Synthesis of poly(N,N,N-trimethyl–N-2-methacryloxyethyl) ammonium chloride initiated by anodically generated Sn^{2+} cation

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Abstract

Cationic polymerization of N,N,N-trimethyl–N-2-methacryloxyethyl ammonium chloride (DMAEM-MC) was studied using a new synthesis technique and new initiator system, Sn^{2+}. The Sn^{2+} was produced by the electrolysis of a sacrificial anode. The polymer was prepared in a batch reactor using only Sn material as electrodes. Factors affecting the conversion and average molecular weight of the polymer by electrolysis were obtained. On the one hand, the results indicated that the agitation rate, initial pH, current density and assembly of electrodes significantly affected both conversion and polymer molecular weight. On the other hand, temperature and monomer concentration were minor factors in the electropolymerization, while these two factors were the major factors in conventional chemical methods. The optimal pH_i and agitation rate were 5.50 and 0 rpm, respectively. The reaction rate increased with current density; however, the current efficiency decreased with increase in current density. The results also revealed that the optimum reaction temperature and monomer concentration were 25 °C and 0.73 M, respectively.

List of symbols

redox	reduction–oxidation
DMAEM-MC	N,N,N-trimethyl–N-2-methacryloxyethyl ammonium chloride
pH_i	initial pH
$[DMAEM-MC]_i$	initial concentration of DMAEM-MC (M)

1. Introduction

Poly(N,N,N-trimethyl–N-2-methacryloxyethyl) ammonium chloride or its copolymers, the cationic water-soluble polymers, have quaternary ammonium groups which cause this type of polymer to have high polarity and a strong affinity for anionic substances. Such properties can be used in various applications such as the paper industry [1], wastewater treatment [2–5] and others such as mining and tertiary oil recovery [6]. In general, aqueous polymerization, a clean and safe polymerization process, with redox initiators is the most widely used chemical method to produce this type of polymer [7–9]. The popular reducing agents are bisulfites [10], amines [11], amino acids [12, 13], alcohols [14, 15], acids [16, 17], aldehydes [18], thiols [19] or polymers with these functional groups. In general, these reducing agents are very active and unstable. There are both safety and pollution issues associated with the use of these reducing chemicals.

Electropolymerization is one of the most promising methods for polymerization because of its specific features [20, 21], namely, a rigorous control of the initiation and termination steps of polymerization, the orientation of macromolecules at the electrode surface, narrow molecular weight distribution, and less variance of physicochemical properties. Several investigators, such as Dong [22, 23], Hsu [13, 24], Erbil [12, 25], Behari [26] and Qiu [27] have studied the polymerization of acrylamide using Ce^{4+} as oxidant and showed that

Ce^{4+}-reductant pairs were effective initiators for aqueous polymerization.

Sarac [28, 29] further studied the electropolymerization of acrylamide by using poly(aminocarboxylic acid)-Ce^{4+} as initiator and showed that many advantages were associated with the electrolysis method compared with nonelectrolytic methods at a very low initiator concentration.

Since Sn^{2+} is a strong reducing agent, the Sn^{2+}-amino acid pairs may be expected to be effective initiators for polymerization or electropolymerization in aqueous solution. However, few studies have concerned these initiator pairs for electropolymerization. In general, the Sn^{2+} cation in the reaction medium is oxidized to the Sn^{4+} cation or reduced to Sn metal. Both Sn^{4+} cation and Sn metal are inactive for the polymerization of vinyl monomers, but the Sn^{4+} cation can be cathodically reduced to the Sn^{2+} cation and Sn metal can be anodically oxidized to the Sn^{2+} cation. This so-called induced chemical-electrochemical process is especially suitable for commercial polymerization of vinyl monomers because the initiator can be continuously generated in situ and, theoretically, a lower Sn^{2+} concentration is required compared to the conventional method.

In previous papers [30, 31], the electrolytic polymerization of DMAEM-MC was carried out in a system containing EDTA using Sn^{2+} ion as reducing agent; this was added to the solution before electrolysis or was in-situ generated from an Sn metal anode, respectively. The results showed that the control of polymerization rate and polymer molecular weight were much easier than in conventional chemical methods by using Sn^{2+}–EDTA as initiator for the electropolymerization of DMAEM-MC.

In this study we further simplify the initiator system by only using Sn^{2+} cation as initiator; this is generated in situ by the sacrificial anode method. Thus, the electropolymerization process is simplified and more easily controlled than that of earlier methods.

In this study, the effects of agitation, pH_i value of monomer solution, current density, amount of charge passed, assembly of electrodes, temperature and initial monomer concentration on the conversion and polymer molecular weight were systematically studied.

2. Experimental details

2.1. Materials

Technical grade DMAEM-MC, (75% purity, CPS Chemical Company Inc., USA) was used without further purification. Sodium nitrate and potassium hydroxide were GR grade (E. Merck). Sulfuric acid was AR grade (Ferak). The solvent was deionized water. The nitrogen purity was more than 99.6% and was used without further treatment. The Sn plate with 99.94% purity was used as electrodes.

2.2. Apparatus and procedures

The monomer solution with the desired amounts of monomer and chosen pH_i were introduced to a 1 litre seven-necked Pyrex separable flask equipped with a stirrer and purged with nitrogen. The flask was immersed in a well-controlled water bath which was maintained at the desired temperature $\pm 0.1\,^{\circ}C$. The electropolymerization process was controlled by a potentiostat/galvanostat (Nichia, model NP-G1001 ED).

During reaction, the product solution was periodically sampled and the conversion and the polymer molecular weight of the sample were determined. The sample product was poured into an ethanol solution which was more than 20 fold the volume of the sample to precipitate the polymerized product and the product was then dried at $85\,^{\circ}C$ in vacuo for at least two days. The conversion was determined by weighing the dried polymer. Simultaneously, the polymer molecular weight was determined as described previously [30].

3. Results and discussion

3.1. Effect of agitation rate

The effect of agitation rate on both the conversion and the molecular weight of the polymer was obtained, as shown in Figures 1 and 2. The conversion increases linearly with the reaction time and the higher conversion appears at the lower agitation rates such as 0 and 50 rpm. Figure 2 also shows that the polymer molecular weight apparently decreases with the increase in agitation rate. For example, at 6.0 h reaction time, increasing the agitation rate from 0 rpm through 100 rpm to 200 rpm decreases both conversion and polymer molecular weight from 20.43% and 1.63×10^5 through 16.51% and 2.41×10^4 to 6.74% and 0.37×10^4, respectively. It must emphasize that the largest conversion and polymer molecular weight were found at 0 rpm agitation rate, that is without agitation. Consequently, all the runs in this study were operated without agitation.

3.2. Effect of pH_i value

The effect of pH_i, initial pH value, on both conversion and polymer molecular weight is shown in Figures 3 and 4. The conversion increases linearly with reaction time
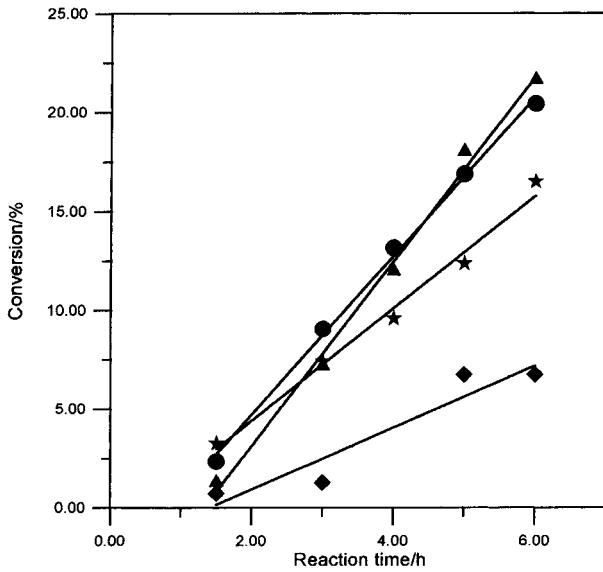
Fig. 1. Effect of reaction time on the conversion at different agitation rates. Temperature 45 °C; pH_i 5.50; current density 7.08 A m^{-2}; [DMAEM-MC]$_i$ 0.98 M. Agitation rates: (●) 0, (▲) 50, (★) 100 and (◆) 200 rpm.
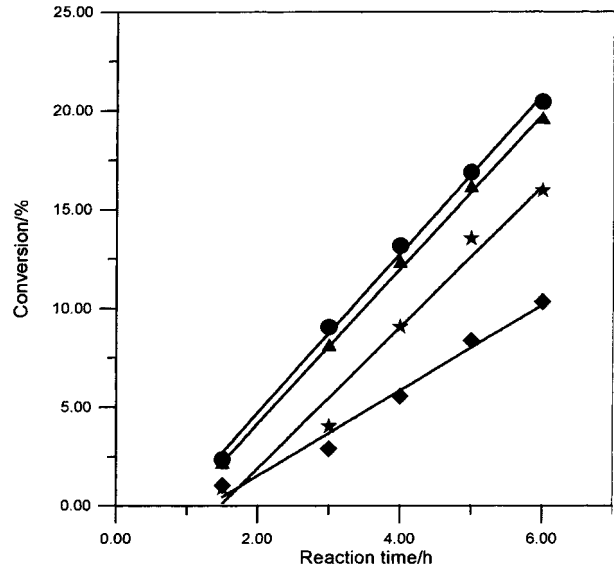

Fig. 3. Effect of reaction time on the conversion at different pH_i. Temperature 45 °C; current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M. Initial pH: (◆) 2.50, (★) 4.00, (●) 5.50 and (▲) 7.00.
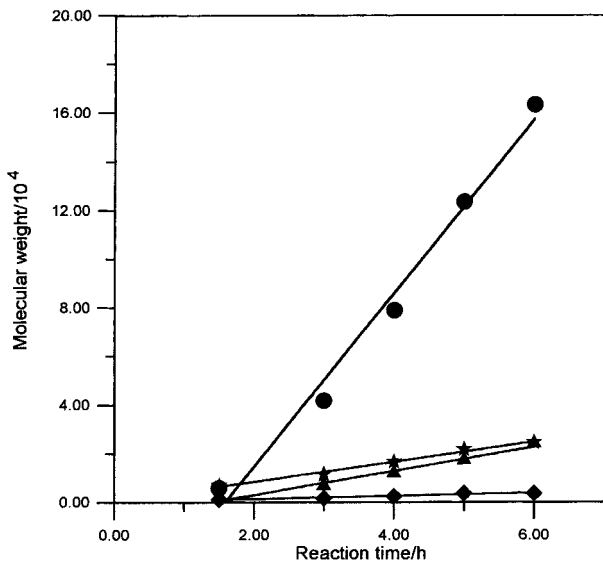

Fig. 2. Effect of reaction time on the molecular weight at different agitation rates. Temperature 45 °C; pH_i 5.50; current density 7.08 A m^{-2}; [DMAEM-MC]$_i$ 0.98 M. Agitation rates: (●) 0, (▲) 50, (★) 100 and (◆) 200 rpm.
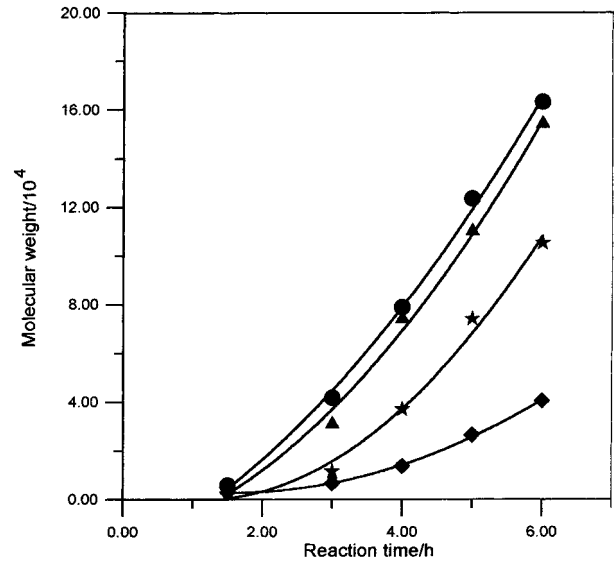

Fig. 4. Effect of reaction time on the polymer molecular weight at different pH_i. Temperature 45 °C; current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M. Initial pH: (◆) 2.50, (★) 4.00, (●) 5.50 and (▲) 7.00.

and the largest conversion appears at about pH_i 5.5 and pH_i 7.0 as shown in Figure 3. The results show that the reaction rate (slope of straight line) is 3.83×10^{-2} h^{-1} except at pH_i 2.5, when the slope is 2.16×10^{-2} h^{-1} which is smaller than for other pH_i values. The relationship of molecular weight with reaction time is similar to the conversion reaction time relationship as shown in Figure 4. The highest polymer molecular weight appears at pH_i 5.5 and 7.0. Based on the above results, pH_i 5.5 is the optimum reaction condition since it gives the largest conversion and the highest polymer molecular weight and the less pH adjustment is required.

3.3. *Effect of current density*

The effect of current density on both conversion and polymer molecular weight is shown in Figures 5 and 6. The conversion increases with current density as shown in Figure 5. For example, at 3.0 h increasing the current density from 1.77 through 7.08 to 14.16 A m^{-2} increases the conversion from 0.8 through 9.04 to 11.2%. The results are reasonable, since higher current density results in higher active [Sn^{2+}] concentration in the solution and generates a larger reaction rate. The current efficiency decreases with increase in current density as shown in Figure 6. The increasing rates of polymer molecular weight also have similar trends to the current efficiency. Side reactions, such as Sn^{2+} reduction on the cathode, or H$_2$O electrolysis in the solution, took place to a greater extent at higher current densities. Thus, the current density is controlled and the rate of free radical generation is controlled, so that both polymerization rate and polymer molecular weight are easily controlled by current density. This behaviour is quite different from that found in the conventional chemical method where the rate of free radical gener-ation is mainly controlled by the temperature.

3.4. *Effect of cathodic area*

The effect of cathodic area on both conversion and polymer molecular weight is shown in Figures 7 and 8. At the same anode current density, 7.08 A m^{-2}, the conversion and the polymer molecular weight using

smaller cathodic area are higher than that using larger cathodic area as shown in Figure 7. This may be explained by Figure 8 which shows the plot of applied potential against reaction time at different current densities. The results show, on the one hand that the applied potential apparently increases with reaction time at a 125 A m^{-2} cathode current density as shown in Figure 8. On the other hand, at a 7.08 A m^{-2} cathode current density, the change in applied potential with

Fig. 6. Effect of amount of charge passed on both conversion and polymer molecular weight at different current densities. Temperature 45 °C; pH$_i$ 5.50; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M; reaction time 6 h. Current density: (★,☆) 0.59, (●,○) 7.08 and (◆,◇) 14.16 A m^{-2}.
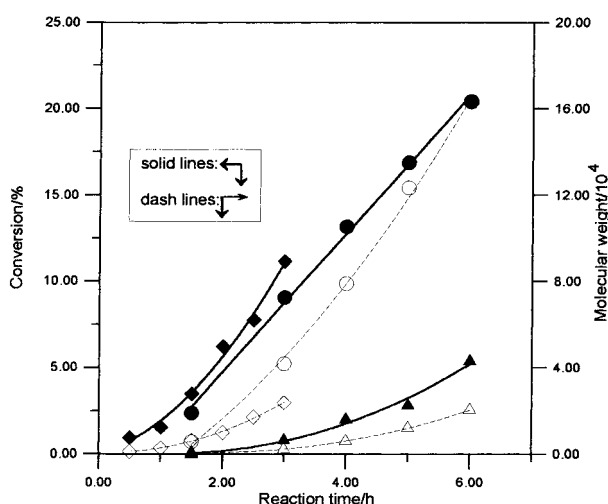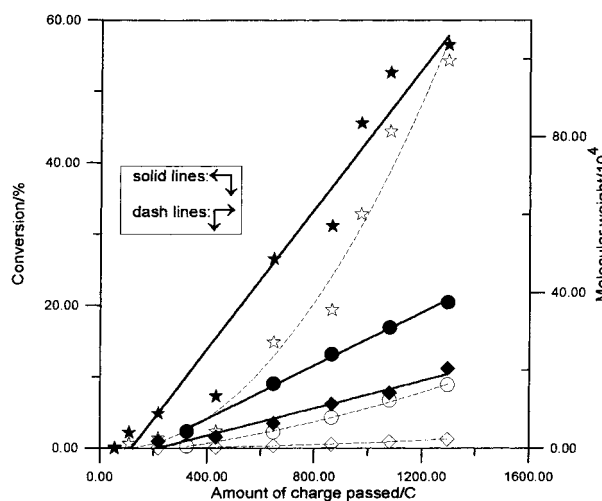

Fig. 5. Effect of reaction time on both conversion and polymer molecular weight at different current densities. Temperature 45 °C; pH$_i$ 5.50; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M. Current density: (▲,△) 1.77, (●,○) 7.08 and (◆,◇) 14.16 A m^{-2}.
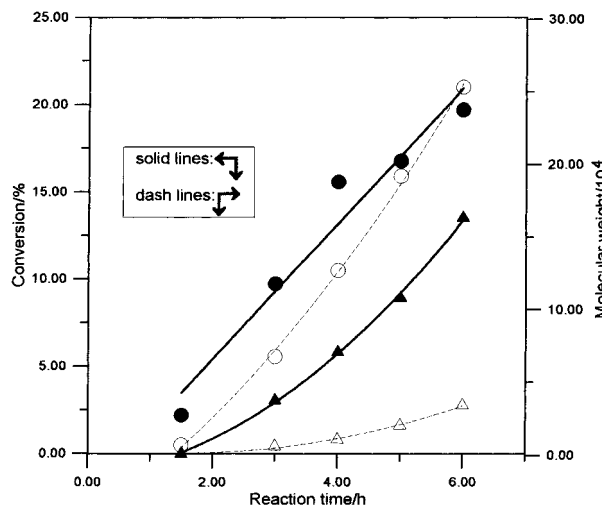

Fig. 7. Effect of reaction time on both conversion and polymer molecular weight at different cathode current densities. Temperature 65 °C; pH$_i$ 5.50; anode current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M. Current density: (△,▲) 7.08 and (○,●) 125 A m^{-2}.

reaction time is small. Comparing the curves in Figure 7, it is apparently that the *I–R* drop increases with both conversion and polymer molecular weight. Accordingly, the active Sn^{2+} should have the longer residence time and larger concentration at 125 A m^{-2} cathodic current density than that at 7.08 A m^{-2} and result in larger conversion and polymer molecular weight.

3.5. *Effect of temperature*

The effect of temperature on both conversion and polymer molecular weight is shown in Figures 9 and 10. A plot of conversion against reaction time results in a straight line, except at 55 °C, as shown in Figure 9. The reaction rates , or the slopes of the plot in Figure 9, are about 3.91×10^{-2} h^{-1} in the temperature range 25 to 45 °C. However, at the temperature of 15 and 65 °C, the reaction rates are 2.73×10^{-2} and 2.95×10^{-2} h^{-1}, respectively. The lower reaction rate at 15 °C may be explained by the fact that the low reactivity of the monomer at low reaction temperature induces the low reaction rate. The results also show the surprising phenomenon that for temperatures above 45 °C, the reaction rate decreases with increase in reaction temperature. A similar trend in the reaction rate was also observed by Erbil [12, 32], Sarac [30], Akar [33], and Palit [34]. This is possible due to a good portion of the initiating species being destroyed by side reactions at higher temperature. A plot of polymer molecular weight

against reaction time is shown in Figure 10, which shows that the trends of increasing rate of polymer molecular weight are similar to the reaction rate as shown in Figure 9. The highest polymer molecular weight appears at 25 °C and the lowest polymer molecular weight appears in the range 55 to 65 °C, as shown in
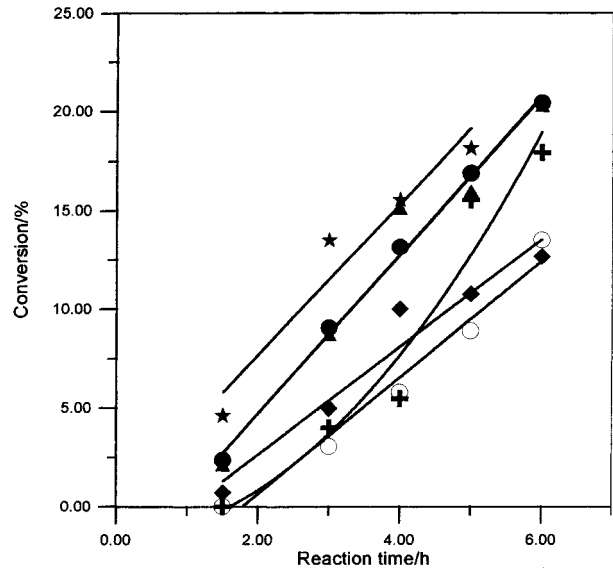
Fig. 9. Effect of reaction time on the conversion at different reaction temperatures. pH_i 5.50; current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M.Temperature: (◆) 15, (★) 25, (▲) 35, (●) 45, (+) 55 and (○) 65 °C.
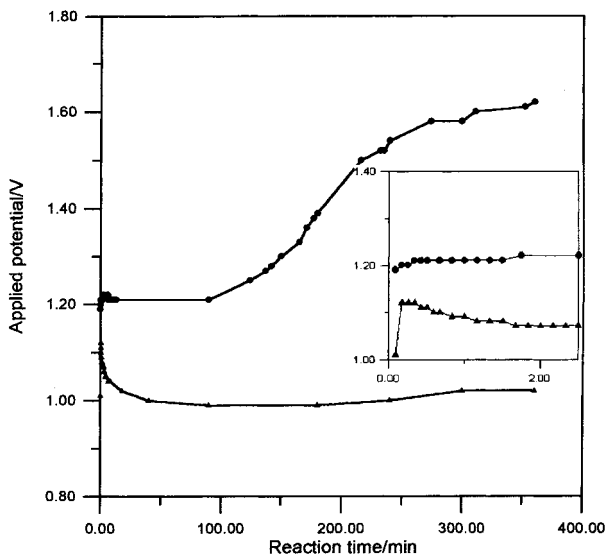
Fig. 8. Plot of applied potential against reaction time at different cathode current densities. Temperature 65 °C; pH_i 5.50; anode current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M. Current density: (▲) 7.08 and (●) 125 A m^{-2}.
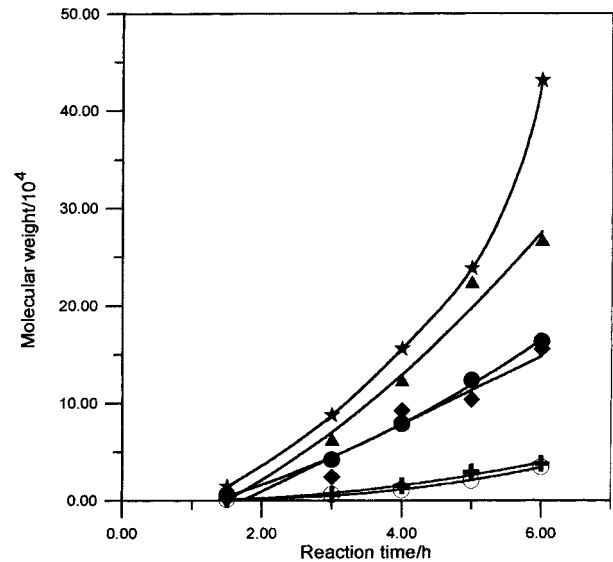
Fig. 10. Effect of reaction time on the polymer molecular weight at different reaction temperature. pH_i 5.50; current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M. Temperature: (◆) 15, (★) 25, (▲) 35, (●) 45, (+) 55 and (○) 65 °C.

Figure 10. Based on the above results, the optimum reaction temperature is 25 °C.

Generally, the reaction rate depends strongly on temperature and increases with the reaction temperature in the chemical reaction system. However, the results show that electropolymerization is different from conventional chemical methods and the temperature is a minor factor in the electropolymerization.

3.6. Effect of monomer concentration

A plot of conversion against reaction time results in a straight line, except at 1.48 M initial monomer concentration, as shown in Figure 11. The reaction rates are about 4.15×10^{-2} h^{-1} in the concentration range 0.73 to 1.23 M. Additionally, the reaction rate of 1.48 M initial monomer concentration is 3.90×10^{-2} h^{-1} at 5.0 h from the beginning of the run. The lower reaction rate after 5.0 h may be due to the Trommsdorff effect [35] in the higher conversion of higher reaction monomer concentration. The reaction rate of 0.48 M is 2.24×10^{-2} h^{-1} which is lower than for other concentrations. This is reasonable and similar to that found in chemical methods. However, in the range 0.73 to 1.23 M, the effect of monomer concentration on the reaction rate is insignificant. This phenomenon is quite different from that in chemical methods.

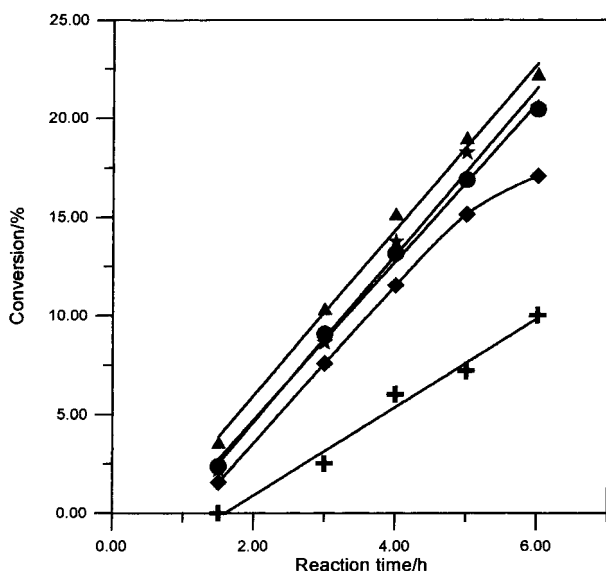Figure 12 shows that the optimal initial monomer concentration for obtaining the highest polymer molec-
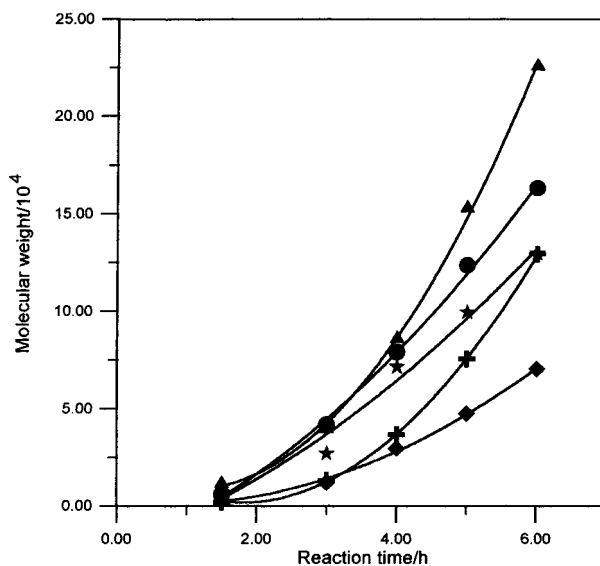

Fig. 12. Effect of reaction time on the polymer molecular weight at different monomer concentrations. Temperature 45 °C; pH$_i$ 5.50; current density 7.08 A m^{-2}; agitation rate 0 rpm. Concentration: (+) 0.48, (▲) 0.73, (●) 0.98, (★) 1.23 and (◆) 1.48 M.

ular weight is 0.73 M. It is similar to the conversion as shown in Figure 11. However, the molecular weight to reaction time relationships are different from the conversion reaction time plots. For example, at 6.0 h reaction time, the conversions are 20.43 and 20.55% at 0.98 and 1.23 M initial monomer concentration, respectively. Nevertheless, the polymer molecular weights are 1.63×10^5 and 1.30×10^5 corresponding to 0.98 and 1.23 M initial monomer concentrations, respectively. Furthermore, the conversions are 10.0 and 17.1% at 0.48 and 1.48 M initial monomer concentrations, respectively. However, the molecular weights are 1.29×10^5 and 7.03×10^4 corresponding to 0.48 and 1.48 M, respectively. This indicates that the termination is disproportionation in the range of higher reaction monomer concentrations and is not mutal termination. This phenomenon is reasonable since the diffusivity of active polymer chains decreases with increase in viscosity and the solution viscosity also increases with increase in both concentration and conversion.

3.7. Comparison with earlier electrochemical methods

In previous work [30], the initiator was added prior to electrolysis and this induced an extent of polymerization which was not controllable. However, in the present method, the polymerization was only initiated by the anodically generated Sn^{2+}. Apparently, the polymerization can be more easily controlled.

Fig. 11. Effect of reaction time on the conversion at different monomer concentrations. Temperature 45 °C; pH$_i$ 5.50; current density 7.08 A m^{-2}; agitation rate 0 rpm. Concentration: (+) 0.48, (▲) 0.73, (●) 0.98, (★) 1.23 and (◆) 1.48 M.
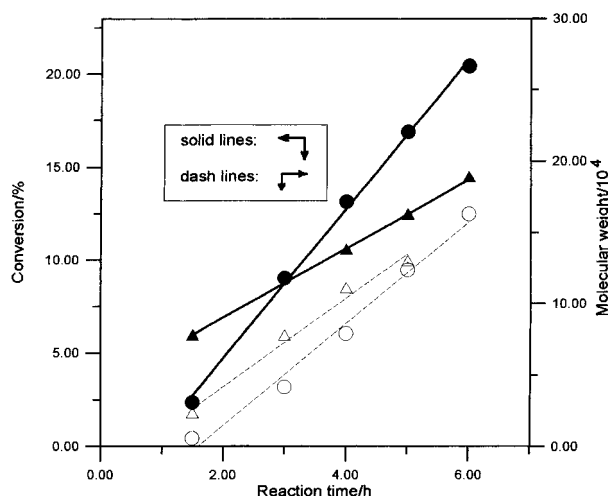
Fig. 13. Effect of reaction time on both conversion and polymer molecular weight with or without EDTA. Temperature 45 °C; current density 7.08 A m^{-2}; agitation rate 0 rpm; [DMAEM-MC]$_i$ 0.98 M; with EDTA: pH$_i$ 1.75; without EDTA: pH$_i$ 5.50. Key: (●,○) [EDTA] 0 M; (▲,△) [EDTA] 1.61 ×10^{-3} M.

The comparison of both conversion and polymer molecular weight with and without EDTA at optimal pH$_i$ is shown in Figure 13. The reaction rate and the increasing rate of polymer molecular weight using this method are 4.00 ×10^{-2} h^{-1} and 3.56 × 10^4 h^{-1}, respectively. However, the reaction rate and the increasing rate of polymer molecular weight in the earlier method [31] were 1.86 × 10^{-2} h^{-1} and 3.10 × 10^4 h^{-1}, respectively, which are smaller than in the present method.

4. Conclusions

A new synthesis technique for poly(DMAEM-MC) initiated by using a sacrificial Sn anode was explored and the results show that it is a very promising aqueous system method. The factors controlling both conversion and polymer molecular weight were determined. The pH$_i$, current density and assembly of electrodes were major factors affecting both conversion and polymer molecular weight. The optimal pH$_i$ was 5.50. The reaction rate increased with current density; however, the current efficiency decreased with increase in current density . The results also show that the reaction rate and polymer molecular weight can easily be controlled using the current density.The effect of temperature is a minor factor in the range 25 to 45 °C and is quite different from that in the chemical method . The effect of monomer concentration is also a minor factor.

References

1. R.F. Lang and U. Zellstoff, *Papier* **20** (1971) 143.
2. A.E. Stafford, Br. *Polym. J.* **4** (1972) 231.
3. S. Friberg and K. Roberts, *in* 'Environmental Engineering', edited by, G. Lindner and K. Nyberg (D. Reidel, Dordrecht-Holland, 1973), p. 227.
4. J.E. Morgan, M.A. Yorke, J. E. Boothe, *in* 'Ions in Polymers', Advanced Chemistry Series No. 187, edited by A. Eisenberg (American Chemical Society Washington, DC, 1980), p. 235.
5. L. Eriksson and B. Alm, *Water Sci. Techol.* **28**(1) (1993) 203.
6. J.A. Kitchener, *Br. Polym. J.* **4** (1972) 217.
7. P.L. Nayak and S. J. Lenka, *J. Macromol. Sci., Macromol. Chem.* **C19**(1) (1980) 83.
8. D. Hunkeler and A.E. Hamielec, *Polym. Mater. Sci. Eng.* **58** (1988) 789.
9. H. Tanaka, *J. Polym. Sci.: Polym. Chem. Ed.* **24** (1986) 29.
10. Fre'de'ric Mabire, Roland Audebert and Claude Quivoron, *Polymer* **25**, Sept. (1984) 1317.
11. S.K. Saha and A.K. Chaudhuri, *J. Polym. Sci. Part A.* **1**(10) (1972) 797.
12. C. Erbil, C. Cin, A.B. Soydan and A.S. Sarac, *J. Appl. Polymer Sci.* **47** (1993) 1643.
13. W.C. Hsu, C.Y. Chen, J.F. Kuo and E.M. Wu, *Polymer* **35**(4) (1994) 849.
14. G. Renders, G. Broze, R, Jerome' and Ph.Teyssie', *J. Macromol. Sci. Chem.* **A16**(8) (1981) 1399.
15. M.D. Ferna'ndez and G.M. Guzma'n, *J. Polm. Sci., Part A: Polym. Chem.,* **27** (1989) 3703.
16. S.V. Subramanian and M. Santaooa, *J. Polym. Sci. Part A* **1**(6) (1968) 493.
17. G.S. Misra and J. I. Khatib, *Colloid Polym. Sci.* **261** (1983) 188.
18. S.V. Subramanian and M. Santappa, *Makromol. Chem.* **112** (1968) 1.
19. N.K. Chakrabarty and A. K. Chaudhuri, *J. Macromol. Sci. Chem.* **A22**(22) (1985) 1691.
20. G.S. Shapoval and T.E' Lipatova, 'Electrochemical Initiation of Polymerization' [in Russian] (Naukova Dumka, Kiev 1977).
21. V.D. Bezuglyi and T.A. Alekseeva, 'Electrochemistry of Polymer' [in Russian] (Osnova, Kharkov, 1990).
22. J.H. Dong, K.Y. Qiu and X.D. Feng, *Makromol. Chem. Phys.* **195**(3) (1994) 823.
23. J.H. Dong, D.H. Liu, K.Y. Qiu and X.D. Feng, *Macromolecular Reports* **A(31)** suppl. 5 (1994) 491.
24. W.C. Hsu, J.F. Kuo and C.Y. Chen, *J. Polm. Sci., Part A: Polym. Chem.,* **31** (1993) 3213.
25. C. Erbil, A.B. Soydan, A.Z. Aroguz and A.S. Sarac, *Die Angew. Makromol. Chem.* **213** (1993) 55.
26. K. Behari, U. Agrawal and R. Das, *Polymer* **34**(21) (1993) 4557.
27. K.J. Qiu, Z.H. Lu, A.J. Tang and X.D. Feng, *Chinese J. Polym. Sci.* **10**(4) (1992) 366.
28. A.S. Sarac, H. Basak, A.B. Soyden and A. Akar, *Die Angew. Makromol. Chem.* **198** (1992) 191.

496

29. A.S. Sarac, C. Erbil and A.B. Soydan, *J. Appl. Polym. Sci.* **44** (1992) 877.
30. T.-Y. Lin, T.-C. Chou, *J. Electrochem. Soc.* **144**(3) (1997) 835.
31. T.-Y. Lin, T.-C. Chou, submitted to *J. Electrochem. Soc.*
32. C. Erbil, A. B. Soydan, A. Z. Aroguz, A. S. Sarac, *Die Angew. Makromol. Chem.* **213** (1993) 55.
33. A. Akar, O. Galiglu, A. Gocmen and A. S. Sarac, *J. Appl. Polym. Sci.* **39** (1990) 1657.
34. S. R. Palit and R. S. Konar, *J. Polm. Sci.* **58** (1962) 85.
35. G. V. Schulz and G. Haborth, *Makromol. Chem.* **1** (1948) 106.