Macromolecules 1982, *15*, 255–258

Formation of Macrozwitterions in the Cationic Polymerization of 2-Methyl-2-oxazoline Initiated by *o*-Sulfobenzoic Anhydride

Man Jung Han*

Department of Chemical Engineering, Ajou University, Suweon 170, South Korea

Ji Young Chang and Youn Young Lee

Department of Chemistry, Seoul National University, Seoul 151, South Korea.

Received April 28, 1981

ABSTRACT: The cationic polymerization of 2-methyl-2-oxazoline in acetonitrile initiated by *o*-sulfobenzoic anhydride is investigated. The polymerization proceeds via a zwitterionic mechanism, and the resulting polymers are found to be macrozwitterions, i.e., poly(2-methyl-2-oxazoline), having *o*-(iminocarbonyl)benzenesulfonate anion at the one end and 2-methyl-*N*-alkyloxazolinium cation at the other end, in accordance with characteristics of their IR and NMR spectral data. The existence of negative charge on the polymer chain is proven by electrophoresis after destruction of the oxazolinium ion with NaOH. No transfer or chain branching occurred during the polymerization. The molecular weight of the polymer can be controlled by changing the mole ratio of monomer to initiator, and it coincides with the degree of polymerization. The isolated polymer can start a new polymerization.

Introduction

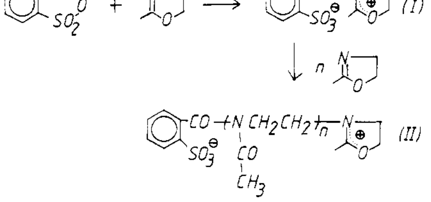
Macrozwitterion is defined as a polymer molecule having a cation at one end and an anion at the other end of the polymer chain. Macrozwitterions, contrary to conventional polymers, are expected to have characteristic physical properties due to the ionic end groups. By being cast as a thin film in an electrical field, for example, the macrozwitterions will exhibit the property of ferroelectricity.

The macrozwitterion, a new material in polymer chemistry, is difficult to obtain in a pure form, though many laboratories have tried to synthesize it. A direct reaction between initiator and monomer in the ionic polymerization forms a zwitterion, and then by the propagation either on the cation or on the anion of the zwitterion, the macrozwitterion can be built.[1-3] This mechanism has been repeatedly proposed for the ionic polymerization of numerous heterocyclic or vinyl monomers,[4-9] but few of them, however, have been proven to be an actual process in cationic[10] and anionic polymerization.[1-3] Moreover, the isolation of pure macrozwitterion in cationic polymerization failed due either to instability of the ions or to chain branching.

The failure in proving the zwitterionic mechanism in the cationic polymerization is rooted in the following reasons: (1) Most cationic initiators (i.e., Lewis acids) require a third substance (cocatalyst) in order to start the polymerization, so the initiation product is considered not to be a zwitterion but to be an ion pair. (2) Even though zwitterions are formed in the initiation step, most of the cations (carbonium or oxonium ions) are too unstable to be proven experimentally. It is known that proton or hydride transfers occur frequently in the active species in cationic polymerization, so zwitterion structures could be destroyed during the polymerization or storage of the polymer.

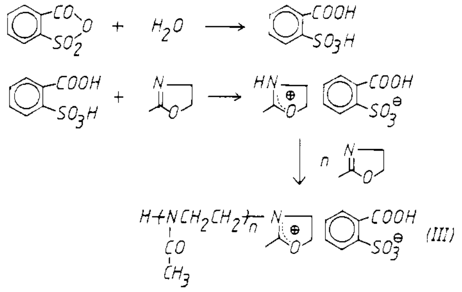
In the hope of demonstrating that the zwitterionic mechanism is operative in cationic polymerization and that stable macrozwitterions can be isolated, 2-methyl-2-oxazoline (MeOXZ), as a monomer, and *o*-sulfobenzoic anhydride (SBA), as an initiator, are chosen in this study. At the initiation of the polymerization, the nitrogen atom of the enamine in MeOXZ attacks the carbon atom of the carbonyl group in the initiator to produce a zwitterion (I), which starts the polymerization (see reaction 1).

N-Methyl-2-methyl-2-oxazolinium ion was found to be stable in the presence of tosylate anion.[11] Since the anionic end group, *o*-(iminocarbonyl)benzenesulfonate anion, is a very weak base and nucleophile, it was expected that the sulfonate ion could not react with oxazolinium ion. Consequently, the probable mutual destruction of the opposing ions during the polymerization is unlikely to take place. Furthermore, during the ring opening of the oxazolinium ion, while no carbonium ion was expected to be formed as an intermediate, the transfer reactions resulting from hydride or proton transfers could not occur.



(1)

As an alternative mechanism, by a trace of water present in the system the initiator could be hydrolyzed to a dibasic acid, which then can start polymerization as illustrated in reaction 2. In this case the initiation is the same as the usual cocatalysis mechanism.



(2)

In addition, Saegusa and co-workers[12] have reported several combinations of nucleophilic and electrophilic monomers that produce alternating copolymers where zwitterions were considered to be essential intermediates responsible for the initiation and alternating propagation.

Experimental Section

Materials. *o*-Sulfobenzoic anhydride (SBA) was distilled in vacuo [bp 138 °C (4 torr)] and recrystallized three times from dry benzene. 2-Methyl-2-oxazoline (MeOXZ) and acetonitrile were dried with 4A molecular sieves and distilled (bp 110 and 81.6 °C). Analysis by GC showed that the purity of MeOXZ and acetonitrile was higher than 99.5%. *n*-Butylamine was dried over KOH pellets and distilled (bp 77.8 °C). Dimethyl sulfate was distilled in vacuo [bp 76 °C (15 torr)].

Polymerization. *o*-Sulfobenzoic anhydride (2.17 g, 12 mmol) was added to a solution of 15 mL of monomer in acetonitrile (4.0 mol/L), and the polymerization was carried out with stirring in

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Table I
Polymerization of MeOXZ in Acetonitrile at 60 °C and Physical Data of Polymers

polymer	initiator	$[M]/[I]^a$	polymn time, h	conversion, %	ion conc,^{b} mol/g of polymer: anion	cation	deg^b of polymn	$M_n{}^b$
A	SBA	5	1.5	75	1.7×10^{-3}	1.7×10^{-3}	4.9	600
B	SBA	10	2.0	75	9.0×10^{-4}	8.9×10^{-4}	10.8	1100
C	SBA	20	2.0	75	5.3×10^{-5}	5.0×10^{-5}	20.2	1900
D^c	DMS^d	50	5.0	80				

[a] Mole ratios of monomer to initiator. [b] Calculated by the NMR spectra of the polymers. [c] Polymerization was carried out at 80 °C. [d] Dimethyl sulfate.

a thermostat. After 1.5 h an excess amount of diethyl ether was added to the reaction mixture, and the precipitate was filtered. The polymer was purified by dissolving it in acetonitrile and reprecipitating with diethyl ether repeatedly. The polymer was dried in vacuo at room temperature (yield 75%). Polymers having different molecular weights are obtained by changing the mole ratios of initiator to monomer.

Dimethyl sulfate (0.11 mL, 1.2 mmol) was added to a solution of 15 mL of monomer in acetonitrile (4.0 mol/L), and the polymerization was carried out at 80 °C for 5 h. Isolation and purification of the polymers were done as described above (yield 80%).

Spectra. IR, UV, and NMR spectra were recorded with a Unicam SP1000 infrared spectrometer, a Hitachi 200-20 UV spectrometer, and a Varian XL100 spectrometer, respectively.

Hydroxyl-Terminated Polymer (IV). Polymer A (0.6 g, 1 mmol) was dissolved in 4 mL of 1.5 M NaOH solution at 0 °C, and the excess NaOH was neutralized by titrating with H_2SO_4 in an ice bath. The precipitate (Na_2SO_4) formed by addition of excess MeOH was filtered. The filtrate was poured into acetone. The precipitated polymer was filtered and dried in vacuo.

Synthesis of *n*-Butylammonium *o*-[(*n*-Butylamino)carbonyl]benzenesulfonate (BSBA). To a solution of 1.8 g (0.01 mol) of *o*-sulfobenzoic anhydride in 20 mL of acetonitrile was added 2 mL of *n*-butylamine. The resulting solution was refluxed for 1.5 h. After an additional 2 h of stirring at ambient temperature, a white precipitate was isolated. The product was purified by recrystallization from acetonitrile (mp 142 °C, yield 70%). The NMR spectrum in D_2O showed signals at δ 7.41 and 7.81 for phenyl, δ 2.80 for $^+NCH_2$, and δ 3.20 for $CONCH_2$ protons. Anal. Calcd: C, 54.52; H, 7.93; N, 8.48. Found: C, 54.25; H, 7.90; N, 8.44.

Determination of Molecular Weight. Number-average molecular weights (M_n) of the polymers were measured at 37 °C in water and acetonitrile by VPO (Hewlett-Packard). Mannitol (M_w = 182.17) and benzophenone (M_w = 182.22) were standards for water and for acetonitrile, respectively.

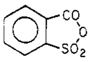
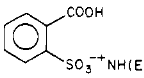
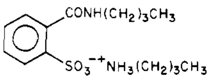
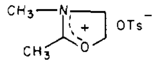
Electrophoresis. Thin-layer electrophoresis was carried out on a cellulose sheet (25 cm × 3 cm, Eastman chromatogram sheet no. 6065), which was immersed in a buffer solution of pH 8.0 at a constant 300 V for 1.5 h. The bands separated were identified by UV (1 A).

Results and Discussion

Polymerization. The polymerization was carried out in acetonitrile. Since polymer, monomer, and initiator are soluble in this solvent, the polymerization proceeded in a homogeneous phase. To facilitate end group analysis, low molecular weight polymers were made by starting the polymerization with high concentrations of initiator. So that the unconverted initiator could be removed, the polymer was purified by dissolving it in acetonitrile and then precipitating it with additions of diethyl ether repeatedly. Spectroscopic analyses showed that no initiator was present in the purified polymer. The results of several polymerizations are given in Table I.

At the onset of the polymerization it was observed that the solution became turbid and then within 1 min turned back to clear. Since it was found in the kinetic measurement of the polymerization that initiation reactions were completed within 30 s, the zwitterions (I) formed in the initiation step seem to be insoluble, and they become soluble as the chain is lengthened by propagation. The fact that the model compound BSBA is slightly soluble in acetonitrile supports this observation. The low molecular weight polymer A was a pale yellow powder, and it became colorless by increasing the molecular weight (e.g., as in polymer C). The polymer was soluble in polar solvents such as acetonitrile, alcohol, and water, whereas it was insoluble in nonpolar solvents such as benzene, toluene, hexane, and ether. High molecular weight polymer D was prepared for the purpose of comparing its end group to those of other polymers.

Table II
Model Compounds and Spectral Data

model compound	IR^a: freq, cm^{-1}	assign	NMR: δ	assign
 SBA	1750	CO	8.02^b	phenyl
 TBS[10]	1720	CO	7.85, 7.32^c	phenyl
 BSBA	1650	CO	7.42, 7.82^c 3.20^c 2.80^c 1.40^c 0.81, 0.89^c	phenyl $CONCH_2$ $^+NCH_2$ CH_2 CH_3
 MMOT[11]			4.06^d 4.80^d 3.20^d 2.29^d	NCH_2 OCH_2 NCH_3 CCH_3

[a] Spectra were taken using KBr pellets. [b] In Me_2SO-d_6. [c] In D_2O. [d] In CD_3CN.

As is shown in Table I, the mole ratios of monomer to initiator coincide with the degrees of polymerization that were calculated from anionic concentrations in the polymers determined by NMR spectra of the polymers. This result leads to the conclusion that all initiators start the polymerization. The conversions of the monomer were found to be 75%. The purification process is responsible for the rather low yield since the low molecular weight polymer is soluble in the solvent mixture ether–acetonitrile.

Polymerization Mechanism. So that the polymerization mechanism could be elucidated and the polymer structures analyzed, the spectroscopic analyses for the polymer end groups were used as the main tools. For the purpose of comparison, several model compounds such as triethylammonium *o*-carboxybenzenesulfonate (TBS), *n*-butylammonium *o*-[(*n*-butylamino)carbonyl]benzenesulfonate (BSBA), and *N*-methyl-2-methyloxazolinium tosylate (MMOT) were synthesized, and their spectral data

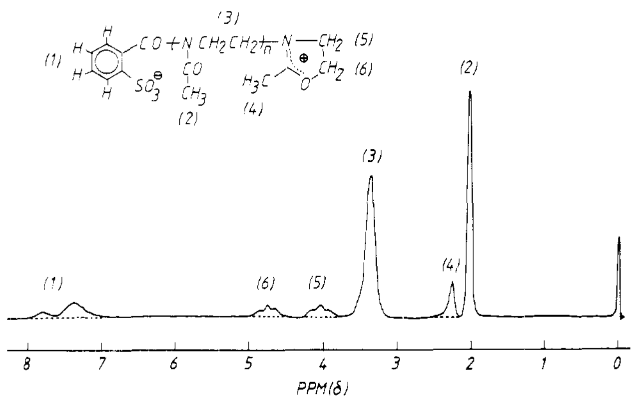


Figure 1. NMR spectra of poly(2-methyl-2-oxazoline) in $CDCl_3$: (—) polymer A, initiated by *o*-sulfobenzoic anhydride; (---) polymer D, initiated by dimethyl sulfate.

are summarized in Table II.

Since the basicity of the monomer ($pK_a = 5.5$)[13] is much higher than that of water, the initiator will react with the monomer prior to water. If initiation is caused by cocatalysis with water (reaction 2), it is expected that the resultant polymer should contain *o*-carboxybenzenesulfonate anion as the counterion. The peak corresponding to the carbonyl group of TBS at 1720 cm^{-1} was not observed in the IR spectrum of polymer A. Therefore cocatalysis by water in the initiation step seems to be improbable. In the NMR spectrum of polymer A recorded within 30 s after starting the polymerization, it was found that the peak at δ 8.02, assigned to phenyl protons of the initiator, disappeared, and new peaks at δ 7.42 and 7.82, assigned to phenyl protons of BSBA, appeared. This observation indicates the initiation step is a direct reaction between the initiator and monomer, and it leads subsequently to the formation of the zwitterion (reaction 1).

In the cationic polymerization of propylene sulfide initiated by *o*-sulfobenzoic anhydride, it was observed that the reactive episulfonium ions caused chain branching and resulting polymers were not macrozwitterions but ionic polymers.[10] However, owing to the high stability of the oxazolinium ion and low basicity of the amide nitrogen in the chain and of the sulfonate anion in the end group, chain branching or back-biting was hardly expected in this polymerization system. The oxazolinium ions remained in the polymer without any change in their concentration even after long storage at ambient temperature. A new polymerization can be started with the isolated polymer.

Polymer Structure. The NMR spectra of polymer A (solid line) and of polymer D (dotted line) are presented in Figure 1. The NMR spectrum of polymer A compared with that of polymer D gives additional peaks at δ 7.42 and 7.82, 4.06 and 4.80, and 2.29, which were assigned to the phenyl protons of anionic end group BSBA and methylene and methyl protons of 2-methyl-*N*-alkyloxazolinium ions (cationic end groups MMOT), respectively. As is given in Table I, the concentrations of the cationic and anionic end groups were measured from NMR spectra, and the concentrations of both ions were nearly equal within experimental error, as expected for the macrozwitterions. From these observations it is quite reasonable to assume that the polymer is a macrozwitterion having a cation at one end and an anion at the other end of the polymer chain as shown in structure II.

Molecular Weight. The number-average molecular weights (M_n) of the polymers were calculated on the basis of the ionic concentrations of the end groups and are given in Table I. M_n of polymer B was measured by vapor pressure osmometry in two different solvents, water and acetonitrile, and it was found to be 1100 in water, which was in good agreement with the M_n calculated from end group concentrations.

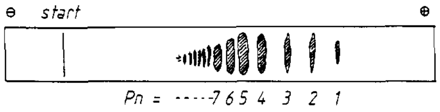
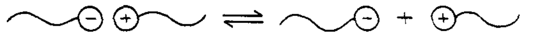


Figure 2. Electrophoresis diagram of polymer IV at a constant 300 V for 1.5 h in a pH 8 buffer solution.

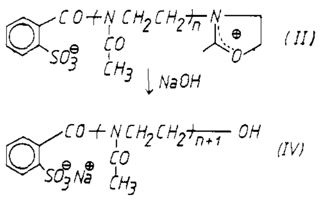
In the M_n measurement by vapor pressure osmometry in acetonitrile, the plot of difference in resistance as a function of concentration did not show a straight line. However, extrapolation of the fraction of straight line at low concentrations of polymer gives $M_n \simeq 1600$. An equilibrium between ion pairs and free ions should be maintained in the macrozwitterions.



(3)

The difference of measured M_n in different solvents is attributed to the fact that macrozwitterions are free ions in a highly polar solvent (water) and exist partly as ion pairs when the polarity of the solvent is decreased (acetonitrile).

Electrophoresis. The result of electrophoresis provides evidence for the presence of anionic end groups in the polymer chains. Macrozwitterions (II) should not migrate in an electric field. If, however, the charge balance of II is destroyed, e.g., by treatment with NaOH, a negatively charged polymer chain (IV) will result, and IV should then migrate to the anode (see reaction 4). This method should prove the presence of the negative charge on the original polymer molecule, since it is hard for any other reaction to occur between the polymer and sodium hydroxide that produces a negative charge on the polymer chain. Reaction 4 occurred under mild conditions as described in the Experimental Section. The disappearance of the peaks at δ 4.06, 4.80, and 2.29 assigned to the oxazolinium ion (MMOT) in the NMR spectrum of polymer IV confirmed that the oxazolinium ions were completely destroyed. Polymer IV was applied on an electrophoresis cellulose sheet, and the electrophoresis was run. The electrophoresis diagram is shown in Figure 2.



(4)

Under the condition that there is a single negative charge in the polymer molecule, the mobility (V) of the molecule is inversely proportional to the two-thirds power of the molecular weight (M):[14]

$$V = KZM^{-2/3} \tag{5}$$

where Z is the net charge and K is a constant. The band at the greatest distance from the starting line corresponds to the polymer having a degree of polymerization of 1, since the blank test of model compound BSBA under the same condition showed a similar distance from the starting line. According to the relationship of eq 5, all bands can be assigned to different degrees of polymerization, as shown in Figure 2.

No trace of polymer IV was detected on the starting line in the electrophoresis diagram. Under the same conditions electrophoresis of macrozwitterions (polymer A) was run, and it was found that the polymer (A) remains at the starting line as a somewhat dispersed shape. All polymer IV molecules have, therefore, a negative charge, whereas the polymer (A) molecules are macrozwitterions. These results lead to the conclusion that transfer or termination reactions did not occur during the polymerization.

Acknowledgment is made to the Ministry of Education for generous financial support of this work.

References and Notes

(1) Jaacks, V.; Mathes, N. *Makromol. Chem.* **1970**, *131*, 295.
(2) Mathes, N.; Jaacks, V. *Makromol. Chem.* **1971**, *142*, 209.
(3) Jaacks, V.; Franzmann, G. *Makromol. Chem.* **1971**, *143*, 283.
(4) Ludwig, E. B.; Gantmacher, A. R.; Medvedev, S. S. *Symp. Macromol. Chem., Wiesbaden* **1959**, Paper IIIA, 12.
(5) Kern, W.; Jaacks, V. *J. Polym. Sci.* **1960**, *48*, 399.
(6) Jaacks, V.; Kern, W. *Makromol. Chem.* **1963**, *62*, 1.
(7) Bown, C.; Ledwith, A.; Matheis, P. *J. Polym. Sci.* **1959**, *34*, 93.
(8) Yamashita, Y.; Okada, M.; Suyama, K. *Makromol. Chem.* **1968**, *111*, 277.
(9) Meerwein, H.; Delfs, D.; Morshel, H. *Angew. Chem.* **1960**, *72*, 927.
(10) Han, M. J. *J. Korean Chem. Soc.* **1978**, *22*, 173.
(11) Saegusa, T.; Ikeda, H.; Fujii, H. *Polym. J.* **1973**, *4*, 87.
(12) (a) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1972**, *5*, 354. (b) Saegusa, T.; Kobayashi, S.; Kimura, Y. *Ibid.* **1977**, *10*, 68, 236, 239. (c) Saegusa, T.; Kobayashi, S.; Furukawa, J. *Ibid.* **1975**, *8*, 703. *Ibid.* **1976**, *9*, 728. *Ibid.* **1977**, *10*, 73. (d) Saegusa, T.; Kobayashi, T.; Chow, T. Y.; Kobayashi, S. *Ibid.* **1979**, *12*, 533.
(13) Weinberger, M. A.; Greenhalgh, R. *Can. J. Chem.* **1963**, *41*, 1038.
(14) Morris, C. J. O. R., et al. "Separation Methods in Biochemistry"; Wiley: New York, 1976.

Molecular Weight Dependence of Lamellar Structure in Styrene/Isoprene Two- and Three-Block Copolymers

George Hadziioannou[†] **and Antoine Skoulios***

CNRS, Centre de Recherches sur les Macromolécules, 67083 Strasbourg-Cedex, France.
Received December 19, 1980

ABSTRACT: The lamellar structure of three homologous series of SI, SIS, and ISI block copolymers, 50% by weight polystyrene, was studied as a function of molecular weight with low-angle X-ray diffraction. From the structural standpoint, the three-block copolymers behave identically with the corresponding two-block copolymers of half the molecular weight. Helfand's thermodynamic predictions for the value of the lamellar thickness are in fair numerical agreement with the experimental facts; however, the observed lamellar spacing increases with molecular weight a little more steeply than predicted. Finally, the molecular area, calculated from Helfand's theory as a function of chemical composition at constant lamellar thickness, is independent of the exact position of the interface within the lamella. The general impression is that for two-block copolymers the arrangement of the sequences in the lamellae would be close to a double-layer arrangement. This would imply little interpenetration of the molecules in a direction normal to the interfaces.

Introduction

Since their discovery, the mesomorphic phases of block copolymers have been the subject of many studies. Some of these aimed to establish the generality of the spontaneous liquid-crystalline organization observed and to describe the main structures involved. Others analyzed the dependence of the structure on various factors such as temperature, solvent concentration, composition of the copolymer, and molecular weight.[1-5]

Most of the studies that considered the role of molecular weight were carried out with binary mixtures of copolymer and solvent. They showed that the dimensions of the segregated microdomains were comparable to those of the macromolecules themselves and that they increased monotonically with the length of the blocks.[1,2] Their quantitative analysis is, however, complicated because it is necessary to take into account the particular role of each solvent used. Whether good or bad, the solvents can in fact be preferential to some extent for each type of block.

Several studies have nevertheless been performed in the absence of solvent. Based on scattered results obtained from an incomplete and truncated series of styrene/isoprene or styrene/butadiene block copolymers, the conclusions are still neither very coherent nor convincing. For instance, Vanzo[6] and Kawai[7] pointed out for the case of the lamellar structure that the thickness of the layers is proportional to the square root of the molecular weight. Later, Krömer[8] stated that the dimensions of the segregated microdomains are proportional to the molecular weight raised to the 0.55–0.60 power. Later still, Gallot[9] simply announced that the structural parameters increase with the length of the blocks in a monotonic fashion. Concerning the role of the molecular structure, he added that on going from a given two-block to the related three-block copolymer (obtained from the former by the addition of a new block), the thickness of the lamellae decreases markedly.

Regarding the role of the molecular weight on the occurrence and the stability of the mesomorphic phases, it has not been possible to tackle the problem experimentally. As far as we are aware, only one study has touched on this question. This study[10] concerns the change in the mechanical behavior of styrene/butadiene block copolymers which was observed above a threshold of molecular weight of about 10 000 and which was interpreted as being related to microphase separation.

All previous studies, the earliest of which were made 15 years ago, have been accompanied by theoretical explanations based on thermodynamics.[7,8,11-22] We will return to this later.

In order to try to clarify the situation, we decided to repeat the earlier work and study further styrene/isoprene

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[†] Present address: Polymer Research Institute, University of Massachusetts, Amherst, Mass. 01003.

0024-9297/82/2215-0258$01.25/0