Notes

Ionic Polymerization under an Electric Field. XIV. Evidence Against Electrolytic Mechanism

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In this laboratory, various polymerizations have been studied under an electric field. It was found that the electric field increased the rate and the degree of polymerization for some ionic polymerization systems.[1] It appeared to be possible that three factors were responsible for the observed field effect: Joule heat, electrolytic reactions, and effects of an electric field. The factor of Joule heat could be definitely denied.[2] The contribution of the electroinitiated or electrolytic polymerization[3] was also ruled out on the basis of the study on the living anionic polymerization under electric field.[4] In this note, we study the possible influence of the electrolytic reactions on cationic polymerizations.

The polymerization of α-methylstyrene catalyzed by boron trifluoride etherate (BF_3OEt_2) in 1,2-dichloroethane (DCE) was chosen, because the accelerating effect of an electric field was fairly large,[2] and because the reproducibilities of the rate of polymerization, the field effect, and the conductivity were satisfactory.

In order to obtain different current intensities at a given electric field strength, five kinds of glass vessels were used in this work, which are shown in Figure 1. The glass vessels, a, b, c, d, and e, have two, three, four, five, and six platinum parallel square plate electrodes, respectively. The distance between top and bottom electrodes is 25 cm for all glass vessels, and the volume is 42 ml. Other electrodes are fixed at intervals of 25/2 cm, 25/3 cm, 25/4 cm, and 25/5 cm for the vessels b, c, d, and e, respectively.

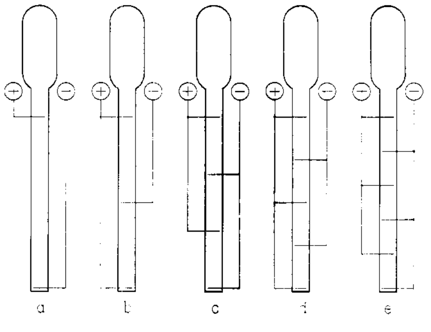

Figure 1. Glass vessels for polymerization under an electric field: ⊖, cathode; ⊕, anode.

TABLE I

DEPENDENCES OF THE POLYMERIZATION RATE ON CURRENT STRENGTH AND ON CURRENT DENSITY AT AN ELECTRIC FIELD STRENGTH OF 1.0 kV/cm[a]

Glass vessel[b]	$R_p \times 10^3$, mol/l. min	Current strength,[c] μA	Current density for anode, μA/cm²	Current density for cathode, μA/cm²
a	3.62	6.6	3.3	3.3
b	4.24	10.3	2.58	5.15
c	3.66	25.0	6.25	6.25
d	3.71	29.8	4.97	7.45
e	4.10	45.0	7.50	7.50

[a] α-Methylstyrene-BF_3OEt_2–1,2-dichloroethane system: $[\alpha\text{-MSt}]_0 = 0.80$ mol/l., $[BF_3OEt_2]_0 = 8.0 \times 10^{-5}$ mol/l., temperature −12.0°; R_p at 0 kV/cm = 2.80×10^{-3} mol/l. min. [b] See Figure 1. [c] At 10 min.

Immediately after the onset of the polymerization, a (dc) high voltage was applied to the polymerizing solution. The electric field strength was 1 kV/cm for all vessels. All polymerizations were performed at −12.0°.

The results obtained are given in Table I. The rate of polymerization R_p was determined as previously.[2] According to our previous experiments[2] with a glass vessel of a volume of 15 ml, the observed temperature rise by Joule heat was 0.6° at 0.21 W. In the present work, the electric power was 0.23 W at most and the glass vessel (42 ml) was larger than that in the previous work.[2] Therefore, we may expect that in the present work the temperature rise should be smaller than 0.6°, which is negligible.

Since the polymerization rate was 2.80×10^{-3} mol/l. min in the absence of an electric field, it is seen from Table I that the field application clearly increased the rate by about 40% beyond the experimental error. If electrolytic reactions were responsible for the observed rate enhancement, the polymerization rate with the field should depend on the current strength and current density. However, Table I shows that the polymerization rate stayed almost constant, whereas the current strength varied about sevenfold and the density changed about twofold. Therefore, the field-accelerating effect mentioned above was not caused by the electrolytic reactions.

A possible objection to this argument is that the range of the current strength used in our experiment might be in a saturation region. This objection can be rejected as follows. The previous data obtained for the same system[2] (Figures 4 and 12 in ref 4) showed that the field effects linearly increased with the field strength, and also with the current strength, which was in a range between 60 and 220 μA. This clearly indicates that the saturation phenomena can be put out of consideration at the present current strength (6.6∼45 μA).

Finally it would be useful to mention additional infor-

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(2) I. Sakurada, Y. Tanaka, and N. Ise, *J. Polym. Sci., Part A-1*, **6**, 1463 (1968).

(3) For example, B. L. Funt, S. N. Bhadani, and D. Richardson, *ibid., Part A-1*, **4**, 2871 (1966); N. Yamazaki, S. Nakahama, and S. Kanbara, *Polymer Lett.*, **3**, 57 (1965).

(4) I. Sakurada, N. Ise, H. Hirohara, and T. Makino, *J. Phys. Chem.*, **71**, 3711 (1967).

mation. No polymer was produced by applying 5kV/cm to an α-methylstyrene–DCE solution ($[\alpha\text{-MSt}]_0$ = 0.80 mol/l.) without BF_3OEt_2 for 5 hr. This result implies that the polymerization can be started neither by an direct electron transfer to monomer nor by an electrolysis of solvent. Furthermore, we subjected a catalyst solution ($[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mol/l.) to an electric field (1.6 kV/cm) for 2 hr before the monomer was added and carried out the polymerization in the absence of the field. The observed polymerization rate agreed with that obtained by using a catalyst solution without the preelectrolysis treatment. According to this finding, it is highly improbable that active species were produced electrolytically from the catalyst and solvent.

The molecular weight of the polymer produced was not reproducible and the field influence on this quantity was undetectable.

Communications to the Editor

The Solvent Effect on the Composition of Styrene Polysulfone

It is well known that the aliphatic olefins, such as ethylene, propylene, and the butenes, form alternating copolymers with liquid sulfur dioxide by means of a radical initiator.[1] Styrene also copolymerizes with liquid sulfur dioxide radically, and forms styrene polysulfones having various copolymer compositions. The composition depends mainly on the polymerization temperature but hardly on the feed composition.[2,3] These results suggest that the familiar equation for copolymer composition, *i.e.*, the Mayo/Lewis equation, cannot be applied to the copolymerization of the styrene/liquid sulfur dioxide system. Thus, Barb[1] has introduced the concept of participation of a 1:1 styrene/liquid sulfur dioxide complex in propagation in order to interpret the kinetics of the copolymerization of styrene with liquid sulfur dioxide. However, an entirely equivalent scheme can be derived without invoking complex participation.[4] Concerning this matter, we have already been investigating the copolymerization of various styrene derivatives with liquid sulfur dioxide, but we could not clarify the mechanism of the propagation.[5-7] The present paper is concerned with the solvent effect on the composition of styrene polysulfone, and the results obtained here offer a key for the solution of the propagation mechanism.

The radical copolymerization of styrene and liquid sulfur dioxide was carried out with α,α′-azobisisobutyronitrile (AIBN) as an initiator at 50 and 80°. The mole fraction of styrene in the feed was kept constant at 0.8 or 0.2, but the initial total monomer concentration of styrene and liquid sulfur dioxide was varied from 1.0 to 9.0 mol/l. by adding such solvents as *o*-dichlorobenzene, cyclohexane, sulfolane, nitrobenzene, and pyridine, respectively. With the exception of the cyclohexane solvent, polymerization proceeds in a homogeneous system. After allowing the copolymerization to proceed to not more than 5% conversion, the copolymer was isolated into methanol, and then it was reprecipitated from dioxane/methanol. The composition of copolymer was determined by carbon analysis.

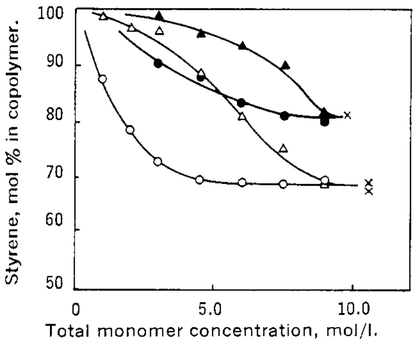

Figure 1. Copolymer composition curves which were obtained from pyridine [—△— (50°), —▲— (80°)] and sulfolane [—○— (50°), —●— (80°)] as added solvents, respectively. The styrene mole fraction in feed was kept constant at 0.8.

The results of the copolymerizations at 50° are summarized in Tables I and II, in which the styrene feed compositions were kept constant at 0.8 and 0.2, respectively. From these tables, it can be seen that the copolymer compositions at fixed feed composition vary not only with the nature of solvents used, but also with the initial total monomer concentrations. The typical results are plotted in Figure 1. It is most likely from Tables I and II and Figure 1 that the solvent effect can be divided into two groups, that is, pyridine and the remaining solvents of which sulfolane is a representative example. The styrene mole fraction in the copolymer increases by the addition of pyridine, which is known to form a strong charge-transfer complex with liquid sulfur dioxide.[8] With the other solvents, mutual interaction with liquid sulfur dioxide is rather small, and it does not have an effect in a region of comparably higher monomer concentrations. However, even in these solvents, at lower monomer concentrations, the styrene mole fraction in the copolymer increases with increasing solvent volume fraction.

It is quite possible to interpret this dilution effect as a characteristic of polymerization involving a charge-transfer complex, providing that a depropagation has

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