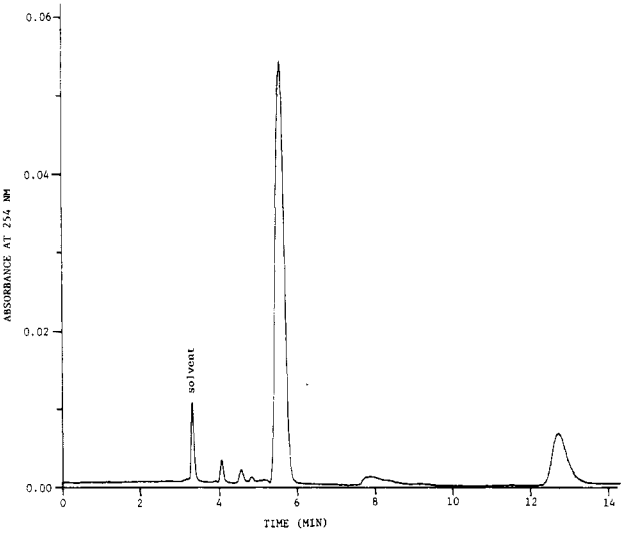
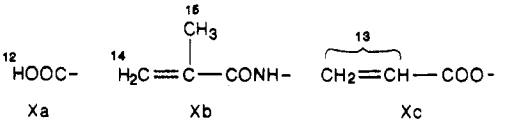


Figure 5. HPLC of benzoylated product mixture: stationary phase, μ-Porasil column; mobile phase, CH_3OH–methylene chloride (1:100).

methacrylamido, and acryloyl with the signal assignments shown in Xa–c. The ^1H NMR spectrum showed a broad



singlet at 12.3 ppm due to carboxyl protons. (The ^1H NMR spectrum in the COOH region of Figure 2 was recorded at room temperature. The COOH proton signal could not be detected at 100 °C due to exchange between COOH and NH protons.) The parts per million values for signals in the olefinic region (signals 13 and 14) were in line with those expected[2] for acryloyl and methacrylamido protons. The singlet at 1.85 ppm was assigned to the

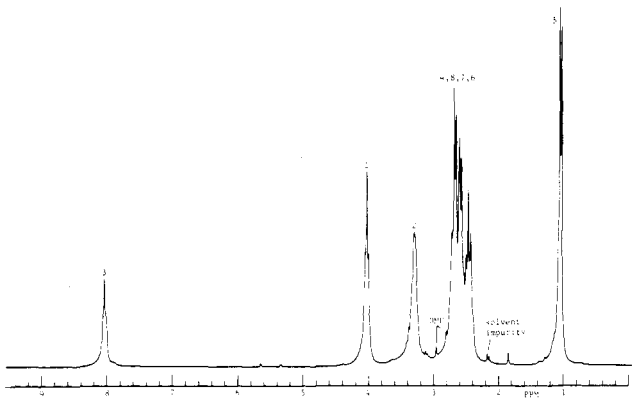


Figure 6. 200.1-MHz ^1H NMR spectrum of IPOMPA polymer (synthesized in DMF at 130 °C) recorded in Me_2SO-d_6 at 25 °C.

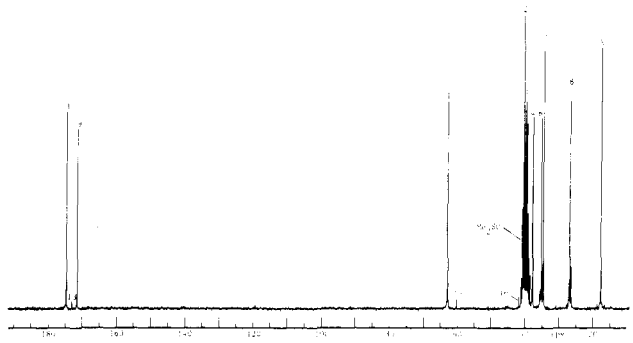


Figure 7. 50.3-MHz ^{13}C NMR spectrum of IPOMPA polymer (synthesized in DMF at 130 °C) recorded in Me_2SO-d_6 at 25 °C.

methyl protons of the methacrylamido group. The bulk polymers synthesized at 100 and 130 °C contained all three end groups with carboxyl end groups predominating over acryloyl and methacrylamido end groups as detected by ^1H NMR. There were approximately equal amounts of acryloyl and methacrylamido end groups. The carboxyl content outnumbered the total of acryloyl and methacrylamido by a factor of 3–4. However, the integration of the COOH proton signal may not be too reliable due to exchange of COOH protons with those from NH (and also residual water present in Me_2SO-d_6 used as the solvent for NMR). [The ^{13}C NMR spectrum (Figure 3) of the 130 °C bulk polymer showed a signal for COOH carbon (signal 13), but the olefinic carbons were not present in sufficient concentration to be detected.] Polymer prepared at 70 °C showed only carboxyl and acryloyl end groups. Methacrylamido end groups increased in concentration with increasing polymerization and became the major end groups for bulk polymers prepared at 160 and 200 °C.

The polymer prepared in DMF solution showed methacrylamido, carboxyl, and (2-hydroxyethyl)amino (Xd) end groups. The latter is not present in polymer prepared in

$HOCH_2CH_2NH-$

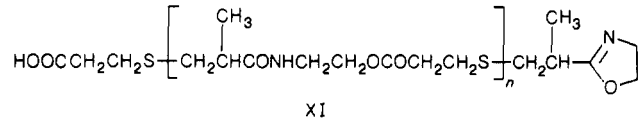
Xd

bulk. The (2-hydroxyethyl)amino end group was detected by OCH_2 and NCH_2 signals (signals 15 and 16) at 59.9 and 41.4 ppm, respectively, in the ^{13}C NMR spectrum (Figure 7). Polymers prepared at 70 and 100 °C showed weak carboxyl and methacrylamido end groups. The methacrylamido end group increased in concentration with increasing temperature and became the major end group for polymers prepared at 130 and 160 °C.

Search for Zwitterion V. The possibility of forming zwitterion V from IPOMPA adduct during polymerization was examined by recording the ^1H NMR spectrum of a 30% solution of the adduct in CD_3CN at 35 and 60 °C. The ^1H NMR of the IPOMPA adduct–F_3CCOOH salt (prepared by mixing IPOMPA adduct with trifluoroacetic acetic acid in CD_3CN) was used as a model for detecting the presence of V. The IPOMPA adduct–F_3CCOOH salt showed a broad NH signal at 7.80 ppm, and many of the other signals were significantly deshielded relative to IPOMPA adduct; e.g., the CH_2O signal was deshielded by almost 0.6 ppm. The ^1H NMR spectra of IPOMPA adduct after heating for 1 and 15 h at 35 °C showed no signals for zwitterion or IPOMPA polymer. A similar experiment performed at 60 °C showed the appearance of signals due to polymer formation but no signals for zwitterion. These results indicate that zwitterions are not present (at least to the extent detectable by ^1H NMR).

Polymerization Mechanism

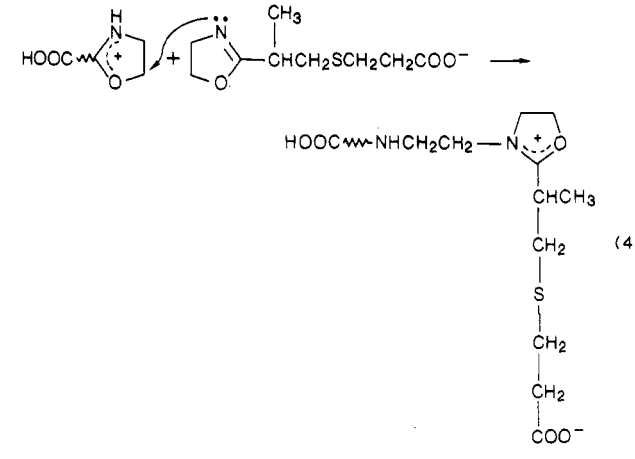
Polymerization of IPOMPA adduct is considered to proceed by the stepwise reaction of an AB type of bifunctional monomer. The polymer growth reaction involves nucleophilic ring-opening attack by the carboxylate oxygen to cleave the CH_2–O bond of the oxazoline ring. Growth proceeds to form different sized molecules of type XI. Zwitterions of type V and counterparts derived from



XI

XI (formed by intra- and/or intermolecular proton transfer from COOH to nitrogen of the oxazoline ring) may be primarily responsible for the growth process. ^1H NMR did not detect the presence of zwitterions but that does not preclude their presence at low concentrations. Zwitterion intermediates are postulated as the reactive intermediate since protonated oxazoline ring and carboxylate anion are much more reactive as electrophile and nucleophile, respectively, compared to unprotonated oxazoline ring and thiol.

Branching occurs in the polymerization of IPOMPA when the nitrogen of an unprotonated oxazoline ring competes with carboxylate anion as the nucleophile for attack on a protonated oxazoline ring. This reaction can occur between two molecules of adduct of XI or one of each. For example, consider the reaction between XI and IPOMPA adduct (eq 4) to yield XII. XII is trifunctional

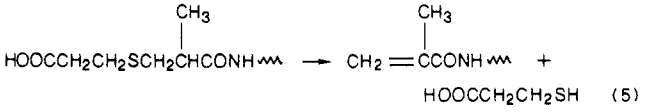


XII (4)

with two carboxyl-propagating centers and one oxazoline-propagating center. Normal propagation by reaction between oxazoline ring and carboxyl group yields IPOMPA branched polymer (IV). The results of our hydrolysis experiments showed that the reaction described by eq 4 was not repeated in a consecutive manner with a second

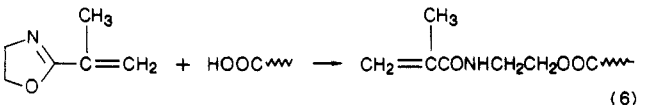
XI or IPOMPA adduct; i.e., homosequences of branch sites did not occur. The successful competition of the oxazoline nitrogen (against the carboxyl group) in the nucleophilic ring-opening reaction has also been reported in zwitterion polymerizations of 2-methyl-2-oxazoline with succinic and phthalic anhydrides and 2-ethyl-2-oxazoline with phthalic anhydride.[3] The degree of branching is lower for polymerization in DMF solution, especially at temperatures of 100 °C and higher, compared to polymerization in bulk or in CH_3CN. Polymerization in DMF takes place as a homogeneous reaction whereas the other two systems are heterogeneous. Heterogeneity favors the branching reaction, but the mechanism for this effect is not known.

The polymer molecular weight is somewhat higher for bulk polymerization (at the lowest reaction temperatures) compared to solution polymerization due to the lower concentration of IPOMPA adduct in solution relative to bulk. However, the highest molecular weight even for bulk polymerization is only 3370. Termination reactions compete very effectively with polymerization to sharply limit polymer molecular weight. Elimination at the carboxyl end of a polymer results in the formation of 3-mercaptopropionic acid and methacrylamideo end groups (eq 5).



(5)

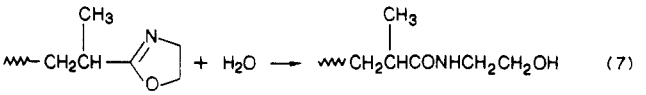
Acrylamido end groups can also be formed by decomposition of IPOMPA adduct to 3-mercaptopropionic (MPA) acid and 2-isopropenyl-2-oxazoline (IPO) followed by reaction of IPO with carboxyl end groups (eq 6). Elimi-



(6)

nation of H_2S from MPA yields acrylic acid which reacts with 2-oxazoline end groups to form polymer chains containing acryloyl end groups. The basicity of the 2-oxazoline nitrogen (in IPOMPA adduct and polymer end group) may be involved in promoting the various elimination reactions. There are other possible reactions for producing methacrylamido and acrylamido end groups. An alternate route for decomposition of IPOMPA adduct is the formation of acrylic acid and 2-(2-mercaptoisopropyl)-2-oxazoline. The reaction of acrylic acid with 2-oxazoline polymer end groups would produce acrylamido end groups. Polymer chain degradation at C–S bonds would produce acrylamido or methacrylamido end groups depending on whether scission occurred at C-4 or C-6 of the polymer repeat unit.

(2-Hydroxyethyl)amino end groups (observed in the polymer synthesized by polymerization in DMF) are formed by the reaction of the small amounts of water present in DMF with 2-oxazoline end groups (eq 7). The



(7)

role of water in this termination was verified by carrying out a polymerization in DMF with 20 mol % added water. The resulting polymer had greatly increased areas for the ^{13}C NMR signals at 41.4 and 59.9 ppm (CH_2N and CH_2O, respectively). The acidity of the carboxyl proton (in IPOMPA adduct and polymer end group) may be involved in promoting this substitution reaction by protonation of the 2-oxazoline ring.

It is interesting to compare the polymerization of IPOMPA adduct with the previously reported[1] polymerizations of 2-(mercaptoalkyl)-2-oxazolines. The latter system proceeds without branching and yields polymers of much greater molecular weight compared to the 2-(carboxyalkyl)-2-oxazoline system. The difference between the two systems is a consequence of the difference in nucleophilicity between the carbonyl and mercapto functions. The pK_a values[4] of RCOOH and RSH are about 4–5 and 12, respectively, which indicates that RS^- is a much stronger nucleophile relative to $RCOO^-$. The greater nucleophilicity of RS^- allows propagation to compete more effectively against elimination reactions (which are very similar in the two systems) in the 2-(mercaptoalkyl)-2-oxazoline system compared to the 2-(carboxyalkyl)-2-oxazoline system. Additionally, branching does not compete with propagation in the 2-(mercaptoalkyl)-2-oxazoline system since the 2-oxazoline ring is a poor nucleophile compared to RS^-.

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Registry No. I, 10471-78-0; II, 107-96-0; IIIa, 114132-85-3; IIIa (homopolymer), 114132-90-0.

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