

Electroinitiated Polymerization of Methyl Methacrylate in Aqueous Sulfuric Acid

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Synopsis

The polymerization of methyl methacrylate electroinitiated at the cathode was examined in concentrated solutions of the monomer containing aqueous sulfuric acid. The initiating reaction is not due to the formation of hydrogen atoms, as demonstrated by varying the nature of the cathode and of the acid, but involves the participation of the polymeric peroxide contained in the monomer. The cathodic material greatly affects the molecular weights and the yields, as does the composition of the solutions. Lead cathodes, which proved to be particularly efficient, showed phenomena of adsorption of both monomer and polymer. Kinetic curves are similar to those obtained in conventional radical polymerizations of MMA; a marked gel effect, limiting the termination reaction and leading to very high molecular weights, was observed.

INTRODUCTION

The electroinitiated polymerization of methyl methacrylate (MMA) in acid solutions has received a certain deal of attention, especially as far as the cathodic process is concerned. In the early papers, the view was generally accepted that the cathode-initiated polymerization was due to the formation of active hydrogen atoms.¹⁻⁵ Indeed, these species are obviously formed in such solutions and, furthermore, the efficiency of the cathodes in inducing the polymerization was seen to depend on their chemical nature. A correlation between hydrogen overvoltage and efficiency was attempted,¹⁻³ but it seemed immediately questionable, for only a few cathode materials were considered and some of them do not follow such a correlation. Albeck⁶ and Shelepin⁷ criticized the theory of initiation by hydrogen atoms; in particular, the second author was able to demonstrate, by very accurate experiments, that no electroinitiated polymerization could occur in highly purified solutions of MMA in H₂SO₄.^{7,8} According to this author, peroxides of MMA may play an important role in its polymerization. Also Schouten⁹ recognized the importance of the presence of such peroxides in the bulk polymerization of MMA. Shelepin has also shown, with overvoltage-current density curves on Pb and Hg electrodes,^{7,8} the importance of adsorption phenomena of both the monomer and the polymer on the cathode.

Apart from the disagreement on the mechanism of initiation, an absolute lack of kinetic investigation was noticed in the above papers, which prevents any comparison between electroinitiated and conventional polymerization.

Also, the influence of the electrolyte composition on the yields and molecular weights has received very scarce attention. Finally, all papers refer to dilute monomer solutions, which prevents the formation of significant amounts of poly(methyl methacrylate) (PMMA), which may be desirable from a practical point of view.

This further investigation seemed to be worthwhile. In this paper, we report the results of a study of the cathodic polymerization of MMA in solutions having a high monomer and sulfuric acid concentrations.

EXPERIMENTAL

Materials

MMA (Fluka product) was purified by fractional distillation under reduced pressure and stored at 4°C. It was employed within a week from distillation, the results being no more satisfactorily reproducible for polymerizations made with more aged monomer.

The presence of peroxides in the monomer was ascertained by a test proposed by Barnes¹⁰; MMA was shaken with a freshly prepared saturated solution of KI; the appearance of a yellow color of I₂ in the MMA layer indicated the presence of peroxides.

Sulfuric Acid, 96% (Merck product), was used without further purification, because its content of impurities was insufficient for any unwelcomed catalytic activity. To ascertain whether traces of H₂SO₃ might exert an activity in the polymerization of MMA, as reported by Mukherjee,¹¹ an experiment was made after oxidation with KMnO₄; polymer was again obtained.

Apparatus and Procedure

The solutions were prepared at room temperature avoiding overheating during the mixing. In fact, it will be later pointed out that MMA-H₂SO₄-H₂O solutions can give a spontaneous polymerization, which is favored by an increase in temperature.

The polymerizations were made at 25°C in two compartment cells having a sintered glass disk in the middle. The electrodes were made with various metals (area, 1 cm²) which were chemically cleaned immediately before the electrolysis to remove any superficial oxides. In blank experiments (without current) it was ascertained, by observation for some days, that the metals do not give any spontaneous polymerization in contact with the solutions. It has been reported that Cu powder in acid solutions of MMA may act as a catalyst.¹²

In preliminary experiments, it was noticed that MMA-H₂SO₄-H₂O solutions may yield polymer in both the cathodic and the anodic compartment. In this work, we limited ourselves to the investigation of the cathodic polymerization; therefore, a H₂O-H₂SO₄ solution was used in the anodic compartment with a platinum electrode.

To minimize the presence of oxygen in the solution and its influence on the polymerization, purified nitrogen was bubbled through the solution at constant rate for ½ hr before the electrolysis and during the reaction.

Yields were determined by pouring the electrolyzed solution into water or methanol; the compact lump of PMMA was then finely minced and washed thoroughly to remove H_2SO_4 and residual MMA. It was then dried at 50°C and weighed. I -versus- V curves were obtained in a cell having a third inlet for the introduction of a reference electrode (saturated Calomel).

The viscosity-average molecular weights \bar{M}_v were obtained by measuring the viscosity of solutions of PMMA in acetone at 25°C and using the following relationship between the intrinsic viscosity $[\eta]$ and the molecular weights¹³:

$$[\eta] = 7.5 \times 10^{-5} \bar{M}_v^{0.70} \text{ (dl/g)}.$$

Usually the PMMA so obtained was completely soluble in acetone. However, sometimes a very small amount of polymer remained undissolved, possibly due to the presence of a small percentage of crosslinks. In these cases, the concentration was recalculated after separation of the insoluble PMMA. NMR spectra were recorded in *p*-dichlorobenzene at 102°C .

Electrolytic resistances were measured in a conventional conductivity cell between unplatinized platinum electrodes, using a conductivity bridge particularly suitable for measuring low resistances.

RESULTS AND DISCUSSION

During this investigation, it was noticed that some of the solutions could give a spontaneous polymerization. This effect was separately examined and proved to be of some importance for elucidating the mechanism of initiation.¹⁴ Care was taken so as to avoid overlapping of the spontaneous polymerization on the electroinitiated one. In the experiments here reported, the solutions were stable for all the electrolysis time. In particular, the solutions used for obtaining the kinetic curves were stable for several days.

TABLE I
Influence of Cathode Materials on Conversions and Molecular Weights

Cathode	$-\eta_{\text{H}_2}$ (V vs. SCE) ^a	Conversion, % ^b	$\bar{M}_v \times 10^{-6}$
Pb	0.68	43.3	1.30
Hg	0.60	18.5	2.00
Sn	0.53	12.1	1.70
Zn	0.85	9.8	1.20
Cu	0.51	9.4	1.65
Cd	0.72	7.0	0.75
Ni	0.04	5.8	0.40
Pt	0.22	4.5	4.80
Al	0.68	4.2	4.00
Ag	0.48	3.1	2.60
Fe	0.40	0.0	—

^a In this column the V values are reported at which a sharp current increase in the I/V curves occurs (see Fig. 1).

^b Determined after 1 hr of electrolysis at 100 mA (25°).

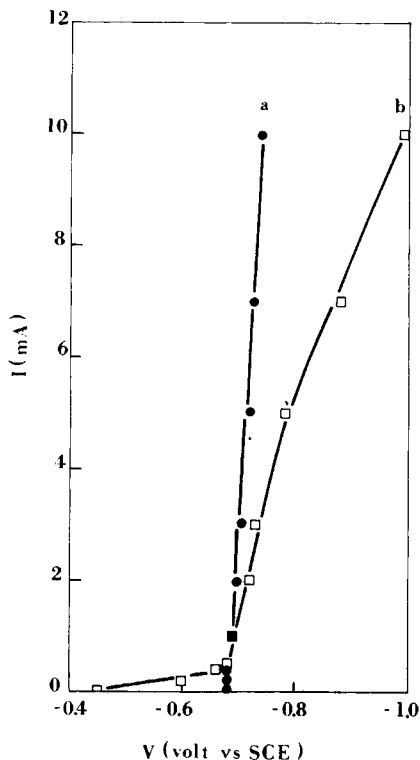


Fig. 1. Polarization curves in the absence (a) and in the presence (b) of MMA. Pb cathode, SCE reference electrode. Composition of the solution for curve (b): 10.0M H₂SO₄, 2.0M H₂O, 4.0M MMA.

Influence of Cathode Material

In Table I, the influence of the cathode material on the yields and molecular weights is reported along with the hydrogen overvoltage (η_{H_2}) determined in the same solutions used for the polymerizations. No obvious correlation may be seen among η_{H_2} and the yields or the molecular weights. It is true that Pb and Hg, i.e., two cathodes having high hydrogen overvoltage, show the higher efficiencies. However, the very high yield obtained with Pb (43.3%) certainly cannot be explained on this basis, especially considering that its η_{H_2} is lower than that of Zn and Cd (yields, 9.8% and 7.0%, respectively). Shelepin has shown that on Pb,⁷ as well as on Hg,⁸ adsorption phenomena take place concerning both the monomer and the polymer. MMA is adsorbed on the cathode probably in the form of a protonated species¹⁵; in this way, it accelerates the evolution of hydrogen, as shown by a decrease in overvoltage. The effect of the polymer formation is opposite, in that its adsorption leads to an increase in overvoltage. We have verified these results with our solutions on a Pb cathode and found an analogous trend (Fig. 1); at low currents, adsorption of MMA lowers η_{H_2} , but as soon as polymer is formed and adsorbed on Pb, η_{H_2} is shifted to more negative values. As we did not use a Luggin capillary to minimize IR drops, the increase in η_{H_2} observed in the presence of MMA for potentials higher than 0.68 V must be taken with

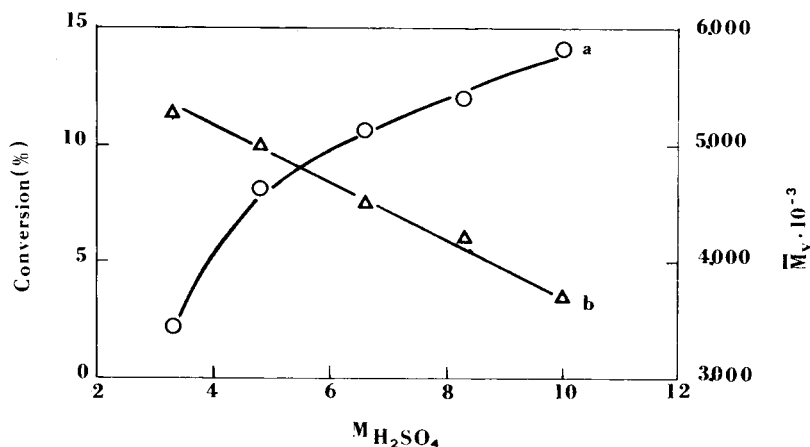


Fig. 2. Formation of PMMA (a) and molecular weights (b) as a function of H_2SO_4 concentration. H_2O , 1.0M in all solutions. 45 mA, 4 hr, Pt cathode.

some care. However, the effect of polymer adsorption seems to be real, as demonstrated by the rapid increase of the cathode potential at fixed current, before the occurrence of any appreciable polymerization in the bulk of the solution (the last would increase the resistance, so raising the measured potential). An increase in η_{H_2} would favor the occurrence of the cathodic process giving rise to the polymerization reaction.

Influence of Sulfuric Acid Concentration

An increase in the concentration of H_2SO_4 is beneficial for the conversions, as shown in Figure 2. A progressive increase in the H_2SO_4 /MMA ratio raises both the viscosity and the conductivity of the solutions (at 9.4M H_2SO_4 the conductivity is seven times greater than that measured at 3.3M H_2SO_4). Both these factors seem to favor the polymerization. The former positively affects the gel formation, which will be discussed later in more detail. The latter may be important on the basis of a greater dissociation of H_2SO_4 , as also suggested by the effect of increasing the H_2O content (see below); if this is so, a certain importance may be attributed to the HSO_4^- anions, as the H^+ ions cannot be taken responsible any longer for the initiation reaction.

A third possibility exists, i.e., the increasing concentration of undissociated acid may play some role in the polymerization. Lower molecular weights are obtained with increasing acid content; this may be related to some chain transfer of the macroradicals with H_2SO_4 . However, it is more probable that this trend is connected with the fact that a higher acid content creates more centers of initiation, so giving rise to shorter chains (the same effect is observed by increasing the catalyst concentration in conventional polymerizations of MMA).

Influence of Water Concentration

Figure 3 shows the importance of the amount of H_2O added to a 10M H_2SO_4 solution. The yield, as a function of H_2O concentration, exhibits a

maximum. This may possibly be rationalized considering that an initial dilution produces a dissociation of H_2SO_4 , which may favor the initiation reaction. It has to be noted that the viscosity of these solutions remained practically unchanged, since small amounts of H_2O replaced small amounts of MMA; therefore, this confirms the importance of a dissociation process of H_2SO_4 .

Further dilution will give rise to a concentration of H^+ capable of competing more successfully at the cathode with the process producing the active polymerization centers.

The molecular weights increase rapidly in the range of small amounts of H_2O added and then very slowly. The rapid increase is probably connected with the occurrence of a gel effect in the solutions. This effect, which is beneficial for both the yields and molecular weights (see below), is much more consistent when H_2O is added.

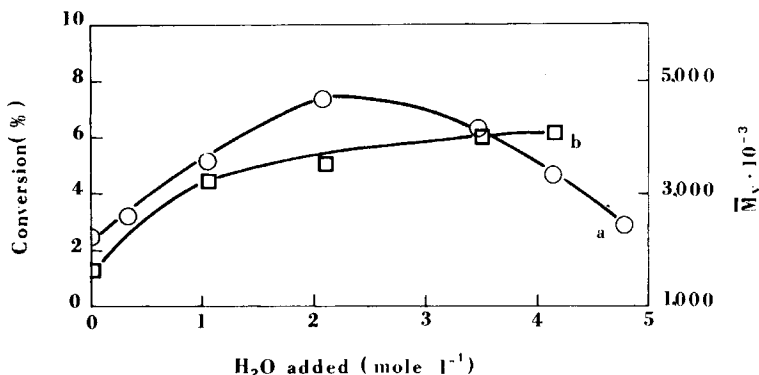


Fig. 3. Formation of PMMA (a) and molecular weights (b) as a function of H_2O added. H_2SO_4 , 10.0M in all solutions; 100 mA, 1 hr, Pt cathode.

Influence of Current Density

The decreasing trend of \bar{M}_v with increasing current of electrolysis (Fig. 4) is typical of radical polymerizations and may again be explained in terms of increasing number of active centers which lead to shorter chains. The \bar{M}_v values are quite high under all conditions in spite of the fact that relatively high current densities and temperatures were employed (see Table I and Figs. 1, 2, and 3). In some experiments at 0°C and 1 mA with a Pt cathode, $[\eta]$ values were obtained giving \bar{M}_v higher than any value reported in the literature. It is apparent that the high initial viscosity of the solutions (H_2SO_4 has a η of 25.4 cp at 20°C) and the progressive increase of this viscosity due to the solubility of PMMA favor chain propagation. Schulz¹⁶ has shown that the termination rate decreases when the viscosity of the solution increases; such an effect is favorable for obtaining high molecular weights.

Conversion/Time Curves

The kinetic curves of Figure 5 have the typical shape of curves obtained when MMA is polymerized with conventional radical initiators.¹⁷ At all cur-

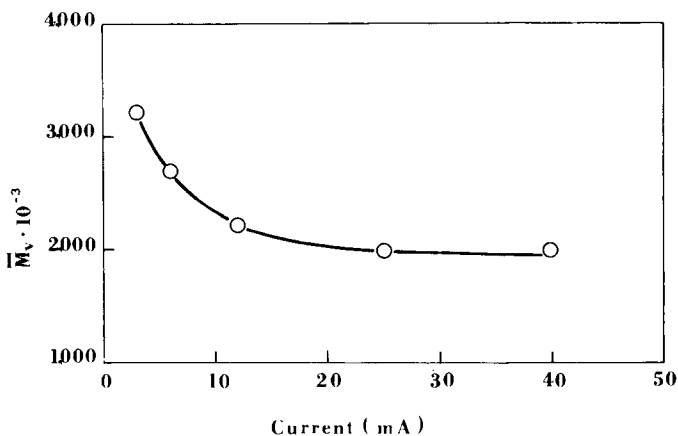


Fig. 4. Variation of molecular weights with current. H_2SO_4 , 4.0M; H_2O , 1.0M in MMA; Pb cathode, 1 hr.

rents examined, an acceleration is observed in the early stages of the polymerization, and the curves level off before complete conversion is achieved. The gel effect theory^{17,18} of the radical polymerization of MMA is applicable in this case, too. As the viscosity of the medium is increased by the polymer dissolved in it, the radicals become less free to move, so the rate of termination R_t is progressively reduced. As the monomer, on the contrary, still retains its ability to reach the growing macroradicals, the propagation rate R_p is not reduced by the decreased mobility of the chains. Thus, the R_p/R_t ratio will increase, and this will result in the observed acceleration and in an increase of the molecular weights.¹⁸ When the solution becomes highly gelled, however, a sharp decrease in the propagation rate occurs (see, for instance,

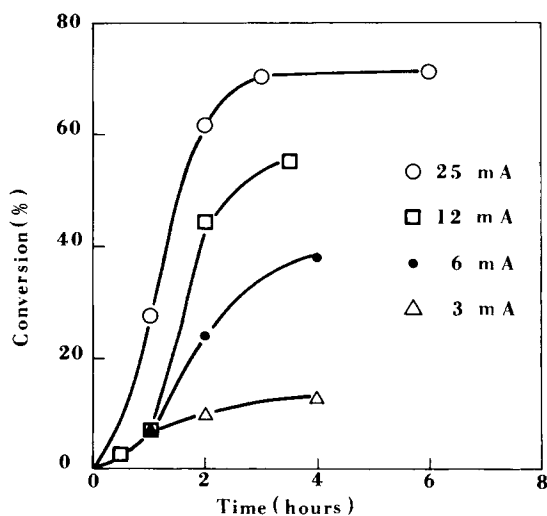


Fig. 5. Conversion/time curves at various currents. H_2SO_4 , 4.0M; H_2O , 1.0M in MMA; Pb cathode.

the curve at 25 mA) due to the inability of the monomer to diffuse toward the radicals, which, on the other hand, are buried in the polymer network.

Figure 5 also shows the importance of a sufficiently high current density for obtaining satisfactory conversions. At low currents, the conversions level off very early; evidently, the concentration of the macroradicals is low, whereas the solution, due to its high viscosity, is rapidly turning to a gel, so creating the conditions in which the propagation rate itself is reduced to zero.

Some experiments were made to evaluate the existence of a post effect. Electrolyses were done for $\frac{1}{2}$ hr at 3 and 12 mA; the solutions were then allowed to polymerize for 18 hr in the absence of current. Polymer yields were 4.1% and 15.8%, respectively; these values, compared with the yield after $\frac{1}{2}$ hr (2.0%, see Fig. 5), indicate the existence of a further propagation of the radicals. However, these yields are lower than those obtained with continuous electrolyses. This probably means that, although most of the active centers are produced at the beginning of the electrolysis, some radical formation takes place also at later stages.

As pointed out by Burnett¹⁸ and confirmed by the curves of Figure 5, no stationary-state conditions can apply over the entire conversion range. Possibly, these conditions are valid in the early stages of the polymerization, in which occlusion of the macroradicals is not yet very important. However, no attempt to verify this assumption has been made in this work.

Mechanism of Polymerization

Clean-cut evidence was obtained about the radical nature of the polymerization. Indeed, (a) the use of protic solvents such as H_2O and CH_3OH (the latter used in some experiments) would have an inhibiting effect on an anionic process; (b) the very high \bar{M}_v values and their decrease as a function of the current density are typical of radical processes; (c) an electrolysis made at 12 mA for 2 hr under O_2 gives only 0.08% PMMA (compared with 44% obtained under N_2). Points (a) and (c) allow to exclude any significant participation of concurrent ionic processes.

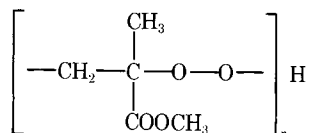
It remains to ascertain how radicals may be generated in the system investigated, the hydrogen atom theory once is discarded. Experiments in which H_2SO_4 was replaced by HCl , HNO_3 and $HClO_4$ (again used at high concentrations) were negative. Only HNO_3 gives a product soluble in CH_3OH and insoluble in H_2O , having a low molecular weight ($[\eta] = 0.03$; $\bar{M}_v \simeq 5000$), which is probably an oligomer of MMA. This evidence supports that obtained from the behavior of different cathodes, i.e., the discharge of H^+ ions is not responsible for the initiation reaction. However, it has to be pointed out that in dilute HCl solutions, the formation of PMMA has been observed.^{3,4,5} On the other hand, Tsvetkov⁴ has noticed that an increase in HCl concentration caused the polymerization to slow down.

To ascertain whether the peroxides of MMA^{10,19} may play a fundamental role, as suggested by Shelepin,^{7,8} in the electroinitiated polymerization of this monomer, we made some experiments using MMA immediately after distillation. The test of Barnes¹⁰ did not show any visible presence of peroxides, and both the preparation of the solutions and the electrolyses were made under purified nitrogen. An electrolysis at 25 mA for 1 hr gave 5.2% PMMA (compared to 27% obtained with a two-day-old MMA); an electrolysis at 6 mA did not give a polymer within 2 hr. This clearly points to the participa-

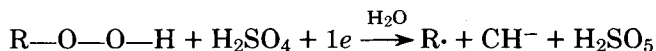
tion of the MMA peroxides in the electrode reaction in which radicals are generated. The small conversion obtained with freshly distilled monomer may be due either to residual peroxides⁹ or to the concurrence of a process not involving the peroxides. Both Shelepin⁷ and Jovanovic²⁰ were unable to obtain PMMA under rigorous conditions, so that the second hypothesis seems less probable.

We obtained fairly reproducible yields and molecular weights when using MMA after one to seven days from distillation. With more fresh or more aged MMA, the reproducibility was less satisfactory, because the peroxide content was too low or too high.

The importance of the peroxides as radical generating species once being recognized, the influence of H₂SO₄ on the radical formation may possibly be accounted for on the basis of the following observations. It is known that H₂SO₄ may react with hydrogen peroxide to form H₂SO₅.²¹ Shelepin⁷ has shown that addition of H₂O₂ to aqueous H₂SO₄ solutions of MMA induces a radical polymerization on Pb. According to Barnes,¹⁹ the peroxide of MMA is a copolymer of MMA and oxygen with a terminal hydroperoxide group, i.e.,



It is possible that a reaction similar to that between H₂O₂ and H₂SO₄ takes place at the electrode, involving the copolymer peroxide:



H₂SO₄ proved to be the only acid capable of giving a spontaneous polymerization in aqueous MMA solutions.¹⁴ This may be taken as further evidence of a specific reaction between the above peroxide and H₂SO₄ leading to radical formation. The KBr test²² was applied to a MMA-H₂SO₄-H₂O solution and seems to confirm the formation of persulfuric acid. H₂SO₄-H₂O solutions and MMA alone did not give the yellow color and the gaseous evolution of Br₂ observed when adding KBr to a polymerizing solution. However, the possibility of the formation of other compounds capable of oxidizing KBr cannot be ruled out completely.

The proposed initiation mechanism cannot obviously explain the results of the authors who obtained PMMA in dilute HCl.^{3,4,5} However, in these cases, too, the participation of the MMA peroxide in the initiation reaction is out of discussion.²⁰

Structure of PMMA

NMR was taken of the polymer dissolved in *p*-dichlorobenzene to receive information on its structure. The main features are the following: (1) the monomer units are linked in head-to-tail sequences; (2) the polymer is not significantly branched (less than 0.5%), thus indicating a small degree of transfer to polymer; (3) the percentage of the three possible forms is 65% syndio-, 30% hetero-, 5% isotactic; a similar composition was reported for conventional PMMA.⁹

Conclusions

The polymerization of MMA electroinitiated at the cathode in solutions of aqueous H_2SO_4 provides a useful tool for obtaining fairly high yields of high molecular weight PMMA. Due to the high MMA content of the solutions, this polymerization may be considered almost a bulk polymerization, so that the weight of PMMA formed per volume unity of the solution is satisfactorily high. The molecular weights depend to a large extent on current density, composition of the solution, and nature of the electrodes. It is possible to program the course of the polymerization to obtain the desired \bar{M}_v . In particular, from Table I it can be seen how widely \bar{M}_v can be varied using different cathodes.

From a practical point of view, the optimum \bar{M}_v values are those sufficiently high to ensure good mechanical properties and sufficiently low to allow processibility under standard conditions. For instance, a PMMA (obtained in this work) $\bar{M}_v = 3,500,000$, a value which represents a good improvement compared with 1,200,000 of commercial PMMA (Plexiglas), could not be used as a molding powder, since its melt flow index is too low (0.23 g/10 min) to make it suitable for injection molding.

Work is now in progress to optimize both the yields and the molecular weights. The accomplishment of such task would perhaps make this technique interesting from an industrial point of view, owing to its overall nonsophisticated character.

The authors wish to thank Dr. B. Scrosati for helpful discussions concerning the electrochemical part of this work.

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Received July 31, 1975

Revised November 11, 1975