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An Anomalous Cathode-Initiated Copolymerization of Styrene and Methyl Methacrylate on the Electrode

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ABSTRACT

The cathode-initiated copolymerization of styrene and methyl methacrylate (MMA) in dimethylformamide yielded a copolymer which was found to be a mixture of the high and low molecular weight copolymers. The composition of the former, rich in MMA, was similar to that of a typical anionic copolymer. The latter, of anomalously high styrene content, was assumed to be produced on the cathodic surface via an anionic process, where styrene monomer was preferentially adsorbed. This was confirmed by capacitance measurement of the electrode and sequence analysis of the copolymer.

Electroinitiated polymerization is affected by the solvent, supporting electrolyte, electrode material, etc. [1, 2]. In the electroinitiated copolymerization of styrene and methyl methacrylate (MMA), initiation and propagation processes and monomer composition in the copolymers produced varied drastically by the

solvent and supporting electrolyte used [1]. In tetrahydrofuran (THF) the anionic copolymerization of styrene and MMA was initiated at the cathode, and cationic polymerization initiated at the anode was suppressed. On the other hand, in 1,1-dichloroethane, only anodically initiated cationic copolymerization proceeded. Ammonium salts, such as tetrabutylammonium tetraphenylborate and bromide, as supporting electrolytes, hindered cationic chain growth in 1,1-dichloroethane, but not anionic chain growth.

Dimethylformamide (DMF) has been regarded as a suitable solvent for anionic polymerization. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) does not have an appreciable effect on anionic propagation. Therefore, the cathode-initiated copolymerization of styrene and MMA carried out in DMF with Bu_4NBF_4 ruled out normal anionic copolymerization [1]. The styrene composition in the copolymer was nearly equal to that in the feed, which was far different from the usual anionic copolymerization. Some comments were offered by Funt et al. to explain the anomalous behavior [1]; (1) Specific solvation of monomers with DMF and complex formation with the salt reduce the variation in the reactivity of the monomer pair. (2) A high dielectric-constant solvent, such as DMF, results in an increased concentration of free growing anions whose relative reactivities may be comparable in DMF. (3) The adsorption of styrene monomer on the electrode surface, which may possibly enhance the incorporation of styrene in the copolymer, is not the case.

In our opinion, it is worthwhile to call attention to the third point. There were some evidences for the adsorption of butadiene and isoprene on the platinum anode in Kolbe electrolysis [3]. The methyl radical from Kolbe electrolysis attacked butadiene and isoprene to yield trans-3-hexene and cis-3-methyl-3-hexene to the exclusion of cis-3-hexene and trans-3-methyl-3-hexene, respectively. The observed stereospecific mode of addition suggests the adsorption of the intermediates on the electrode surface.

Some experimental results obtained in this study also suggested that the adsorbed monomer on the cathodic electrode surface influenced the electrolytic copolymerization. The polymer produced was found to be a mixture of two copolymers by gel-permeation chromatography (GPC) and was separated into a MMA-rich and a styrene-rich copolymer, with the latter contributing to the anomalous behavior. The electrode, solvent, and supporting electrolyte affected the formation of the styrene-rich copolymer, and the effect was related with the adsorption of styrene monomer on the electrode surface as suggested by the capacitance measurement of the electrode. It is considered that the MMA-rich copolymer is produced via normal anionic process and that another anionic polymerization, which occurred on the surface of the platinum electrode and involved the adsorption of styrene monomer, yielded the styrene-rich copolymer.

EXPERIMENTAL

Materials

Monomers. Styrene and MMA were dried over calcium hydride and distilled into the electrolysis cell through a vacuum line.

Solvents. DMF was dried over potassium hydroxide by stirring overnight. Furthermore, it was dried over calcium hydride and distilled twice under reduced pressure. THF and dimethoxyethane were dried over LiAlH_4 and distilled. Other solvents were purified by the method similar to that used for DMF.

Supporting electrolytes. Tetra-*n*-butylammonium tetrafluoroborate, perchlorate, and hexafluorophosphate were synthesized from tetra-*n*-butylammonium iodide and potassium tetrafluoroborate, perchlorate, and hexafluorophosphate, respectively, and recrystallized from ethyl acetate. Other tetra-alkylammonium iodides, special grade, were used without further purification.

Electroinitiated Copolymerization

Electrolysis was conducted at 0°C in the H-type glass cell, which was separated into cathodic and anodic compartments by sintered glass. The smooth platinum electrodes ($1.0 \times 2.5 \text{ cm}^2$) were sealed into the apparatus. The cell, which contained 0.23 g of Bu_4NBF_4 , was dried under vacuum ($<10^{-4}$ Torr) for about 6 hr, and then styrene (65 mmoles), MMA (65 mmoles) and DMF (35 ml) were distilled on a vacuum line into the cell. After 0.10 to 0.15 mF of current was passed, catholyte and anolyte were treated by methanol individually. No polymer was found in the anolyte. The copolymer obtained from the catholyte was filtered off and washed with methanol. After the filtrate was evaporated to dryness under reduced pressure, the copolymer was extracted from the residue by ether which did not dissolve Bu_4NBF_4 . The methanol-soluble and -insoluble copolymers were combined and purified by the freeze-drying method from benzene solution. The styrene/MMA ratio in the copolymer was estimated from the absorbances at 706 and 1720 cm^{-1} which were attributed to styrene and MMA units, respectively.

Capacitance Measurement

Capacities of microplatinum and dropping mercury electrodes were measured at varying potentials under conditions similar to that of electrolysis by employing Universal Bridge, Model 4255A, Yokokawa-Hewlett-Packard.

RESULTS AND DISCUSSION

As shown in Fig. 1, the monomer-polymer composition curve for the electroinitiated styrene-MMA copolymerization was obtained in accordance with the result of Funt et al. [1] within experimental error. The curve itself has not a significant meaning because the polymer produced was found to be consist of two copolymers by GPC measurement. From a comparison of the curve (dashed line) for adsorption at 260 nm and the curve (solid line) for differential refractive index vs elution volume in the GPC chart (Fig. 2), it was obvious that the lower molecular weight copolymer was rich in styrene units and the higher molecular weight copolymer included only a small amount of styrene units in its chain. Figure 3 shows the GPC curves of the copolymers before and after the extraction with cyclohexane. The extraction of the styrene-rich copolymer from the mixture was not satisfactory. The composition curves of the each copolymer, cyclohexane-soluble and -insoluble, are revealed again in Fig. 4. The composition diagram for the MMA-rich copolymer almost coincides with that for typical anionic copolymerization.

The other curve of the styrene-rich copolymer cannot be interpreted by an ordinary mechanism. The total styrene content decreased a little with an increasing amount of current passed as shown in Fig. 5, and the anomalous behavior was still observed up to 40% conversion. The styrene-rich copolymer, which was

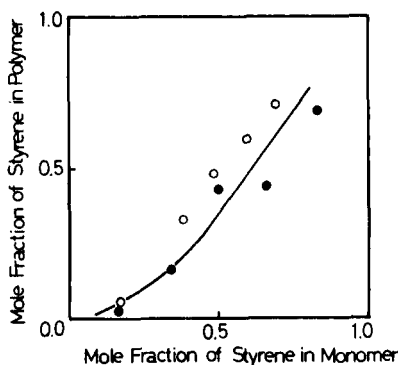


FIG. 1. The monomer-polymer composition curve for the electroinitiated styrene-MMA copolymerization. Solvent, DMF. Supporting electrolyte, Bu_4NBF_4 . Temperature of electrolysis, 0°C . (○) Results of Funt et al. [1], (●) Results of this study.

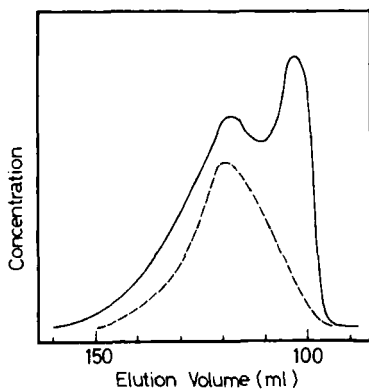


FIG. 2. Gel-permeation chromatogram of the styrene-MMA copolymer produced electrolytically. The concentration of the eluate was measured by differential refractive index (—) and absorbance at 260 nm (- -). Electrolysis conditions as described in the Experimental section. Flow rate, 1.0 ml THF/min.

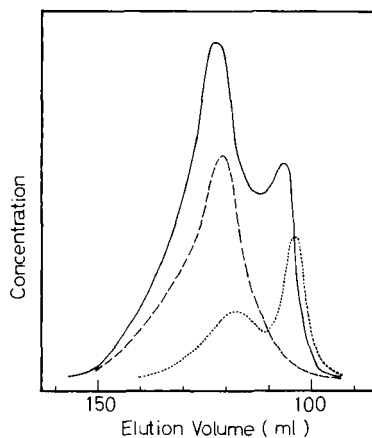


FIG. 3. Gel-permeation chromatograms of the cyclohexane soluble (- -) and insoluble (· ·) copolymers. The concentration of the eluate was measured by differential refractive index. The solid line shows the GPC of the original copolymer before extraction. Electrolysis conditions as described in the Experimental section. Flow rate, 1.0 ml THF/min.

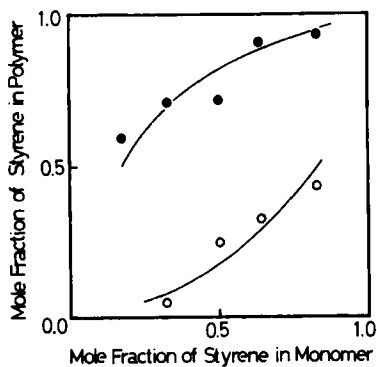


FIG. 4. The composition diagrams of the MMA-rich (○) and styrene-rich (●) copolymers. Electrolysis conditions as described in the Experimental section.

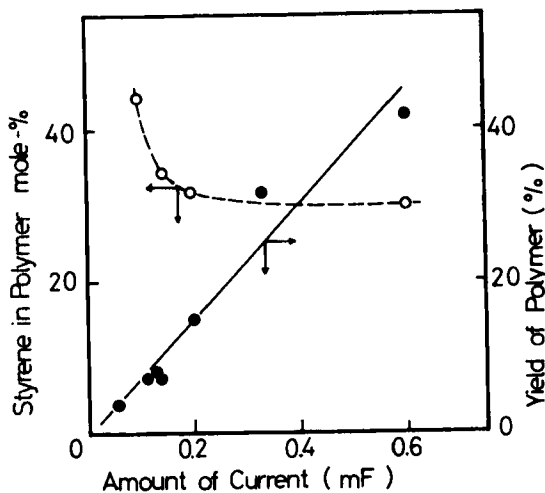


FIG. 5. The styrene content in the copolymer and the yield of the copolymer vs the amount of current passed. Electrolysis conditions as described in the Experimental section except for the amount of current passed.

produced by the anomalous cathode-initiated copolymerization, was considered to be formed via an anionic process from the following results. Radical inhibitors, such as hydroquinone and DPPH, had no effect on the formation of the styrene-rich copolymer at the cathode. A significant amount of styrene and MMA blocks were found to be included in the styrene-rich copolymer by NMR measurement, indicating anionic propagation. The triad sequences of (SSS) and (MMM) (S, styrene unit; M, MMA unit) were 80% and those of (SMS) and (MSM) were less than 2% on the assumption that the cotacticity, σ , was 0.48 [4]. It is unlikely that cationic copolymerization takes place in the cathodic compartment.

The addition of Bu_4NBF_4 to a typical copolymerization mixture, i.e., styrene, MMA, *n*-butyllithium, and DMF, did not result in the styrene rich-copolymer, but in a usual MMA-rich copolymer. This indicates that Bu_4NBF_4 has not a sufficient effect to vary the reactivities of the monomers.

The adsorption of styrene monomer on the electrode surface may be involved in the formation of the styrene-rich copolymer. As shown in Table 1, the styrene-rich copolymer was produced with platinum, copper, nickel, silver, and carbon electrodes, but not with a mercury electrode. From the capacitance measurements of the electrode, it was suggested that styrene monomer was adsorbed on the platinum electrode surface and desorbed from the mercury electrode surface at a certain potential in the Bu_4NBF_4 -DMF solution. As shown in Fig. 6, the addition of styrene to the Bu_4NBF_4 -DMF solution caused a decreasing of the capacity of the platinum electrode when the electrode potential was changed in the less noble direction, and the

TABLE 1. Effect of Electrode Materials on Monomer Composition in the Copolymer^a

Electrode material	Styrene unit composition (%)	Polymer yield (%)
Mercury	1	11.4
Platinum	35	6.4
Copper	43	5.0
Nickel	43	4.6
Silver	35	5.8
Glassy carbon	32	6.8

^aConditions of polymerization: amount of current passed, 0.11 ~0.14 mF; temp, 0°C; monomer, styrene 65 mmoles, MMA 65 mmoles; solvent, DMF 35 ml; supporting electrolyte, Bu_4NBF_4 , 0.67 mmole.

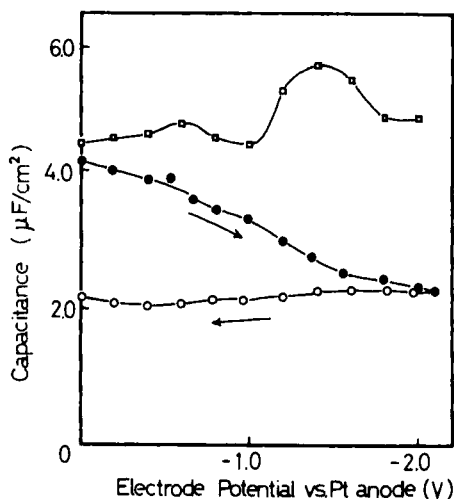


FIG. 6. Capacitance of platinum electrode vs electrode potential. Surface area of the microplatinum electrode is $2.48 \times 10^{-2} \text{ cm}^2$. Capacitance was measured at 0°C in the DMF (30 ml)-Bu₄NBF₄ (0.5 g) solution (□) in the presence of styrene (●, cathodic scan; ○, anodic scan).

hysteresis effect was observed in the reverse scanning, suggesting the adsorption of styrene monomer on the electrode. On the other hand, the addition of MMA did not affect the capacity of the platinum electrode. With the mercury electrode, adsorption and desorption peaks of styrene monomer were observed, but not of MMA (Fig. 7). As enough potential to desorb styrene monomer was impressed at the electrolysis, the styrene-rich copolymer was not produced with the mercury electrode.

Adsorption of styrene monomer on the platinum electrode was not observed in *N*-methylpyrrolidone in the capacitance curve shown in Fig. 8. This is consistent with the result that the styrene-rich copolymer was not formed at the platinum cathode in *N*-methylpyrrolidone. As shown in Table 2, only two solvent used in this study, DMF and hexamethylphosphortriamide, were suitable for the formation of the styrene-rich copolymer.

R₄NI (R; ethyl, propyl, and butyl) exhibited an effect similar to the case of Bu₄NBF₄ in the formation of the styrene-rich copolymer, whose molecular weight was lower than that of the MMA-rich copolymer (Fig. 2). These results suggested that the R₄N⁺ ion, which was enriched in the vicinity of the cathode, terminated the

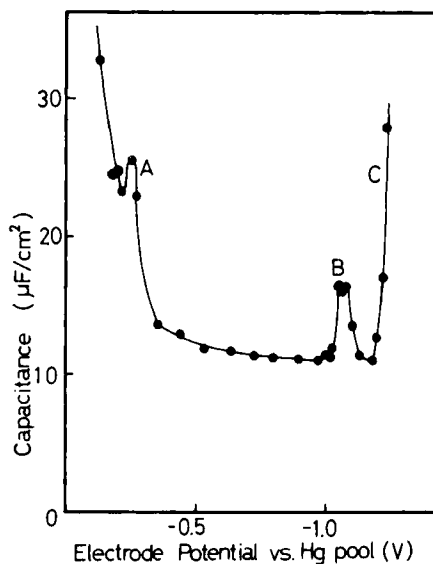


FIG. 7. Capacitance of dropping mercury electrode vs electrode potential. Capacitance was measured at 0°C in the DMF (30 ml)- Bu_4NBF_4 (0.5 g) solution in the presence of MMA (1.0 ml) and styrene (2.0 ml). (A) Adsorption peak of styrene. (B) Desorption peak of styrene. (C) Electron transfer to MMA.

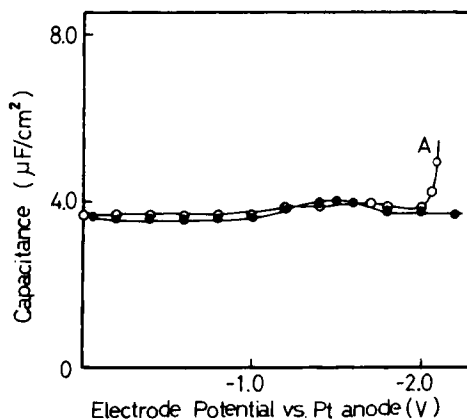


FIG. 8. Capacitance of platinum electrode vs electrode potential. Capacitance was measured at 0°C in the N-methylpyrrolidone (30 ml)- Bu_4NBF_4 (0.5 g) solution in the absence (\bullet) and the presence (\circ) of styrene (2.0 ml). (A) Electron transfer to styrene.

TABLE 2. Effect of Solvent on Monomer Composition in the Copolymer^a

Solvent	Styrene unit composition (%) ^b	Polymer yield (%)	Amount of current (mF)
DMF	35	6.4	0.14
HMPA	20	6.4	0.03
Dimethylacetamide	12	13.4	0.06
N-Methylpyrrolidone	7	14.8	0.07
Dimethoxyethane	10	13.0	0.02
Dimethylsulfoxide	3	2.6	0.14
Bulk	2	1.0	0.01

^aConditions of polymerization: temp, 0°C; monomer, styrene, 65 mmoles, MMA, 65 mmoles; electrode, platinum; supporting electrolyte, Bu₄NBF₄, 0.67 mmole.

^bTotal styrene content.

anionic chain growth to produce the low molecular weight copolymer on the cathodic surface in preference to that in the solution. Using (CH₃)₄N⁺ instead of higher alkyl ammonium salt, the polymer gave only one peak on the GPC chart and had an extraordinarily higher styrene content than that of the conventional anionic copolymer. This seems to be due to the lack of termination with (CH₃)₄N⁺ because it has no reactive β-proton [5]. Contrary to quaternary ammonium ion, exclusively normal anionic copolymerization proceeded in DMF with sodium tetrafluoroborate.

The temperature and current density of electrolysis had little effect on the anomalous behavior of this electroinitiated copolymerization in the range of -35 to 40°C and 1 to 10 mA/cm².

From the results obtained in this study on the cathode-initiated copolymerization of styrene and MMA in the Bu₄NBF₄-DMF solution, it is considered that two types of anionic copolymerization took place; one was normal in the cathodic solution and the other yielded the styrene-rich copolymer on the platinum electrode surface, where styrene monomer was preferentially adsorbed.

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