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Polymerization via Zwitterion. VII. Alternating Ring-Opening Copolymerization of 2-Methyl-2-oxazoline with 3-Hydroxy-1-propanesulfonic Acid Sultone

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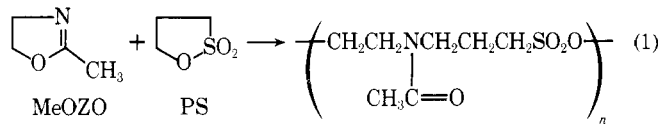
ABSTRACT: Ring-opening copolymerization of 2-methyl-2-oxazoline (MeOZO) with 3-hydroxy-1-propanesulfonic acid sultone (PS) was studied. The copolymerization took place without added initiator to produce 1:1 alternating copolymer of MeOZO and PS. The structure of the copolymer was determined by ir and NMR spectra, elemental analysis, as well as an alkaline hydrolysis experiment. The values of the apparent monomer reactivity ratio also support the 1:1 alternating copolymerization. The reaction scheme of the copolymerization via the zwitterion mechanism (eq 3–5) was proposed.

Recently, we have reported several combinations of nucleophilic monomers (M_N) and electrophilic ones (M_E) to produce alternating copolymers.[2-8] These copolymerizations occurred without any added initiator, in which a zwitterion (^+M_N–M_E^-) is considered to be an essential key intermediate responsible for the initiation and the alternating propagation. As M_N monomers 2-oxazolines,[2-4,7] 5,6-dihydro-4*H*-1,3-oxazines,[7] 2-iminotetrahydrofurans,[5] and 1,3,3-trimethylazetidine[6] have been examined. As M_E monomers, on the other hand, β-propiolactones,[2,3,5] acrylic acid,[4-6] and acrylamide[7] have been disclosed. In the present study, 2-methyl-2-oxazoline (MeOZO) and 3-hydroxy-1-propanesulfonic acid sultone (PS) were employed as M_N and M_E monomers, respectively. It was found that the combination of MeOZO and PS yielded the alternating copolymer, in which a zwitterion of a structure of 2-methyl-2-oxazoliniumpropane sulfonate was proposed.

Results and Discussion

Copolymerization and Characterization of Copolymer. An equimolar mixture of MeOZO and PS (10 mmol each) in 8 ml of dimethylformamide (DMF) was kept at 130°. With the progress of the reaction the mixture became pale yellow and viscous. After 15 min the mixture was poured into a large amount of benzene to precipitate copolymer, which gave 1.76 g (85% yield) of a glassy, pale yellow solid after drying in vacuo.

The solid is soluble in highly polar solvent such as DMF, methanol, dimethyl sulfoxide (DMSO), and water, slightly soluble in chloroform, and insoluble in toluene, benzene, and diethyl ether. The value of η_{sp}/c was 0.06 in DMF at 30°. Poly-MeOZO is soluble in chloroform, whereas poly-PS is soluble only in DMSO. A small amount of the $CHCl_3$-soluble part was found by NMR spectroscopy to have the same composition as that of the $CHCl_3$-insoluble part. These solubility data suggest that the product solid consists of only copolymer of MeOZO and PS. The structure of the copolymer was determined by ir and NMR spectroscopy, elemental analyses, as well as the alkaline hydrolysis experiment of the copolymer.



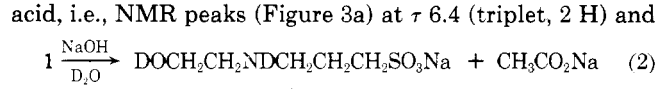
(1)

1

The ir spectrum of the copolymer (Figure 1) shows strong absorption bands at 1640 cm^{-1} due to the amide carbonyl group and at 1180 and 1040 cm^{-1} due to the sulfonate ester group. These band positions are very close to those of the corresponding bands of the respective homopolymers. The NMR spectrum of the copolymer (Figure 2) shows a triplet like at τ 5.7 (2 H), a multiplet at τ 6.7 (4 H), a triplet at τ 7.1 (2 H), and a sharp singlet at τ 8.0 overlapping with a broad peak (total 5 H). They are assigned respectively to protons of OCH_2, $-CH_2NCH_2-$, CH_2S, and $CH_3C{=}O$ plus $-CCH_2C-$. These spectral data strongly indicate that the copolymer is of the amide sulfonate structure **1** having almost 1:1 alternating unit.

The elemental analysis of the copolymer further supported the 1:1 composition of MeOZO and PS. Anal. Calcd for $(C_7H_{13}NO_4S)_n$: C, 43.0; H, 6.6; N, 8.3. Found: C, 42.7; H, 7.0; N, 8.3.

The alkaline hydrolysis of the copolymer was carried out to confirm the copolymer structure. **1** was allowed to hydrolyze with an excess amount of NaOH in D_2O for 3 hr at 100°. The NMR spectrum of the reaction mixture (Figure 3a) showed that the hydrolysis was completed. The hydrolysis products consisted of a 1:1 mixture of Na salts of 3-(2-hydroxyethylamino)propanesulfonic acid (**2**) and of acetic acid, i.e., NMR peaks (Figure 3a) at τ 6.4 (triplet, 2 H) and



(2)

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Table I
Solvent Effect on the Copolymerization of MeOZO and PS[a]

Solvent	Copolymer yield, %	MeOZO unit in the copolymer, mol %
DMF	78	52
C_6H_5CN	72	47
$Cl_2CHCHCl_2$	74	50
$C_6H_5CH_3$	34	44

[a] 10.0 mmol of each monomer in 8 ml of solvent for 10 min at 100°.

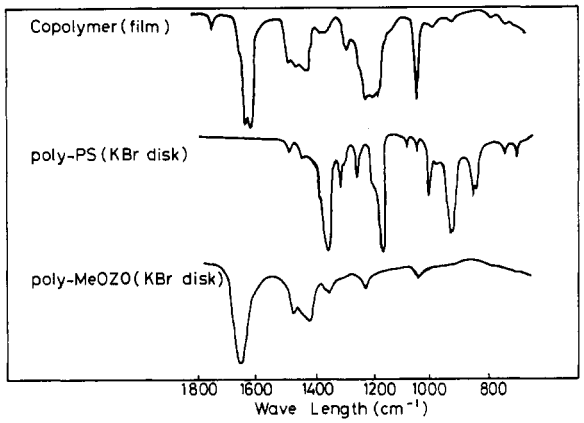


Figure 1. Ir spectra of MeOZO–PS copolymer (top), poly-PS (middle), and poly-MeOZO (bottom).

at τ 7.0–7.6 (two triplets, 6 H), and at τ 8.0–8.3 (sharp singlet and multiplet, 5 H) are due to protons of OCH_2, $-CH_2NCH_2-$, plus CH_2S, and $CH_3C{=}O$ plus $-CCH_2C-$, respectively. The assignment was further confirmed by the comparison of Figure 3a with the NMR spectrum (Figure 3b) of an authentic 1:1 equimolar mixture of Na salts of an isolated sample of **2** and acetic acid in NaOH–D_2O solution. It is evident that the spectra (Figures 3a and 3b) resemble each other.

Copolymerization Conditions. Figure 4 shows the effect of the monomer feed ratio on the copolymer composition at 100° in DMF. With the increase of MeOZO the MeOZO content in the copolymer increased. In the range of more than 50 molar % feed of MeOZO, however, the copolymer composition was almost 1:1 of PS (M_1) and MeOZO (M_2). Based on the data in Figure 4 the apparent monomer reactivity ratios were calculated[9] to be $\gamma_1 = 0.13$ and $\gamma_2 = 0$, respectively. Figure 5 shows the effect of the monomer feed ratio on the copolymer yield, in which the maximum yield was obtained at the 1:1 feed ratio.

Variation of reaction solvents was examined (Table I). The copolymer yield was very much dependent upon the solvent employed, i.e., the higher yield was achieved in highly polar solvents. However, the copolymer composition was less affected by solvents, i.e., almost 1:1 composition was attained regardless of the solvent.

Copolymerization Mechanism. On the basis of the above data, a reaction scheme of eq 3–5 is proposed for the copolymerization of MeOZO with PS, which involves zwitterion intermediates.[1-8] The first step is the reaction of MeOZO with PS to give the genetic zwitterion **3**, which is an important key intermediate in both the initiation and propagation. The reactions of 2 mol of **3** give dimeric zwitterions **4**. The subsequent steps of propagation involve the attack of **3** to **4** to yield a macrozwitterion **5**. The formation of **3** is probably the rate-determining step, since the dipole–

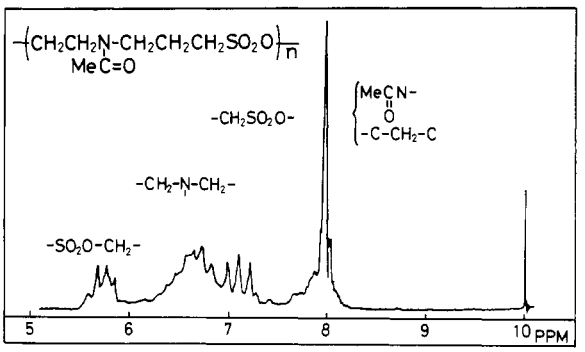


Figure 2. NMR spectrum of MeOZO–PS copolymer in DMF-d_7.

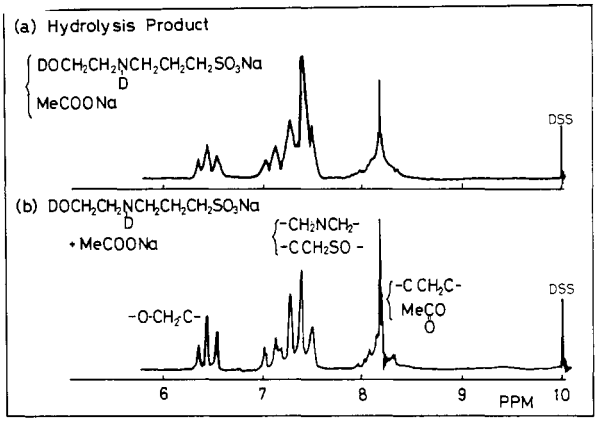
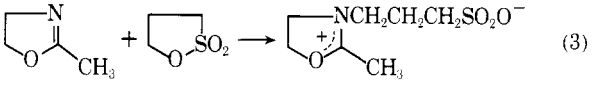
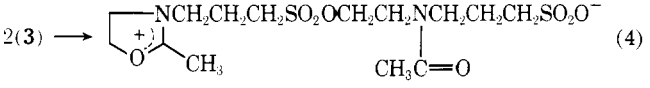


Figure 3. NMR spectra of (a) the alkaline hydrolysis product of the MeOZO–PS copolymer and (b) a mixture of Na salt of **2** and of acetic acid in D_2O using an internal standard of DSS (see Experimental Section).

dipole reaction (eq 3) to produce the zwitterion **3** is favored in highly polar solvents as seen in Table I. The value of $r_1 = 0.13$ indicates that when PS is present in excess, sulfo-


(3)

3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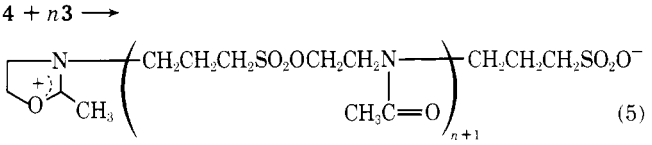
(5)

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nate anion of **3–5** reacts not only with oxazolinium of **3–5** but also with free PS to produce the PS homosequence in the copolymer. Finally the intermolecular reaction between two polymeric zwitterions as well as the intramolecular reaction between the cationic and anionic sites in a single polymeric zwitterion may possibly occur.

The following observations may be taken to support the above mechanism of copolymerization. In an NMR spectrum of a very early stage of copolymerization, a triplet at τ 5.07 and a sharp singlet at τ 7.55 were observed, which were assigned respectively to OCH_2 and CCH_3 of the oxazolinium ring of zwitterions **3–5**. As a model reaction of copolymerization (eq 4 and 5), the reaction between isolated samples of 2-oxazolinium iodide (**6**) and pyridine–PS betaine (**7**) was examined. The reaction between **6** and **7** was completed within 10 min at 100° in CD_3CN–CD_3OD (Fig-

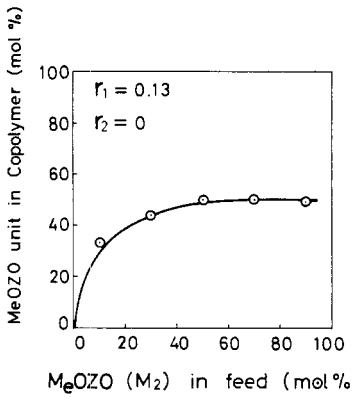


Figure 4. Composition curve in the copolymerization of MeOZO with PS; MeOZO + PS = 40 mmol in 5 ml of DMF, 100° for 1 min.

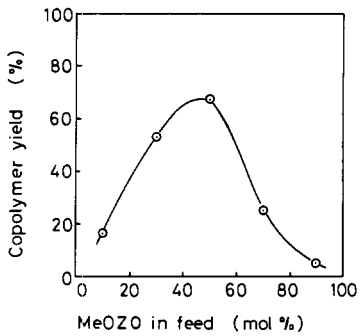
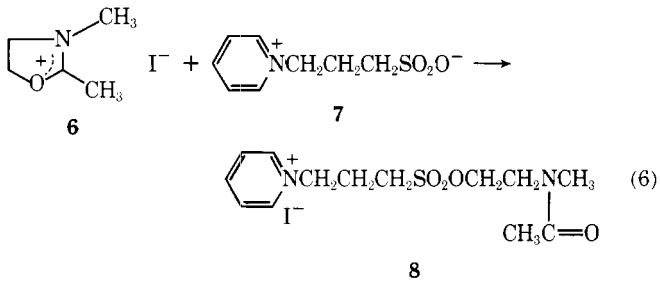


Figure 5. Relationships between monomer feed ratio and copolymer yield in the copolymerization of MeOZO with PS; MeOZO + PS = 40 mmol in 5 ml of DMF, 100° for 1 min.



6 7

(6)

8

ure 6). Characteristic peaks due to **6** disappeared, and instead, a specific new peak (triplet at τ 5.72) appeared, which was assigned to SO_2OCH_2 of the reaction product **8**. Other peak assignments are shown in Figure 6. The quantitative conversion of eq 6 shows the ease of the reaction between 2-methyl-2-oxazolinium and sulfonate anion in the copolymerization of MeOZO with PS.

The molecular weight of the product copolymer is dependent upon the relative rates of three processes, i.e., the formation of dimeric zwitterion from 2 mol of the genetic zwitterion **3** (eq 4), the propagation reaction between oligomeric (or polymeric) zwitterion **5** and **3**, and the intermolecular reaction between two polymeric zwitterions. The formation of lower molecular weight copolymer is ascribed to the fact that the rates of the latter two processes are not very fast in comparison with the rate of the process of eq 4.

The copolymerization of PS with unsubstituted 2-oxazoline (OZO) took place even at 10–40° in DMF or acetonitrile. The copolymer, however, contained the OZO unit in excess, i.e., more than 66 molar % from an equimolar feed of OZO and PS monomers.[10] The copolymerization of PS with 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (PhOZI) yielded the 1:1 alternating copolymer in 40% yield when an equimolar mixture of PS and PhOZI was allowed to react in

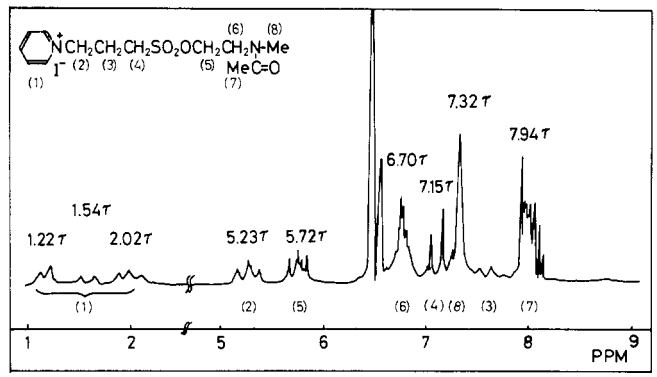


Figure 6. NMR spectrum of the reaction mixture of the oxaolinium iodide **6** and the betaine **7** after 10 min at 100° in CD_3CN–CD_3OD.

acetonitrile at 120° for 3 hr.[10] These findings, coupled with those of the PS–MeOZO system, indicate that the combination of M_N and M_E monomers is the most important factor in producing an alternating copolymer, i.e., a 1:1 alternating copolymer is produced only when the reactivity of M_N^+ and M_E^- in zwitterions is justified properly.

Experimental Section

Reagents. MeOZO was purchased from Aldrich Chemical Co. and purified by distillation, bp 110°.[11] PS was a commercial reagent, which was dried on molecular seives 4A and distilled, bp 130–131.5° (4 mm). 3-(2-Hydroxyethylamino)propanesulfonic acid (**2**) was prepared by the reaction of monoethanolamine with PS, mp 177.9°. Anal. Calcd for $C_5H_{13}O_4NS$: C, 33.0; H, 6.6; N, 7.7. Found: C, 33.0; H, 7.2; N, 7.3. *N*-Methyl-2-methyl-2-oxazolinium iodide (**6**) was obtained as previously reported.[12] Pyridine–PS betaine (**7**) was synthesized according to the literature procedure,[13] mp 271° (lit.[13] mp 270–272°). All solvents were purified by distillation in the usual manner.

Polymerization Procedure. To 8 ml of solvent in a test tube MeOZO and PS (10.0 mmol each) were added at room temperature under nitrogen and the tube was sealed. Then the mixture was kept at a desired temperature. After the reaction the tube was opened and the reaction mixture was poured into a large amount of benzene to precipitate the copolymer. Pale yellow glassy material was obtained after drying in vacuo.

Hydrolysis of Copolymer. To 0.05 g of copolymer was added 0.5 ml of 15% D_2O solution of NaOH at room temperature and the mixture was heated at 98° for 3 hr. Then, the reaction mixture was subjected to NMR measurement using DSS (Na salt of 3-(trimethylsilyl)propanesulfonic acid) as an internal standard, since DSS is miscible in the system.

NMR Measurement. NMR spectra were taken on a JNM-4H100 spectrometer. The internal standard was tetramethylsilane except for the measurement of the alkaline hydrolysis product of copolymer in which DSS was employed.

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