Polymerization of Phenylacetylenes. II. Copolymerization Catalyzed by WCl_6

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ABSTRACT: To obtain information about the mechanism of the polymerization of phenylacetylene by WCl_6, the effect of ring substituents (p-CH_3O, p-CH_3, p-Cl) on the reactivity was investigated. The relation between the relative reactivity and Brown's σ^+ of the substituent showed good linearity, with a slope of −0.47 for the polymerization of phenylacetylene by WCl_6 in benzene at 30°. This value is much less negative than that expected for a conventional cationic mechanism, and reminiscent of a coordination mechanism. On the other hand, ρ^+ was −2.00 in the polymerization of styrene by WCl_6, which supports that the polymerization proceeds by a conventional cationic mechanism. For the sake of comparison, the effects of ring substituents on the ground state of phenylacetylene were studied by means of the CNDO/2 molecular orbital calculation and ^{13}C NMR. The reaction mechanism was discussed on the basis of the results obtained.

In part I of this series, we have obtained the following results on the polymerization of phenylacetylene:[1] (i) WCl_6 and $MoCl_5$ are particularly effective catalysts for the polymerization of phenylacetylene, (ii) the polymerization proceeds fast in a nonpolar solvent such as benzene, and (iii) the molecular weight of the polymer obtained is the highest of those reported so far. The behavior of this polymerization, in particular result (ii), is not explained in terms of a conventional cationic mechanism.

To make the reaction mechanism clear the investigation on the effect of ring substituents on reactivity, that is, the examination of the Hammett relationship, seems to be useful. For example, transition states for various electrophilic additions to olefins were classified on the basis of ρ values.[2] Here, ρ is the reaction constant obtained from the Hammett plots. As to electrophilic additions to styrene, the ρ values of hydration and addition of sulfenyl halide were $-3.42(\sigma^+)$[3] and $-2.20(\sigma)$,[4] which were considered to correlate to β- and α,β-type reactions,[2] respectively. This sort of investigation will be profitable in order to look into the polymerization mechanism of phenylacetylene by WCl_6.

In the present study, we have investigated the effect of ring substituents on the polymerization of phenylacetylene and compared it with those in the polymerization of styrene and in other electrophilic reactions of phenylacetylene. Furthermore the effects of ring substituents on the ^{13}C NMR chemical shifts and on the electron densities were also studied to help understanding of the reaction mechanism.

Experimental Section

Materials. Phenylacetylene was commercially obtained and distilled twice over calcium hydride before use. p-Chlorophenylacetylene and p-methylphenylacetylene were synthesized by the reaction of the corresponding ring-substituted acetophenones with phosphorus pentachloride and the subsequent dehydrochlorination.[5] p-Methoxyphenylacetylene, m-chlorophenylacetylene, and m-nitrophenylacetylene were prepared from the corresponding ring-substituted benzaldehyde by the Knoevenagel or Perkin reaction, followed by bromination, decarboxylation, and dehydrobromination reactions.[5] According to gas chromatographic data, the purities of these monomers except for p-methoxyphenylacetylene were more than 99%, and that of p-methoxyphenylacetylene was ca. 90% because ortho isomer was involved. Ring-substituted styrenes were synthesized by the same method as described elsewhere.[6] Styrenes were purified by the usual method. 2,4-Dinitrobenzenesulfenyl chloride was prepared by the method of Lawson et al.[7] and purified by recrystallization from carbon tetrachloride; mp 95–97° (lit.[7] mp 97–98°). Solvents (benzene and ethylene dichloride) and catalysts (WCl_6 and $SnCl_4$) were purified by the same methods as described in the preceding paper.[1] Trichloroacetic acid (TCA) (Guaranteed Reagent) was used as the cocatalyst of $SnCl_4$ without further purification.

Procedures. Copolymerization was carried out at 30° in an erlenmeyer flask under a dry nitrogen atmosphere. Concentration of the water in the system was ca. 2×10^{-4} M. The consumption rates of both monomers were determined by measuring concentrations of residual monomers by gas chromatography. Monomer reactivity ratios were calculated by Ezrielev's method.[8]

The addition of 2,4-dinitrobenzenesulfenyl chloride to phenylacetylene was carried out in ethylene dichloride at 50°. The relative reactivities of phenylacetylene derivatives were determined by means of competitive additions to phenylacetylene and a phenylacetylene derivative. Aliquots of the reaction solution were taken out at suitable time intervals and drained into methanol containing sodium iodide, and the unreacted phenylacetylenes were measured by gas chromatography.

^{13}C NMR spectra were taken at 25.14 MHz on a JEOL PFT-100 spectrometer. The spectra of neat liquids were obtained with the accumulation of 100 scans by the Fourier transform method. Line positions were referenced against tetramethylsilane.

Theoretical Calculation. Molecular orbital calculations of substituted phenylacetylenes were performed with the CNDO/2 approximation proposed by Pople et al.[9] The parameters determined by Popel et al.[9] and Santry et al.[10] were used without further modification. The criterion for self-consistent conversion is 10^{-3} eV in all molecular orbital energies. The atomic coordinates of the acetylenes were determined from the following bond distances and bond angles: $-C{\equiv}C-$ 1.205 Å, saturated C–H 1.09 Å, acetylenic C–H 1.06 Å, C–C 1.54 Å, aromatic C–C 1.39 Å, aromatic C–H 1.08 Å, saturated C–O 1.43 Å, aromatic C–O 1.42 Å, acetylenic C–C_6H_5 (aromatics) 1.45 Å, Cl–C_6H_5 (aromatics) 1.70 Å, ∠COC 110°, saturated ∠HCH 109°28′, unsaturated trigonal angle 120°. Total energy is the sum of total electron energy and nuclear repulsion energy. Computations were carried out on a FACOM 230-60 computer at the Data Processing Center of Kyoto University.

Results

Copolymerization. Figure 1 shows the composition curves of the copolymerizations of phenylacetylene with ring-substituted phenylacetylenes by WCl_6 in benzene. The monomer reactivity ratios are shown in Table I. Methanol-insoluble reddish brown copolymers were formed in these copolymerizations. As was reported in the preceding paper,[1] a small amount of water accelerated the homopolymerization of phenylacetylene by WCl_6. However, addition of water (twice the catalyst) had no influence on the monomer reactivity ratios in the copolymerization of phenylacetylene with p-methylphenylacetylene (see Table I). The copolymerization was found to be nearly the ideal one from the products of monomer reactivity ratios ($r_1r_2 \simeq 1$). The reactivity of phenylacetylene was increased by introducing an electron-donating substituent.

The results of copolymerizations of styrene with ring-substituted styrenes by WCl_6 are shown in Figure 2 and Table I. There have been no data on the Hammett relation-

Table I
Monomer Reactivity Ratios for the Copolymerizations of Ring-Substituted Phenylacetylenes and Styrenes[a]

M_1	M_2	Catalyst	r_1	r_2	r_1r_2
PA[b]	*p*-CH_3O-PA	WCl_6	0.42 ± 0.08	4.44 ± 0.31	1.86
PA	*p*-CH_3-PA	WCl_6	0.68 ± 0.03	1.69 ± 0.05	1.14
PA	*p*-CH_3-PA	$WCl_6 \cdot 2H_2O$	0.66 ± 0.02	1.81 ± 0.06	1.20
PA	*p*-Cl-PA	WCl_6	1.09 ± 0.04	0.61 ± 0.03	0.67
St[b]	*p*-CH_3O-St	WCl_6	0.03 ± 0.03	22.8 ± 1.4	0.66
St	*p*-CH_3-St	WCl_6	0.57 ± 0.04	2.48 ± 0.09	1.41
St	*p*-Cl-St	WCl_6	2.08 ± 0.06	0.40 ± 0.03	0.83
St	*p*-CH_3O-PA	$SnCl_4 \cdot$ TCA	0.04 ± 0.02	(6.08 ± 0.25)	(0.26)
St	*p*-CH_3-PA	$SnCl_4 \cdot$ TCA	0.46 ± 0.02	(1.97 ± 0.07)	(0.91)
St	PA	$SnCl_4 \cdot$ TCA	1.98 ± 0.11	(0.65 ± 0.06)	(1.30)
St	*p*-Cl-PA	$SnCl_4 \cdot$ TCA	5.69 ± 0.25	(0.27 ± 0.05)	(1.51)

[a] In benzene at 30°. [b] PA = phenylacetylene; St = styrene.

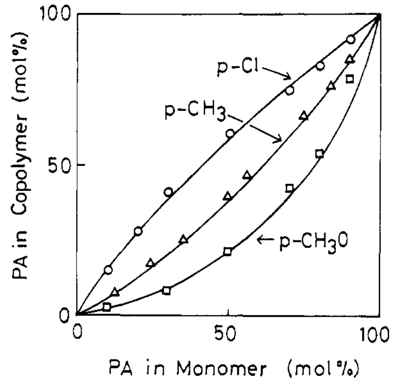

Figure 1. Copolymerizations of phenylacetylene (PA) with ring-substituted phenylacetylenes by WCl_6 in benzene at 30° ($[M]_0$ = 1.0 *M*).

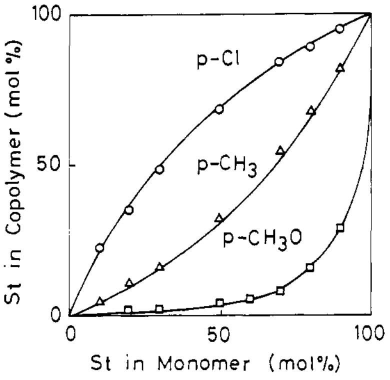

Figure 2. Copolymerizations of styrene (St) with ring-substituted styrenes by WCl_6 in benzene at 30° ($[M]_0$ = 1.0 *M*).

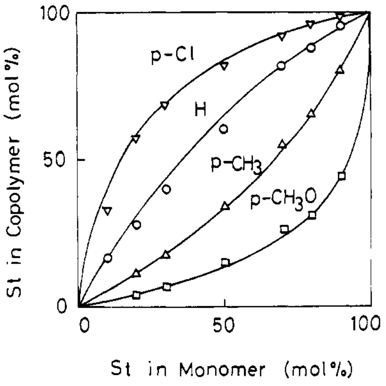

Figure 3. Copolymerizations of styrene with ring-substituted phenylacetylenes by $SnCl_4 \cdot$ TCA in benzene at 30° ($[M]_0$ = 1.0 *M*).

ship for the polymerization of styrene catalyzed by WCl_6, although the relationship has been examined in the case of the $SnCl_4$ catalyst.[11,12] The copolymerizations of the styrenes were much faster than that of corresponding phenylacetylenes; the concentration of catalyst necessary to obtain a comparable rate in the former was only 1/30 as much as in the latter. Methanol-insoluble white powdery copolymers were obtained in these copolymerizations. The results in Figure 2 and Table I show that an electron-donating substituent greatly enhances the reactivity of styrene, and the extent of increasing reactivity is appreciably larger in styrene derivatives than in phenylacetylene derivatives.

The data for the copolymerizations of styrene with ring-substituted phenylacetylenes catalyzed by $SnCl_4 \cdot$ TCA are shown in Figure 3 and Table I. Phenylacetylene does not polymerize by $SnCl_4$.[13] However, the product at high styrene contents in the feed was a methanol-insoluble white powdery copolymer in this copolymerization; the presence of phenylacetylene unit in the product was confirmed by ir and NMR spectroscopies. Therefore, the Mayo-Lewis equation will hold for this system at high styrene contents, that is, the r_1 obtained (M_1 = styrene) will be reliable. On the other hand, the product formed at low styrene contents in the feed was mainly a methanol-soluble oligomer. Hence, the r_2 calculated may not be exactly the ratio of propagation rates (therefore, the values of r_2 in Table I are shown in parentheses). As is clear from comparison of Figures 3 and 1, the substituent effect in these copolymerizations is appreciably larger than that for the copolymerizations of phenylacetylenes by WCl_6.

Copolymerization of phenylacetylene with styrene was attempted by using WCl_6 as catalyst. However, the polymerization of styrene was saturated without completion at an early stage of the polymerization, while phenylacetylene continued to polymerize. This anomalous behavior suggests that phenylacetylene and styrene do not copolymerize randomly by WCl_6 under the same mechanism. Therefore, no monomer reactivity ratios were determined for this system.

Log $(1/r_1)$ obtained from the copolymerizations described above was plotted against Brown's σ^+ (Figure 4). ρ^+ values were obtained from the slopes of the Hammett plots by the least-squares method. The ρ^+ value for the copolymerizations of styrenes by WCl_6 was -2.00. This is very close to the value of -2.03 for the cationic polymerization of styrene.[12] The ρ^+ value for the reaction of phenylacetyl-

Table II
Relative Reactivities of Ring-Substituted Phenylacetylenes in the Addition Reaction of 2,4-Dinitrobenzenesulfenyl Chloride[a]

Substituent	Relative reactivity	
p-CH$_3$O	153	
p-CH$_3$	3.23	
H	1.00	$\rho = -2.20^b$
p-Cl	0.481	$(r = 0.995)^c$
m-Cl	0.196	
m-NO$_2$	0.0356	

[a] Reaction conditions: $[\mathrm{PA}]_{\mathrm{total}} = 0.20\ M$; [sulfenyl chloride] = 1.0 M; 50°; in (CH$_2$Cl)$_2$. [b] Calculated, excluding p-methoxyphenylacetylene. It being included, $\rho = -3.14$, $r = 0.915$; $\rho^+ = -2.38$, $r = 0.986$. [c] r = correlation coefficient.

enes with the propagating end produced from styrene and SnCl$_4$ · TCA (−2.30) is also similar to that for the cationic polymerization of styrene. On the other hand, the ρ^+ value for the polymerization of phenylacetylene by WCl$_6$ (−0.47) is evidently different from the two values determined above.

Electrophilic Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Phenylacetylenes. The transition state for the addition of sulfenyl chloride to olefins and acetylenes has been depicted as episulfonium ion.[14] Kharasch et al. have reported that the rate of addition of 2,4-dinitrobenzenesulfenyl chloride to phenylacetylene in acetic acid is proportional to each reactant concentration.[15]

The addition of 2,4-dinitrobenzenesulfenyl chloride to ring-substituted phenylacetylenes was examined to obtain the ρ value for the addition to phenylacetylene in which the transition state is a bridged ion. Relative reactivities of phenylacetylene derivatives are listed in Table II. The Hammett plots of the relative reactivities against σ gave a good linear correlation when p-methoxyphenylacetylene is excluded. The ρ value was −2.20, which is very similar to that for the addition of the sulfenyl chloride to ring-substituted styrenes (−2.20).[4] The rate of addition to p-methoxyphenylacetylene was exceptionally large and deviated from the straight line. It is to be noted that p-methoxystyrene also largely deviates from the Hammett plot for the addition reaction to styrenes.[4]

Electronic Structure of Phenylacetylene. It is well known that the ^{13}C chemical shift can be correlated with the total electron density of the carbon. In Table III are given the chemical shifts of phenylacetylene derivatives. Figure 5 shows the Hammett plots of chemical shifts of the β and α carbons. From the Hammett plots with the β carbon, a slope of 3.90 ppm/σ was obtained. This value is smaller than that reported for styrene derivatives (ρ = 5.75 ppm/σ).[16] The same tendency has been observed also between the ρ values for the β-carbon shifts of phenylpropyne (ρ = 5.38 ppm/σ) and *trans*-β-methylstyrene (ρ = 6.64 ppm/σ).[17]

In Table IV are shown the total and the atomic orbital electron densities of phenylacetylene derivatives calculated by the CNDO/2 molecular orbital method. The total electron density on C$_\beta$ of phenylacetylene was obviously larger than 4, and it increased when an electron-donating substituent was introduced. The atomic orbital electron density of 2p$_z$ of C$_\beta$ also increased by introduction of an electron-donating substituent. On the other hand, the electron density of 2p$_y$ of C$_\beta$ decreased, but the extent was small.

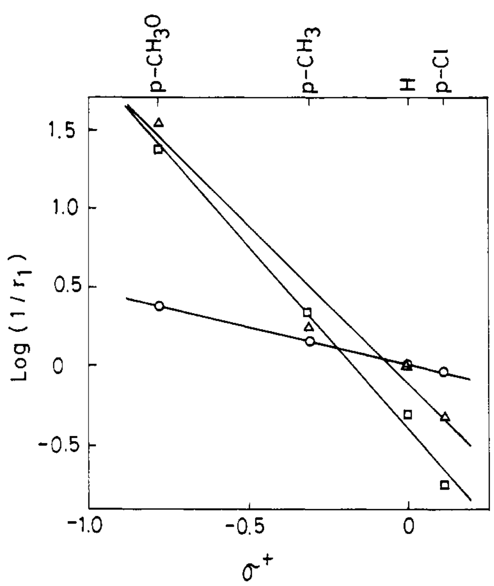

Figure 4. Hammett plots of log (1/r_1) against σ^+ for several copolymerization systems: (○) PA-p-substituted PA–WCl$_6$–benzene (ρ^+ = −0.47), (△) St-p-substituted St–WCl$_6$–benzene (ρ^+ = −2.00), (□) St-p-substituted PA–SnCl$_4$ · TCA–benzene (ρ^+ = −2.30).

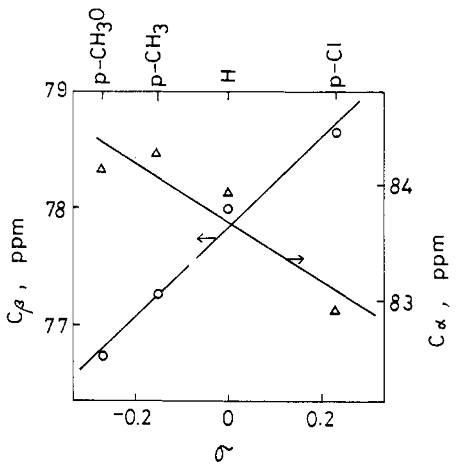

Figure 5. Hammett plots of ^{13}C chemical shifts of phenylacetylenes.

Discussion

Copolymers must have been formed in the copolymerizations between phenylacetylene homologues by WCl$_6$, be-

Table III
The ^{13}C Chemical Shifts of Ring-Substituted Phenylacetylenes[a]

Substituent	C_β	C_α	C_{joint}	Ortho	Meta	Para	Others
p-CH$_3$O	76.71	84.14	114.47	133.74	114.18	160.15	54.97
p-CH$_3$	77.25	84.28	119.47	132.19	129.28	138.28	21.33
H	77.97	83.94	122.53	132.29	128.89	128.50	
p-Cl	78.65	82.92	121.03	133.50	128.79	135.05	

[a] In ppm downfield from TMS.

Table IV
Total and Atomic Orbital Electron Densities in Substituted Phenylacetylenes

		p-CH$_3$O	p-CH$_3$	H	p-Cl^a
Total energy, eV		−2399.80	−1898.25	−1661.60	−2072.38
Total electron density	C_β	4.1162	4.1159	4.1126	4.1089
	C_α	4.0049	4.0057	4.0065	4.0064
Atomic orbital electron density	C_β				
	2s	1.0942	1.0942	1.0946	1.0949
	2p$_x$	0.9586	0.9585	0.9590	0.9596
	2p$_y$	1.0585	1.0606	1.0611	1.0576
	2p$_z$	1.0049	1.0026	0.9980	0.9968
	C_α				
	2s	1.0653	1.0661	1.0656	1.0638
	2p$_x$	0.9698	0.9707	0.9702	0.9679
	2p$_y$	0.9666	0.9649	0.9646	0.9673
	2p$_z$	1.0033	1.0040	1.0061	1.0074

[a] sp calculation.

Table V
The ρ Values for the Electrophilic Additions and ^{13}C Chemical Shifts of Phenylacetylene and Styrene

	Phenylacetylene	Styrene
Hydration	$-4.79(\sigma^+)^{18}$	$-3.42(\sigma^+)^{3}$
Bromination	$-5.17(\sigma^+)^{19}$	$-4.21(\sigma^+)^{20}$
Addition of sulfenyl chloride	$-2.20(\sigma)$	$-2.20(\sigma)^{4}$
Polymerization by SnCl$_4$^{a}	$-2.30(\sigma^+)$	$-2.03(\sigma^+)^{12}$
Polymerization by WCl$_6$	$-0.47(\sigma^+)$	$-2.00(\sigma^+)$
^{13}C chemical shift of C_β	3.90(ppm/σ)	5.75(ppm/σ)^{16}

[a] Reaction with styryl cation.

cause the reaction product is of such high molecular weight as to be methanol insoluble and the product r_1r_2 is close to unity. This is also the case for the copolymerizations between styrene homologues by WCl$_6$. Copolymer was formed also in the copolymerization of styrene with phenylacetylenes by SnCl$_4$ · TCA, when the styrene content was high. However, its copolymerization rate and the molecular weight of the copolymer decreased sharply with increasing phenylacetylene content in the feed. The remarkable reluctance of phenylacetylene to polymerize may be ascribed to very slow initiation and/or to low reactivities of both α-phenylvinyl cation and phenylacetylene. In the attempted copolymerization of styrene with phenylacetylene by WCl$_6$, phenylacetylene polymerized further after the polymerization of styrene was saturated without completion. Therefore, it is probable that copolymerization did not take place.

In Table V are shown both the reaction constants in several electrophilic additions and the sensitivity constant in the ^{13}C chemical shift for phenylacetylene and styrene.

The transition states for hydration and bromination of styrene and phenylacetylene are close to carbenium ions. As Table V shows, the reaction constants of these reactions of phenylacetylene are similar to but a little more negative than those of styrene. The reaction constants for the sulfenyl chloride addition to phenylacetylene and styrene are very similar to each other (see Table V). On the basis of these three pairs of reaction constants, the reaction constant for phenylacetylene is considered to be approximately equal to or slightly more negative than that for styrene in the same electrophilic addition reactions. This is anticipated also with the polymerizations of phenylacetylene and styrene; that is, if the reaction mechanism is the same, the reaction constants for the polymerizations of phenylacetylene and styrene will be similar.

The polymerization of styrene by SnCl$_4$ is a typical cationic polymerization, and the reaction constant has been reported to be −2.03.[12] This value is close to that for the addition of sulfenyl chloride. This indicates that the rate-determining step for the cationic polymerization of styrene is of α,β-attack type.[2] The reaction constant for the polymerization of styrene catalyzed by WCl$_6$ (−2.00) is very similar to this value. It is, therefore, concluded that the polymerization of styrene by WCl$_6$ proceeds by a conventional cationic mechanism.

In contrast to the case of styrene, the ρ^+ value was a very small negative (−0.47) in the polymerization of phenylacetylene by WCl$_6$. This value clearly demonstrates that the reaction does not proceed by a conventional cationic mechanism. Meanwhile, the ρ^+ value was −2.30 in the copolymerization of styrene with ring-substituted phenylacetylenes by SnCl$_4$ · TCA. The mechanism of reaction of phenylacetylene with styryl cation should be similar to that of the propagation reaction in the conventional cationic polymerization of styrene.

It was made clear from molecular orbital calculation and ^{13}C chemical shift that the electron density on the β carbon of phenylacetylene increases when an electron-donating substituent is introduced. The polymerization of phenylacetylene by WCl$_6$ was favored by an electron-donating substituent. Therefore, this reaction should be electrophilic, though its mechanism is not a conventional cationic one.

As described above, the substituent effect on the polymerization of phenylacetylene by WCl$_6$ is obviously different from that expected for a conventional cationic polymerization. WCl$_6$, which is used as catalyst in this experiment, is well known as a very effective catalyst component for the metathesis reaction of olefin. Consequently, it is very probable that the present polymerization is a novel coordination polymerization. The features of this polymerization will be made clearer in further investigations.

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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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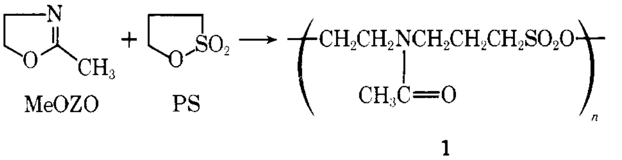
ABSTRACT: Ring-opening copolymerization of 2-methyl-2-oxazoline (MeOZO) with 3-hydroxy-1-propanesulfonic acid sultone (PS) was studied. The copolymerization took place without added initiator to produce 1:1 alternating copolymer of MeOZO and PS. The structure of the copolymer was determined by ir and 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.



$$-\!\!\left(CH_2CH_2N(C(=O)CH_3)CH_2CH_2CH_2SO_2O\right)_n\!\!- \quad (1)$$

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

$$1 \xrightarrow[D_2O]{NaOH} DOCH_2CH_2NDCH_2CH_2CH_2SO_3Na + CH_3CO_2Na \quad (2)$$

2