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Zwitterion Polymerization of 2-Methyl-2-oxazoline and Methacrylic Acid

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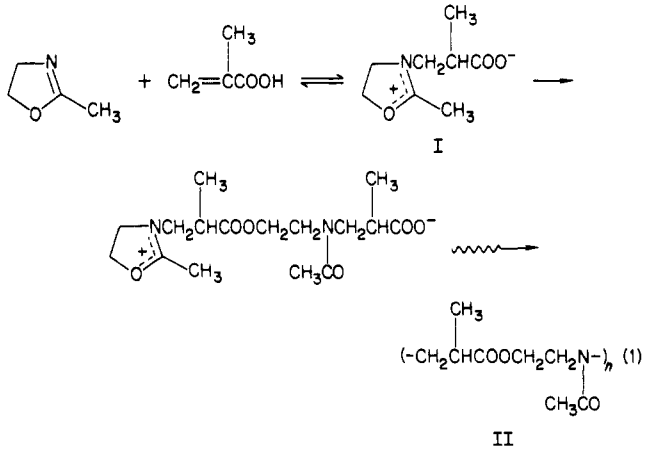
ABSTRACT: The reaction of 2-methyl-2-oxazoline (MeOXO) and methacrylic acid (MAA) has been studied in bulk and solution (acetonitrile) at 60–70 °C. The products were separated by high-performance liquid chromatography and analyzed by ^1H and ^{13}C NMR spectroscopy. Contrary to previous reports by Balakrishnan and Periyasamy (*Makromol. Chem., Rapid Commun.* **1980**, *1*, 307) the reaction of MeOXO and MAA does not yield high molecular weight alternating copolymer but only very low molecular weight products. All of the products contain olefinic and acetamido end groups with varying amounts of MeOXO and MAA units in between the end groups. A mechanism is proposed to account for the observed products and to explain the reported results of Balakrishnan and Periyasamy.

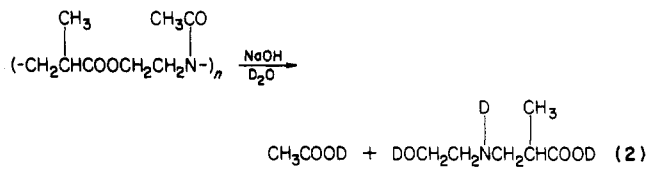
Introduction

2-Methyl-2-oxazoline, a nucleophilic type monomer, has been reported to undergo zwitterion polymerization with a number of electrophilic type monomers such as acrylic acid,[1-3] methacrylic acid,[4] acrylamide,[5] 2-hydroxyethyl acrylate,[6] succinic anhydride,[7] ethylenesulfonamide,[8] and 3-hydroxy-1-propanesulfonic acid sultone[9] to yield low molecular weight alternating copolymers. Balakrishnan and Periyasamy[4] studied the 2-methyl-2-oxazoline–methacrylic acid (MeOXO–MAA) system and proposed a reaction mechanism involving the initial formation of genetic zwitterion I followed by propagation through the reaction of I with itself and with larger-sized zwitterions to yield the alternating copolymer II.



Balakrishnan and Periyasamy isolated a pale brown gum by pouring the MeOXO–MAA reaction mixture into diethyl ether followed by drying at 70 °C. ^1H NMR spectra of the gum and its alkaline hydrolysate were presented in support of copolymer structure II. However, our interpretation of the published spectral data does not support structure II. The ^1H NMR spectrum of the gum was reported as consisting of singlets at 1.95 (α-CH_3) and 2.05 (CH_3CO) ppm and multiplets at 3.6 (CH_2NCH_2 and CH) and 4.3–4.4 (OCH_2) ppm. The singlet at 1.95 ppm, assigned to the α-CH_3 protons of the methacrylate unit, is too far downfield for that type of proton.[10] For example, the α-CH_3 protons of methyl isobutyrate are found at 1.2 ppm.[11] Furthermore, the α-methyl signal for II should be a doublet as it is for methyl isobutyrate. The ^1H NMR spectrum reported by Balakrishnan and Periyasamy shows only the 1.9–5 ppm region. The ratio of various signal areas in the reported spectrum also fails to support structure II. The 1.95, 2.05, 3.6, and 4.3–4.4 ppm signals show areas in the approximate ratio 1.1:2.5:2.6:1 instead of 3:3:5:2 as required for structure II and the spectral assignments by Balakrishnan and Periyasamy.

The published ^1H NMR spectrum of the hydrolyzed gum also does not support structure II. The gum was hydrolyzed by NaOH in D_2O and should yield equimolar amounts of deuterated acetic and *N*-(2-hydroxyethyl)-3-amino-2-methylpropionic acids based on structure II.



The ^1H NMR of the hydrolysate was reported as consisting of singlets at 1.9 (α-CH_3) and 2.0 (CH_3COOD) ppm, triplets

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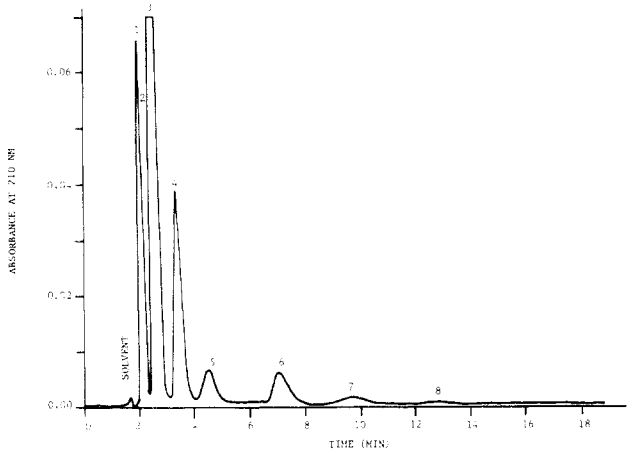


Figure 1. HPLC of polymerized reaction mixture (experiment 4) on a μ-Bondapak C_{18} column. Mobile phase: methanol/water/TFA (200:800:0.25).

at 2.7 (CH) and 4.4 (OCH_2) ppm, and a multiplet at 3.5 ppm (CH_2NCH_2). The 1.9 ppm signal is too far downfield; the α-CH_3 protons of isobutyric acid absorb at 1.2 ppm.[11] Furthermore, the α-methyl proton signal should be a doublet not a singlet. The signal areas in the ^1H NMR spectrum of the hydrolysate do not correspond to those expected for structure II. For example, the signal areas for the CH_2NCH_2, CH, and α-CH_3 protons are in the approximate ratio 1.3:1.7:1 instead of 4:1:3.

In view of the discrepancies described we have reinvestigated the zwitterion polymerization of the MeOXO–MAA system and the results are reported in this paper.

Experimental Section

Materials. Acetonitrile, MeOXO, and MAA (Aldrich) were dried and purified in the manner as previously reported.[3] Methanol (HPLC, Fisher), *p*-methoxyphenol (Aldrich), and anhydrous diethyl ether (Fisher) were used as received.

Polymerization. MeOXO (60 mmol), MAA (60 mmol), along with acetonitrile (10 mL) and *p*-methoxyphenol (to prevent radical polymerization of MAA) when necessary, were mixed inside a drybox, placed in a sample tube, cooled with liquid nitrogen, sealed under vacuum, and then heated at 70 °C for 48 h. The reaction mixture was precipitated into 300 mL of anhydrous diethyl ether at ambient temperature. The ether solution was decanted to give a white solid product. The ether solution was evaporated under vacuum at ambient temperature to give a light yellow gummy product. Both products were dried in a vacuum oven at 35 °C overnight.

High-Performance Liquid Chromatography (HPLC). Analytical and preparative HPLC were used for various analyses and separations. Analytical HPLC was carried out at room temperature by using a Waters system consisting of a Model M-6000 solvent delivery unit, a U6K universal liquid chromatography injector, a Model 450 variable-wavelength UV monitor with 8-μL flow-through cell, and fitted with a μ-Bondapak C_{18} column. The mobile phase was $CH_3OH/H_2O/CF_3CO_2H$ (100:900:0.25) at a flow rate of 2 mL/min maintained by a pressure of 2000–2500 psi. Distilled water, methanol (Fisher HPLC grade), and trifluoroacetic acid (Fisher) (TFA) were filtered prior to use. The recorder chart speed was $^1/_2$ in./min. Sample size was in the range 1–10 μg of polymer injected in volumes of 1–25 μL. The UV detector was set at 210 nm at 0.1 AUFS (absorbance units for full scale).

The polymerized reaction mixture in experiment 4 was fractionated by preparative HPLC with a Waters Prep LC System 500 using a μ-Bondapak C_{18} column with methanol/water/TFA (60:940:0.25) as the mobile phase. A solution of the polymerized reaction mixture, 3 g in 10 mL of mobile phase system, was injected into the column and eluted at a flow rate of 100 mL/min; 50-mL fractions of the eluent were collected and examined by analytical HPLC for purity. After fraction 4 (see Figure 1) eluted from the column, the mobile phase was changed to methanol/water/TFA (100:900:0.25). Pure fractions (i.e., fractions containing one component as determined by HPLC) of the same component were combined. To each 500 mL of the eluent, 5 mg of *p*-methoxyphenol was added (to prevent radical polymerization), and the solution was concentrated by using a Rotovapor evaporator under reduced pressure (temperature of the distilling pot was maintained at 30–35 °C) to a volume of 10 mL, freeze-dried, and dried in a vacuum desiccator overnight.

Table I
Copolymerization of MeOXO–MAA

expt	conditions	temp, °C	time, h	product yield,[a] % ether-insoluble	product yield,[a] % ether-soluble gum
1	solution (CH_3CN)[b]	70	48	10.8	85.2
2	bulk[c]	70	48	14	65
3	solution (CH_3CN)[d]	60	23		85.1
4	solution (CH_3CN)[c]	70	48	3.5	90.9

[a] Based on total initial amount of MeOXO and MAA. [b] No *p*-methoxyphenol. [c] 0.32 mmol of *p*-methoxyphenol. [d] 2.7 mmol of *p*-methoxyphenol.

NMR Spectroscopic Analysis. ^1H NMR spectra (80 MHz) were recorded at 25 °C on an IBM NR 80 FTNMR spectrometer using 3–5% (w/v) solutions in Me_2SO-d_6 with Me_4Si as an internal standard and the acquisition parameters: 30° pulse angle, 7.9-s delay between pulses, and 100–200 acquisitions. Natural abundance ^{13}C NMR spectra were recorded at 32 °C on the NR 80 spectrometer operating at 20.1 MHz using 12–20% (w/v) solutions in D_2O with CH_3CN as an internal standard (CH_3CN methyl protons at 1.70 ppm relative to Me_4Si) and the acquisition parameters: 30° pulse angle, 1.6-s delay between pulses, and 21 226–42 890 acquisitions.

Results and Discussion

Copolymerization of MeOXO and MAA in bulk and acetonitrile gave similar results (Table I). A very low yield of an ether-insoluble white solid product was isolated by pouring the reaction mixture into a $2^1/_2$-fold excess of diethyl ether. Most of the reaction mixture dissolved in the ether during this workup. Evaporation of the ether gave a high yield of a light yellow gummy product. Both the ether-insoluble and ether-soluble products were soluble in polar solvents such as DMF, Me_2SO, methanol, and water. The yields obtained in our studies differ considerably from those reported by Balakrishnan and Periyasamy.[4] Balakrishnan and Periyasamy reported a 47.3–49.4% yield of ether-insoluble pale brown gummy material under the same reaction conditions as in experiment 3 with no workup of the ether solution. The discrepancy in yields between our results and those of Balakrishnan and Periyasamy is most likely due to a difference in the amount of ether used for precipitation (although the amount used by Balakrishnan and Periyasamy is not reported). The experiments reported in Table I differ primarily in the amount of *p*-methoxyphenol. (The temperature difference between experiment 3 and experiments 1, 2, 4 is not significant.) Experiment 3 was performed with a relatively high concentration (2.7 mmol) of *p*-methoxyphenol (conditions similar to those of Balakrishnan and Periyasamy). Experiments 2 and 4 were performed with 0.32 mmol *p*-methoxyphenol while no *p*-methoxyphenol was present in experiment 1. The amount of ether-insoluble product decreased within a narrow range with increasing amount of *p*-methoxyphenol. These results are discussed further at the end of this paper. The low yield of ether-insoluble product compared to the MeOXO–acrylic acid system[3] indicates that the MeOXO–MAA system yields mostly low molecular weight products.

Small amounts of the polymerized reaction mixture from each experiment were subjected to analytical HPLC.

Table II
Composition of Polymerized MeOXO-MAA Reaction Mixture

	mol % of fraction							
expt	1	2	3	4	5	6	7	8
1	16.0		57.2	15.3	4.3	3.6	3.0	0.6
2	11.5	0.8	62.9	15.3	5.4	4.1		
3	31.5	2.4	43.4	12.5	4.2	2.3	3.2	0.5
4	14.7	1.0	56.2	16.0	4.5	4.1	2.7	0.8
ether-insoluble product	3.2	2.2	23.0	30.6	14.9	10.5	9.0	6.6

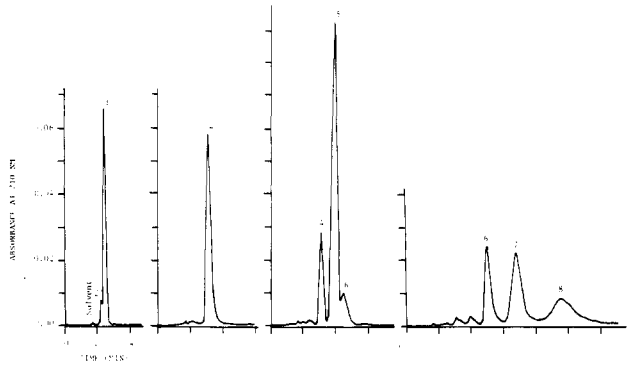


Figure 2. HPLC of purified fractions on a μ-Bondapak C_{18} column. Mobile phase: methanol/water/TFA (200:800:0.25).

Figure 1 shows the results for the reaction mixture from experiment 4. Eight different fractions were observed. Fraction 2, although not seen in Figure 1, appears between fractions 1 and 2 when the HPLC is run by using a mobile phase with a lower methanol content (CH_3OH:H_2O:TFA = 50:950:0.25 instead of 200:800:0.25). The mole percent of each fraction was calculated from the HPLC peak areas assuming all fractions to have the same extinction coefficient (Table II). This assumption is clearly not quantitatively valid since HPLC detection occurs at 210 nm where both amide and ester absorb (almost certainly with different extinction coefficients) and different HPLC fractions contain different amounts of the two chromophores. However, the calculations do allow a comparison of the relative amounts of the various fractions formed in the different experiments. Fractions 1 and 2 were identified as methacrylic acid and *p*-methoxyphenol, respectively, by comparison with authentic samples. HPLC also showed the absence of any unreacted MeOXO in all four experiments. (Experiments with authentic samples showed that MeOXO appears before MAA when the mobile phase has CH_3OH:H_2O:TFA = 50:950:0.25.) The absence of poly(methacrylic acid) as a product was shown by the complete solubility of the polymerized reaction mixture in the HPLC mobile phase.

The compositions of the reaction mixtures from all four experiments are similar with some exceptions. Experiment 2 does not contain fractions 7 and 8 and these fractions are present in only small amounts in the other experiments. The main product is fraction 3 with considerable amounts of fraction 4 and unreacted MAA in all four experiments. The relatively large amount of *p*-methoxyphenol in experiment 3 results in a lower overall conversion with no ether-insoluble product. The ether-soluble product contains a large amount of unreacted MAA and lowered yields of other fractions especially fraction 3. Analytical HPLC of the ether-insoluble product from experiment 4 showed the same eight fractions as the ether-soluble product but with a much smaller amount of MAA and progressively larger amounts of the higher fractions.

The polymerized reaction mixture obtained in experiment 4 was fractionated by preparative HPLC. Analytical HPLC of isolated fractions are shown in Figure 2.

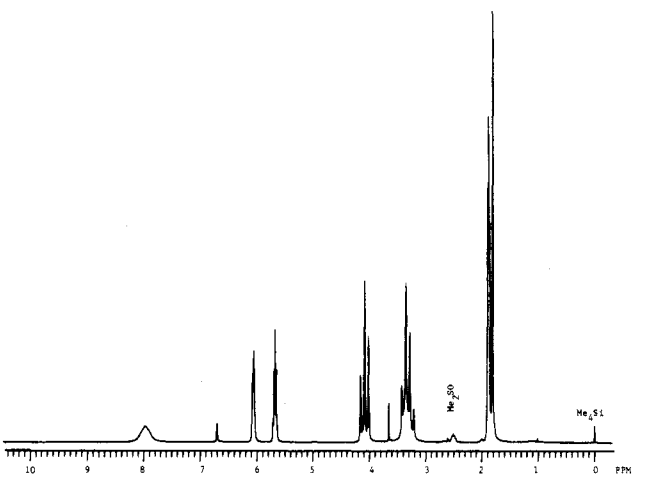


Figure 3. 80-MHz ^1H NMR spectrum of fraction 3.

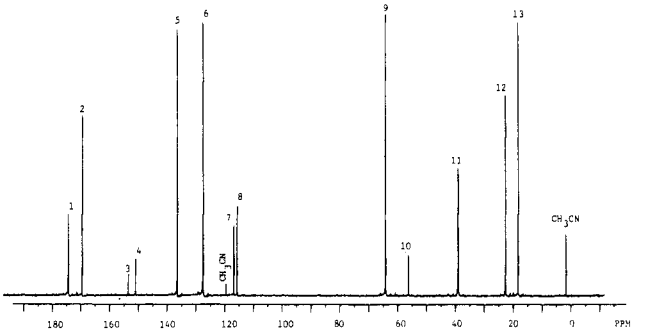
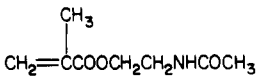


Figure 4. 20.1-MHz ^{13}C NMR spectrum of fraction 3.

Fractions 3 and 4 were obtained in reasonably high purity. Fraction 5 was obtained with 19% and 10% of fractions 4 and 6, respectively, as impurities. Fractions 6–8 were obtained as a mixture containing 28%, 40%, and 26%, respectively, of the three components with minor amounts of other fractions. The isolated fractions were concentrated under reduced pressure, dried, and then subjected to ^1H and ^{13}C NMR.

Fraction 3. The ^1H and ^{13}C NMR spectra of fraction 3 are shown in Figures 3 and 4, respectively. The spectra are compatible with structure III. The ^1H NMR spectrum



III

shows signals for $COCH_3$ (singlet, 3 H, 1.81 ppm), α-CH_3 of the methacrylate group (triplet, 3 H, 1.87 ppm), NCH_2 (multiplet, 2 H, 3.32 ppm), OCH_2 (triplet, 2 H, 4.08 ppm), olefinic protons (multiplets, 1 H each, 5.68 and 6.06 ppm), and NH (1 H, broad, 7.99 ppm). Signals at 3.65 and 6.70 ppm are due to the *p*-methoxyphenol added to prevent radical polymerization during concentration of the fraction.

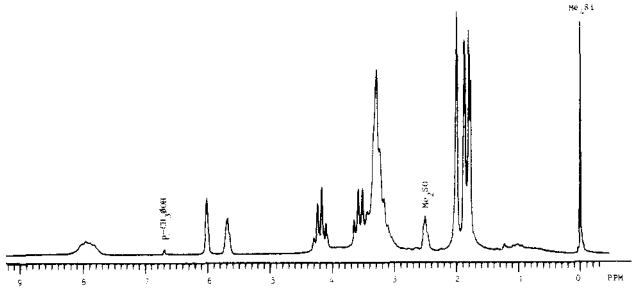
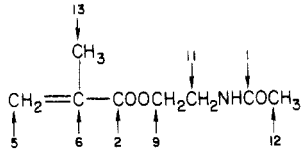


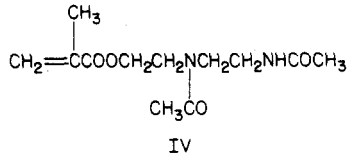
Figure 5. 80-MHz ^1H NMR spectrum of fraction 4.

The various signals in the ^{13}C NMR spectrum were assigned as follows:



based on the chemical shift values of analogously substituted carbons.[10] Signals 3, 4, 7, 8, and 10 are due to *p*-methoxyphenol.

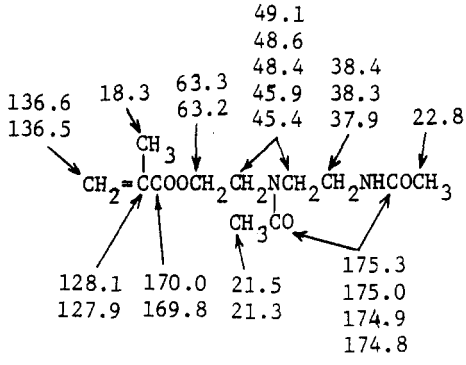
Fraction 4. Fraction 4 was identified as IV based on



IV

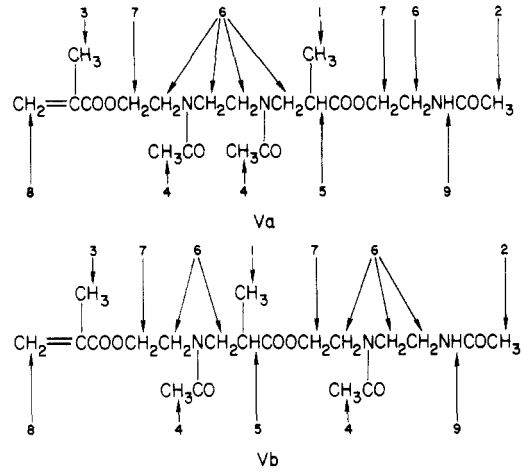
its ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum (Figure 5) shows signals for CH_3CONH (doublet, 3 H, 1.78 ppm), CH_3—C=C (singlet, 3 H, 1.87 ppm), CH_3CON— (singlet, 3 H, 1.99 ppm), $CH_2NCH_2CH_2$ (multiplets centered at 3.35 and 3.55 ppm, 6 H total), OCH_2 (multiplet, 2 H, 4.19 ppm), H_2C=C (doublets, 1 H each at 5.70 and 6.07 ppm), and NH (1 H, broad multiplet, 7.99 ppm).

Various signals in the ^{13}C NMR spectrum were assigned as follows:



The ^{13}C NMR spectrum shows the effect of restricted rotation about the C–N bond, previously described in the 2-methyl-2-oxazoline–acrylic acid (MeOXO–AA) system,[3] as more than one signal is observed for many of the carbons in structure IV. This effect is also seen to some extent in the ^1H NMR spectrum; e.g., the signals for the various methylene protons are not simple triplets. Both the ^{13}C and ^1H NMR data are in good agreement with structure IV for fraction 4.

Fraction 5. Figure 6 shows the ^1H NMR spectrum of fraction 5. A consideration of the chemical shift and integration values of the various signals and comparison with the spectrum for fraction 4 leads to structures Va and Vb for fraction 5 with indicated assignments of the ^1H NMR

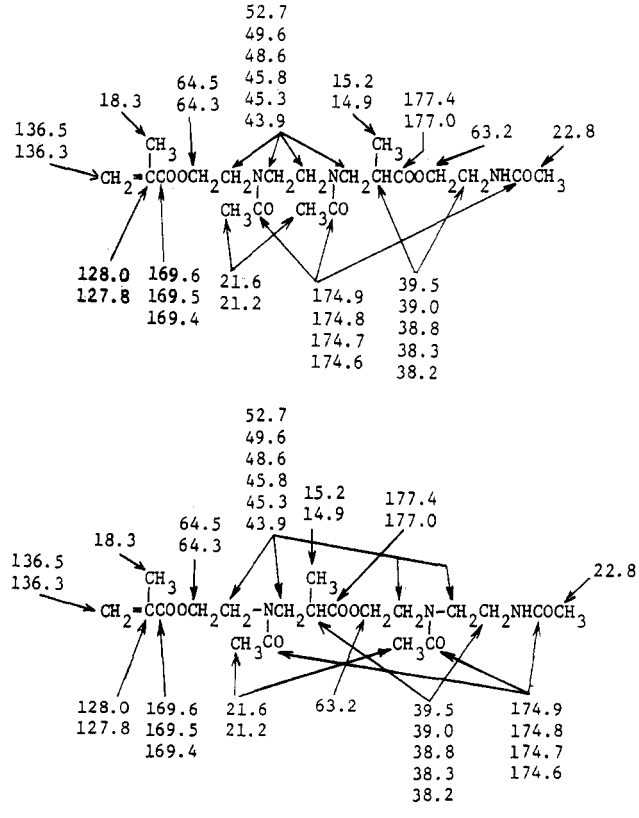


Va

Vb

signals. The ^1H NMR spectrum does not allow one to distinguish between Va or Vb. Fraction 5 is either Va or Vb or a mixture of the two structures. The effect of C–N restricted rotation is seen in Figure 6 for most of the protons. The ^1H NMR at higher temperature (125 °C) shows much less effect of C–N restricted rotation; e.g., signal 1 for the α-methyl protons appears as a doublet and signal 7 for the two different OCH_2 groups appears as a pair of triplets.

The ^{13}C NMR spectrum also identified fraction 5 as Va and/or Vb. The various ^{13}C NMR signals were assigned as follows:



Fractions 6–8. These three fractions were obtained as a mixture containing 28, 40, and 26 mol % of the three components, respectively, with minor amounts of other fractions. The ^1H NMR spectrum of this mixture is very similar to that for fraction 5. Signals were observed for CH_3CHCOO (quartet, 1.12 ppm), CH_3CONH (singlet, 1.80 ppm), CH_3—C=C (singlet, 1.88 ppm), CH_3CON— (doublet, 2.00 ppm), CH (multiplet, 2.80 ppm), CH_2N (multiplet, 3.40 ppm), CH_2O (multiplet, 4.01 ppm), C-H_2=C (doublets at 5.74 and 6.01 ppm), and NH (broad,

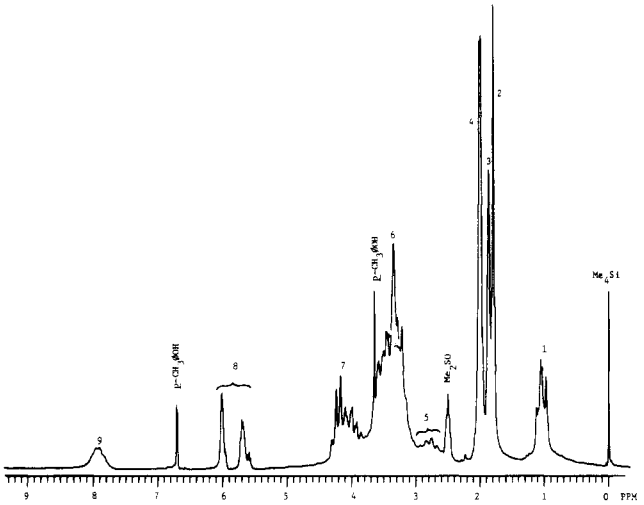
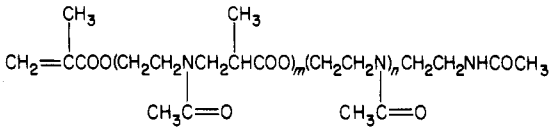


Figure 6. 80-MHz ^{1}H NMR spectrum of fraction 5.

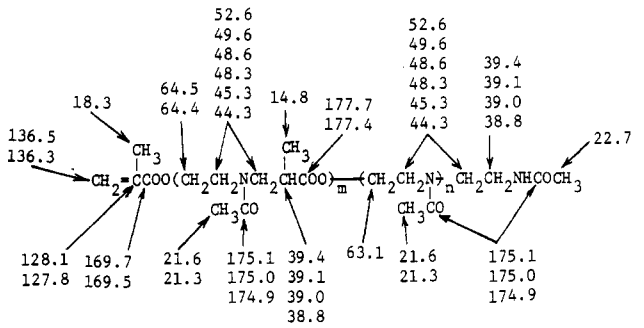
7.90 ppm) with respective areas in the ratios 2:1:1:5:2:9:3:1:1. The general structure VI is assigned to



VI

fractions 6–8 with average values of approximately 2 and $2^1/_2$, respectively, for m and n.

The ^{13}C NMR spectrum supports structure VI for the mixture of fractions 6–8. The ^{13}C NMR signals were assigned as follows:

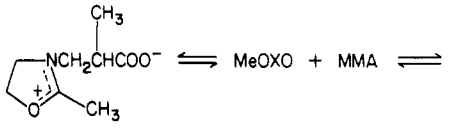


Comment on Work of Balakrishnan and Periyasamy. Our results for the MeOXO–MAA system differ from those reported by Balakrishnan and Periyasamy.[4] We found only low molecular weight products (III–VI) while Balakrishnan and Periyasamy reported the alternating copolymer (II) as the only product. Our interpretation is that they also obtained the low molecular weight products but these were converted to polymer by vinyl polymerization during the workup procedures. Balakrishnan and Periyasamy obtained their product by precipitation with diethyl ether followed by drying at 70 °C. Since we obtained very little ether-insoluble product, it is assumed that the amount of ether used for the precipitation by Balakrishnan and Periyasamy was sufficiently greater than in our procedure to precipitate a larger fraction of the products III–VI. The radical inhibitor p-methoxyphenol goes into the ether layer during the precipitation step. Subsequent drying of the product at 70 °C in the absence of p-methoxyphenol would result in polymerization through the double bonds of the methacrylate end groups of III–VI. Our workup procedure involved vacuum evaporation of ether and drying of the product at 30–35 °C. We did, in fact, observe vinyl polymerizations during the concentration of fractions obtained by HPLC if p-methoxyphenol was absent and the temperature was appreciably above 30–35 °C.

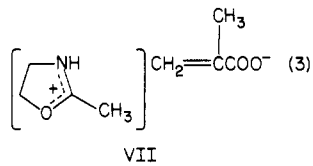
The actual ^{1}H NMR spectra reported by Balakrishnan and Periyasamy support our interpretation. We indicated in the Introduction section that their spectrum for the ether-insoluble product (reported only for the 1.9–5 ppm region) is inconsistent with the alternating copolymer II. The spectrum is compatible with the products from polymerization of III–VI. Signals are present for CH_3CONH and CH_3CON–, CH_2N and CH_2O protons at about the same ppm as the corresponding signals in III–IV as expected (1.8–2, 3.1–3.7, and 3.9–4.4 ppm, respectively). The CH protons of non-end-group MAA units in V and VI are present in amounts too small to be clearly seen in the spectrum but the base line in the 2.5–2.8 ppm region is clearly not flat. Since the reported spectrum does not include the regions below 1.9 or above 5.0 ppm, one cannot corroborate the absence or presence of a number of pertinent signals—CH_2 and CH_3 of polymerized methacrylate end groups, α-CH_3 of non-end-group MAA units (present in V and VI), NH, and CH_2=C.

Mechanism of MeOXO–MAA Reaction. Unlike the MeOXO–AA system, which yields both low and moderate molecular weight products, MeOXO–MAA yields only low molecular weight products. The latter closely resemble the ether-soluble low molecular weight products from MeOXO–AA polymerization.[3b] All of the MeOXO–MAA products contain olefinic and acetamido end groups derived from MAA and MeOXO, respectively, with varying amounts of MeOXO and MAA units in between the end groups. The overall material balance on the MeOXO–MAA system was obtained in two ways. The HPLC of the polymerized reaction mixture showed a considerable amount of unreacted MAA with no unreacted MeOXO. This result was corroborated by NMR which showed that the various reaction products contain considerably more MeOXO than MAA. The MeOXO:MAA ratios are 1:1, 2:1, 3:2, and $5^1/_2$:3 for fraction 3, 4, 5, and 6–8, respectively.

By analogy to our mechanism for MeOXO–AA polymerization, it is proposed that the initial reaction of MeOXO and MAA is the formation of the genetic zwitterion I by nucleophilic attack of MeOXO on MAA and the protonated MeOXO species VII by proton transfer

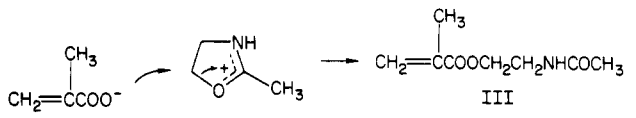


I



VII

Fraction 3, the major product, is formed from VII by ring-opening nucleophilic attack of the methacrylate anion on the oxazolinium ring

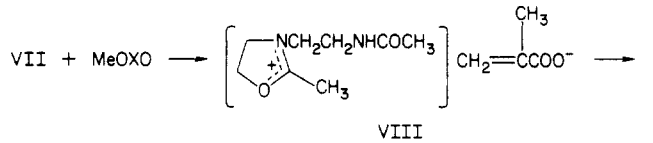


III

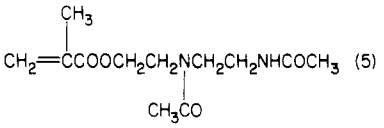
(4)

Fraction 4 is formed by reaction of MeOXO with VII followed by ring-opening nucleophilic attack of meth-

acrylate anion on the oxazolinium ring

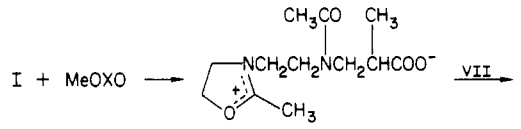


VIII

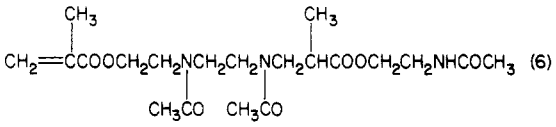


IV

Structure Va of fraction 5 is formed by reaction of the genetic zwitterion I with MeOXO to form IX followed by reaction with VII

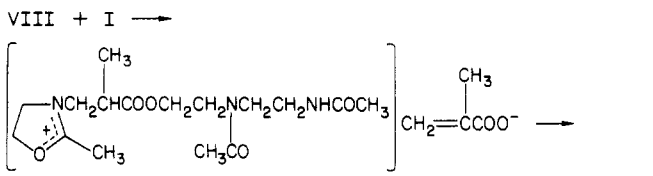


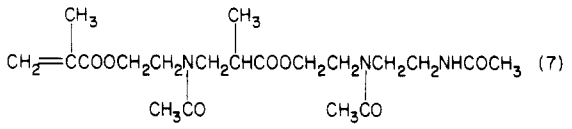
IX



Va

Structure Vb is formed by reaction of VIII with the genetic zwitterion I followed by a ring-opening nucleophilic attack of the methacrylate anion





Vb

Fractions 6–8 (structure VI with varying values of m and n, average values of m and n being 2 and $2^1/_2$, respectively) are formed by variations of the sequences leading to Va and Vb in which more than one MeOXO and/or more than one genetic zwitterion are involved in reactions 6 and 7. For example, the block structure VI with $m = n = 2$ is formed by the addition of two MeOXO molecules to the oxazolinium end of VII followed by the addition of two genetic zwitterions and then a nucleophilic ring-opening attack of methacrylate anion.

It is useful to compare the difference between the MeOXO–AA and MeOXO–MAA systems. MeOXO–AA yields mostly a moderate-sized ($\bar{M}_n$ = 590–2760) alternating copolymer while MeOXO–MAA yields only very low molecular weight products. Molecular growth in both systems resides primarily in reactions of the genetic zwitterion while termination occurs through reaction of the acrylate or methacrylate anion (referred subsequently as the carboxylate anion) with the oxazolinium ring. Termination by reaction of AA with macrozwitterions is an additional termination reaction in the MeOXO–AA system. Differences in the concentrations and/or reactivities of the genetic zwitterions and/or carboxylate anions are most likely responsible for the difference between the MeOXO–MAA and MeOXO–AA systems. MAA is less acidic than AA[12] (due to electron donation by the α-methyl group) and one expects a lower concentration of the carboxylate anion in MeOXO–MAA. (The greater acidity of AA probably accounts for the importance of termination of macrozwitterions by reaction with AA.) The MeOXO–MAA system should also have a lower concentration of genetic zwitterion due to lower electrophilicity of the MAA double bond. Reactivity differences are also expected for the MeOXO–MAA and MeOXO–AA genetic zwitterions and carboxylate anions. Electron donation by the α-methyl group would increase the nucleophilicities of both the carboxylate anion and genetic zwitterion in MeOXO–MAA compared to MeOXO–AA. The steric effect of the α-methyl group would have the opposite effect but its importance relative to the electronic effect is difficult to predict. Exclusive formation of low molecular weight products in MeOXO–MAA would be consistent with a considerably higher concentration and/or reactivity of the MAA carboxylate anion relative to the AA carboxylate anion coupled with little difference in the concentrations and/or reactivities of the two genetic zwitterions.

To determine whether concentration or reactivity differences are of greater importance, we attempted to compare the relative concentrations of genetic zwitterions and carboxylate anions in the two systems by direct ^{1}H NMR of the reaction systems. Both systems at short reaction times showed proton signals at 2.3 ppm, indicative of methyl protons on the oxazolinium ring of either the genetic zwitterion and/or protonated MeOXO. Equal signal areas at 2.3 ppm were observed for both MeOXO–AA and MeOXO–MAA. Neither spectrum showed an NH proton, which would appear to preclude the presence of protonated MeOXO. However, a small concentration of such labile protons would probably not be observed in the presence of much larger concentrations of COOH protons due to rapid exchange. No conclusions can be made as to the relative concentrations of genetic zwitterions and carboxylate anions in the two systems. This prevents one from understanding whether the difference between MeOXO–AA and MeOXO–MAA is caused by concentration or reactivity (or both) differences for the genetic zwitterions and/or carboxylate ions.

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Registry No. (MeOXO)·(MAA) (copolymer), 74218-48-7.

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Mechanism of Living Polymerization of Vinyl Ethers by the Hydrogen Iodide/Iodine Initiating System

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ABSTRACT: The initiation/propagation mechanism of the living polymerization of isobutyl vinyl ether (IBVE) initiated by a mixture of hydrogen iodide and iodine (HI/I_2 initiator) was investigated by NMR and UV/visible spectroscopy in nonpolar media at low temperatures below −15 °C. The initial reaction is the quantitative addition of HI to IBVE to yield a 1:1 adduct (1), $CH_3CHIOCH_2CH(CH_3)_2$. Adduct 1 (or HI) itself can hardly polymerize IBVE but, in the presence of iodine, it does induce a polymerization that yields monodisperse living polymers, the molecular weight of which is determined only by the initial HI concentration. ^1H NMR analysis of the polymerization mixture showed that the living polymers bear a CH–I terminal analogous to that of 1. UV/visible spectroscopy indicated the presence of a constant concentration of unreacted iodine throughout the reaction. From these results, a new polymerization mechanism has been proposed, in which the CH–I bond of 1 is first activated by the electrophilic interaction of added iodine with the terminal iodine and IBVE monomer inserts into the activated CH–I linkage. The resultant dimeric species has again a CH–I terminal that is in turn activated by iodine to allow the insertion of IBVE. Thus, the living polymers form via the successive insertion of the monomer into the covalent CH–I end activated by iodine. The difference between the polymerizations by HI/I_2 initiator and by iodine alone was also discussed on the basis of the proposed mechanism.

Introduction

Quite recently, we have reported the living polymerization of a series of vinyl ethers initiated by a mixture of hydrogen iodide (HI) and iodine, in which monodisperse living polymers with controlled molecular weight are obtained.[1,2] The living processes were also applied to synthesize novel di-[2] and triblock[3] copolymers and amino-functionalized poly(vinyl ethers).[3]

The living polymerization of vinyl ethers by HI/I_2 initiator differs clearly from the conventional cationic polymerization initiated by iodine itself.[1] For instance, even in nonpolar solvents the former proceeds without an induction phase that is usually involved in the latter, and well-defined living polymers can be obtained only with HI/I_2 initiator. Immediate questions arising from these facts are the following: What is the nature of the propagating species derived from the HI/I_2 initiating system that leads to the living processes? What is the difference in mechanism between the polymerizations by HI/I_2 and iodine alone? This study is to unravel these problems.

The mechanism of the iodine-initiated polymerization of vinyl ethers and related monomers has long been discussed mostly on the basis of kinetic investigations,[4–7] none of which, however, provided direct evidence on the nature of the propagating species therein. Ledwith and Sherrington[8] observed by UV spectroscopy equilibrium formation of an adduct (substituted 1,2-diiodoethane) between iodine and isobutyl vinyl ether (IBVE) in methylene chloride and suggested that the diiodo compound would dissociate in the presence of iodine to give an ionic propagating species. A later study by Johnson and Young[9] also indicated the presence of a similar diiode in the polymerization of *n*-butyl vinyl ether by iodine. According to Giusti et al.,[10–12] on the other hand, the adduct between styrene and iodine is inactive per se and may release HI that in turn initiates polymerization. Although these previous studies indicate the intervention of iodine–vinyl ether (or styrene) adducts in the polymerization by iodine, their role in initiation and propagation processes remains unknown.

In this study, we applied NMR and UV/visible spectroscopy, coupled with kinetic measurements, to analyze directly the polymerization systems of IBVE initiated by HI/I_2 and iodine. HI was found to form quantitatively a 1:1 adduct (α-iodo ether; eq 1) with IBVE. We also found that the C–I bond of the HI–IBVE adduct is activated by added iodine and that propagation proceeds via the reaction of IBVE with the activated C–I bond. This mechanism consistently accounts for the difference between the polymerizations by HI/I_2 and iodine alone.

Experimental Section

Materials. IBVE and polymerization solvents [*n*-hexane and carbon tetrachloride (CCl_4)] were purified as described previously.[1] Anhydrous hydrogen iodide was obtained by the dehydration of a 57% aqueous solution (Wako Chemicals) with phosphorus pentoxide[10] and stored as an *n*-hexane or CCl_4 solution in ampules in the dark at −20 °C.[1] Iodine (Wako Chemicals) was sublimed over potassium iodide and stored under dry nitrogen in the dark.

Polymerization Procedures. Reactions and polymerization of IBVE were carried out under dry nitrogen in a test tube equipped with a three-way stopcock.[1] The number-average molecular weight ($\bar{M}_n$) and molecular weight distribution (MWD) of the product polymers were measured by vapor pressure osmometry and gel permeation chromatography, respectively, as described.[1]

NMR Spectroscopy. ^1H and ^{13}C NMR spectra (89.55 and 22.5 MHz, respectively) were recorded on a Jeol FX-90Q Fourier-

0024-9297/85/2218-0611$01.50/0