Postpolymerization of Quaternary Ammonium Acrylate Polymer Produced by Electropolymerization

THONG-YUEH LIN, MIN-HUA CHEN, TSE-CHUAN CHOU

Department of Chemical Engineering, National Cheng-Kung University Tainan, Taiwan, Republic of China, 701

Received 15 May 2000; accepted 2 December 2000

ABSTRACT: Postpolymerization of dimethylaminoethylmethacrylate-methyl chloride (DMAEM-MC) electropolymerization, with Sn^{+2}/EDTA as initiator, was studied. The factors that affect the stable average molecular weight of the polymer (MW_∞) created by postpolymerization were investigated. The results indicate that the major factors affecting the MW_∞ are the current density, pH_i value, and the $[Sn^{+2}]_i/[EDTA]_i$ ratio. On the other hand, original reaction temperature, initial initiator concentration, and initial monomer concentration are minor factors affecting the postpolymerization polymer. Increasing the current density decreases the MW_∞ at fixed operating conditions. The optimum $[Sn^{+2}]_i$ $/[EDTA]_i$ ratio to obtain the highest MW_∞ mainly depends on the pH_i value. At 3.25 and 4.00 pH_i values, the optimum $[Sn^{+2}]_I/[EDTA]_i$ ratio is 5.00. However, at 1.75 and 2.50 pH_i values, the optimum ratios are 1.00 and 2.00, respectively. The results also reveal that increasing the original reaction temperature, initial initiator concentration, and initial monomer concentration increases the molecular weight. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1071–1076, 2001

Key words: postpolymerization; quaternary ammonium acrylate polymer; electropolymerization; Sn^{+2}/EDTA initiator

INTRODUCTION

Polydimethylaminoethyl methacrylate-methyl chloride [poly(DMAEM-MC)] or its copolymers with other monomers (e.g., acrylamide, acrylic acid, acrylonitrile, itaconic acid, etc.) contain an ammonium group, which induces high polarity, strong affinity for anionic substances, and high ionic conductivity. Because of these properties, these types of polymers can be used in various applications; such as, the paper-making industry,[1–4] as a coagulant or flocculant in water treatment,[5–10] for mining and tertiary oil recovery,[11] for drug controlled release,[12–15] as a dispersing agent,[16, 17] and as an antistatic agent.[18] Furthermore, these polymers are very promising materials for the fabrication of sensors[19–21] and solid polyelectrolytes (SPE).[22–24]

In general, aqueous polymerization with redox initiators is the most widely used chemical method to produce this type of polymer.[25] However, electropolymerization has the following positive characteristics:[26, 27] rigorous control of the steps of initiation and termination of polymerization, orientation of macromolecules at the electrode surface, narrow molecular weight distribution, and less variance of physicochemical properties. Electropolymerization is also one of the most promising methods for polymerization.

In a previous study,[28] the electropolymerization of DMAEM-MC was carried out with Sn^{+2}/EDTA as initiator. The results showed that much less initiator concentration was needed to initiate polymerization, the control of polymer molecular weight was easier than with the usual chemical

---

Correspondence to: T.-C. Chou (tcchou@mail.ncku.edu.tw).

Journal of Applied Polymer Science, Vol. 82, 1071–1076 (2001)

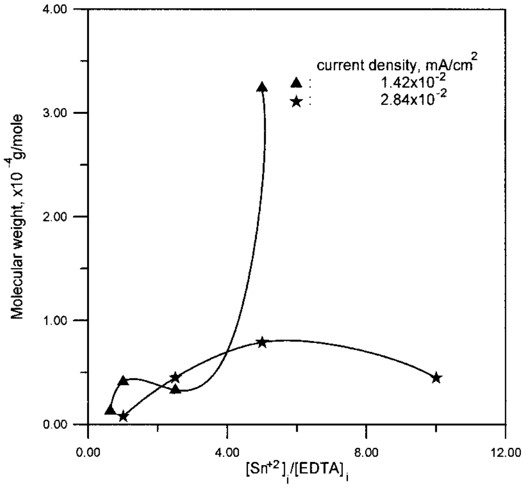

Figure 1 Effect of $[Sn^{+2}]_i/[EDTA]_i$ ratio on the MW_0 of the electropolymerization polymer at different current densities. Temperature, 45 °C; pH_i,7.00; charge,10.8 Coulombs; electrode surface area, 70.42 cm^2; $[Sn^{+2}]_i$, 1.61 $\times 10^{-3}$ M; agitation rate,0 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

method, and the polymerization was via a free radical initiation mechanism. Generally, in free radical electropolymerization, the polymerization should terminate within ~1 s after the electrolysis is discontinued.[29] However, postpolymerization is apparently observed for this Sn^{+2}/EDTA initiator system of DMAEM-MC polymerization. Postpolymerization of acrylate monomers often exists in photo-initiated polymerization[30–32] and radiation-initiated polymerization[33–37] because of the residual photoinitiator and radiation energy, respectively. Unfortunately, only a few studies concerning the postpolymerization of electropolymerization have been published; for examples, methyl methacrylate[38] and acrylamide[39] in mass amounts of organic acid and $ZnCl_2$ solution, respectively. However, few studies have examined the postpolymerization of electropolymerization in the presence of an initiator, especially the Sn^{+2}/EDTA system.

In this work, the postpolymerization polymer was investigated by determining effects of various factors, such as current density, shelf-time, temperature, $[Sn^{+2}]_i/[EDTA]_i$ ratio, pH_i, initiator concentration, and monomer concentration, on the molecular weight.

EXPERIMENTAL

Materials

Poly(DMAEM-MC) was obtained as described in our previous study.[28] Sodium nitrate was G.R. grade (E. Merck). The solvent water was deionized.

Apparatus and Procedures

The polymer obtained by the method described in our previous study[28] was kept at 30 ± 3 °C in a water bath, and the molecular weight of the polymer was periodically sampled and investigated by the viscometric method described in the previous paper[28] until it approached a stable value, which is defined as MW_∞ (MW_0 is the molecular weight of the freshly produced polymer).

RESULTS AND DISCUSSION

Preliminary Test of Postpolymerization

The preliminary test of postpolymerization is shown in Figures 1 and 2. Figure 1 shows that MW_0 increases with both the current densities, 1.42×10^{-2} and 2.84×10^{-2} mA/cm^2, and the highest MW_0 is located at a $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio of 5 and a current density of 2.84×10^{-2} mA/cm^2. Comparing Figures 1 and 2, the postpolymerization is very obvious. For example, at 2.84×10^{-2} mA/cm^2 and a $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio of 2.50, the MW_0 and MW_∞ are 4.50×10^3 and 9.91×10^6 g/mol, respectively. The MW_∞ is 2200-fold the MW_0.

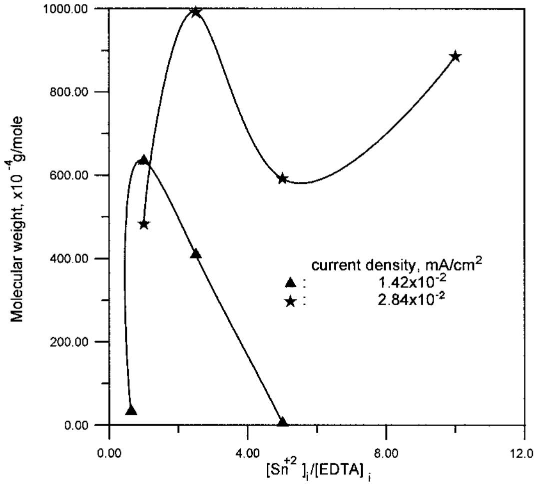

Figure 2 Effect of $[Sn^{+2}]_i/[EDTA]_i$ ratio of electropolymerization on the MW_∞ of the postpolymerization polymer at different current densities. Temperature, 45°C; pH_i, 7.00; charge, 10.8 Coulombs; electrode surface area, 70.42 cm^2; $[Sn^{+2}]_i$, 1.61×10^{-3} M; agitation rate, 0 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

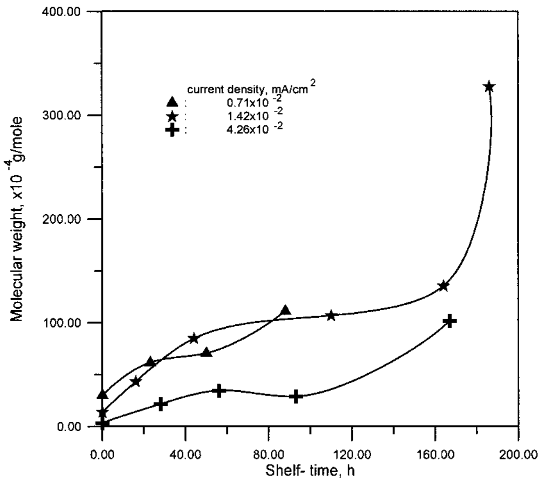

Figure 3 Effect of shelf-time on the molecular weight of the postpolymerization polymer for the electropolymerization at different current densities. Temperature, 45 °C; pH_i, 7.00; $[Sn^{+2}]_i$, 3.22×10^{-3} M; $[Sn^{+2}]_i/[EDTA]_i$, 10.0; reaction time, 3.00 h; agitation rate, 0 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

Effect of Current Density

The effects of current density on the molecular weight of the postpolymerization polymer and MW_∞ are shown in Figures 3–5. At the initial period, the rate of increase of molecular weight of the postpolymerization polymer is similar for different current densities (Figure 3). The effect of current density on the MW_∞ is shown in Figure 4. The MW_∞ decreases with an increase in current density. For example, increasing the current density from 0.71×10^{-2} to 4.26×10^{-2} mA/cm^2 decreases the MW_∞ from 1.12×10^7 to 3.15×10^6 g/mol. The effect of current density on the molecular weight of the postpolymerization polymer for a constant amount of delivered charge passed is shown in Figure 5. The results show that the increase in molecular weight is greater at the higher current density of 1.42×10^{-1} mA/cm^2 than at 1.42×10^{-2} mA/cm^2. However, increasing the current density has the opposite effect on MW_∞; that is, at 1.42×10^{-1} and 1.42×10^{-2} mA/cm^2 current density, the MW_∞ values are 8.54×10^6 and 1.02×10^7 g/mol, respectively.

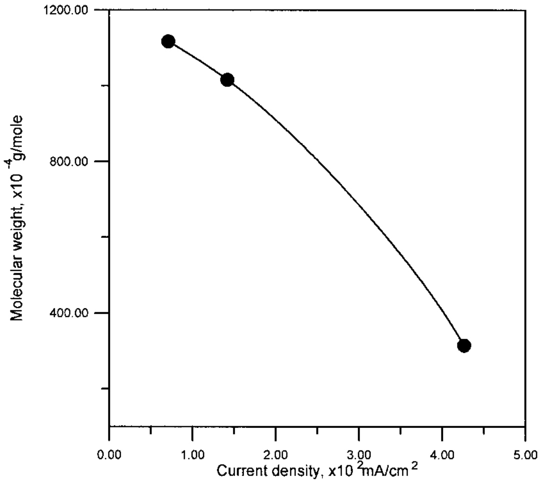

Figure 4 Plot of MW_∞ against current density of electropolymerization. Temperature, 45 °C; pH_i, 7.00; $[Sn^{+2}]_i$, 3.22×10^{-3} M; $[Sn^{+2}]_i/[EDTA]_i$, 10.0; reaction time, 3.00 h; agitation rate, 0 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

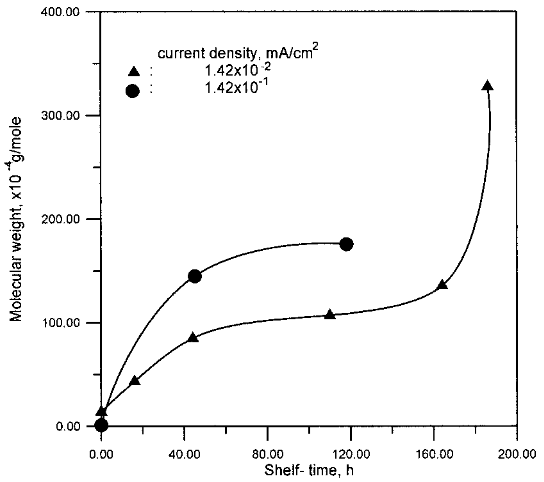

Figure 5 Effect of shelf-time on the molecular weight of the postpolymerization polymer for the electropolymerization at 10.8 Coulombs of charge dispensed. Temperature, 45 °C; pH_i, 7.00; electrode surface area, 70.42 cm^2, $[Sn^{+2}]_i$, 3.22×10^{-3} M; $[Sn^{+2}]_i/[EDTA]_i$,10.0; agitation rate, 0 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

Effect of Shelf-Time

The effects of shelf-time on the molecular weight of DMAEM-MC postpolymerization at different pH_i are shown in Figure 6. The results show that the variation trends in molecular weight due to shelf-time are similar to each other. In addition, the degradation of polymer remains the same. For example, at 4.00 pH_i, increasing shelf-time from 0.0 to 50.0 h increases the molecular weight from 1.40×10^5 to 4.49×10^5 g/mol. Further increasing shelf-time from 50.0 to 217 h decreases the molecular weight from 4.49×10^5 to 3.98×10^5 g/mol.

Effect of Temperature

The relationship of the molecular weight of the postpolymerization polymer with the original re-

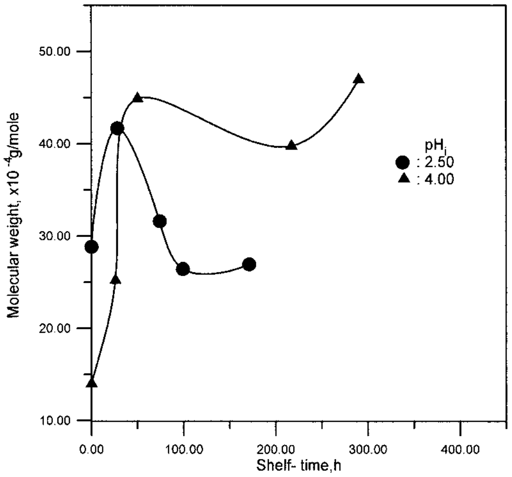

Figure 6 Effect of shelf-time on the molecular weight of the postpolymerization polymer for the electropolymerization at different pH_i. Temperature, 45 °C; current density, 7.08×10^{-2} mA/cm^2; $[Sn^{+2}]_i$, 1.61×10^{-3} M; $[Sn^{+2}]_i/[EDTA]_i$, 5.00; reaction time, 6 h; agitation rate,100 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

action temperature is shown in Figure 7. The results show that MW_∞ increases with the reaction temperature. Nevertheless, the reaction temperature is a minor factor. For example, increasing reaction temperature from 25 to 55 °C increases the MW_0 and MW_∞ from 3.16×10^5 and 7.25×10^5, respectively, to 4.30×10^5 and 1.09×10^6, respectively.

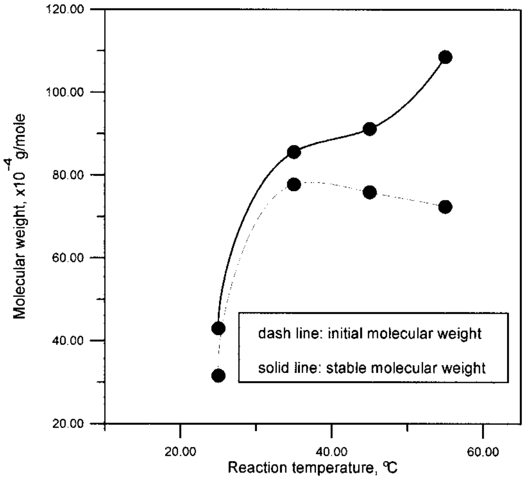

Figure 7 Effect of reaction temperature of electropolymerization on the molecular weight for both the initial product, MW_0, and postpolymerization polymer, MW_∞. pH_i, 2.50; $[Sn^{+2}]_i$, $[EDTA]_i$, 1.61×10^{-3} M; reaction time, 6 h; agitation rate,100 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

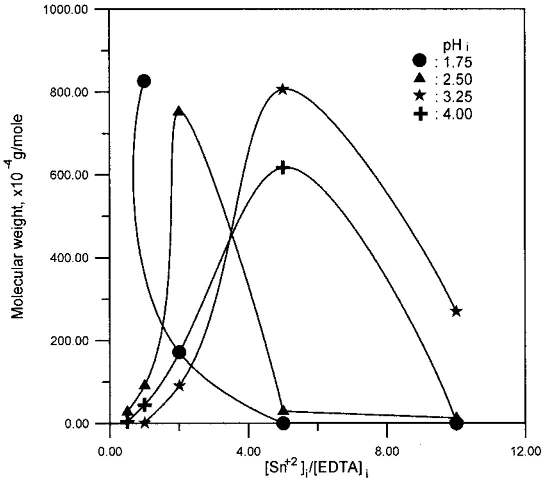

Figure 8 Effect of $[Sn^{+2}]_i/[EDTA]_i$ ratio at different pH_i values of electropolymerization on the MW_∞ of the postpolymerization polymer. Temperature, 45 °C; current density, 7.08×10^{-2} mA/cm^2; $[Sn^{+2}]_i$, 1.61×10^{-3} M; reaction time, 6 h; agitation rate,100 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

Effect of $[Sn^{+2}]_i/[EDTA]_i$ Ratio

The effect of $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio on the MW_∞ is shown in Figure 8. There is an optimum $[Sn^{+2}]_i$/$[EDTA]_i$ ratio for obtaining the highest MW_∞ with respect to different pH_i values. For example, at pH_i 2.50, increasing the $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio from 0.50 to 2.00 increases the MW_∞ from 2.80×10^5 to 7.53×10^6 g/mol, which is also a maximum MW_∞. Further increasing the $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio, from 2.00 to 10.00, results in a decrease in the MW_∞ from 7.53×10^6 to 1.25×10^5 g/mol. Figure 8 also shows that the $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio for obtaining the highest MW_∞ increases with the pH_i. For example, increasing the pH_i from 1.75 through 2.50 to 3.25 increases the $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio from 1.00 through 2.00 to 5.00.

Effect of pH_i Value

The effect of pH_i on the MW_∞ is shown in Figure 9. There is an optimum pH_i value for obtaining the highest MW_∞ with respect to different $[Sn^{+2}]_i$ /$[EDTA]_i$ ratios. For example, at a $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio of 5.00, increasing pH_i from 1.75 to 3.25 increases the MW_∞ from 4.10×10^3 to 8.07×10^6 g/mol, which is also a maximum MW_∞. Further increasing the pH_i from 3.25 to 4.00, the MW_∞ decreases from 8.07×10^6 to 6.17×10^6. Figure 9 also shows that the pH_i value for obtaining the highest MW_∞ increases with the $[Sn^{+2}]_i$ /$[EDTA]_i$ ratio. For example, increasing the $[Sn^{+2}]_i$ /[ED-

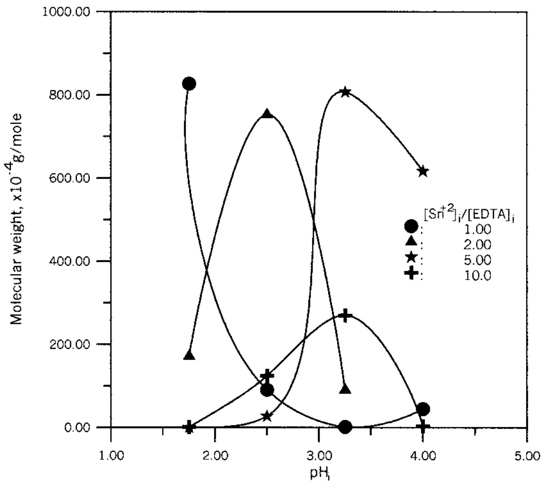

Figure 9 Effect of pH_i values at different $[Sn^{+2}]_i$/$[EDTA]_i$ ratios of electropolymerization on the MW_∞ of the postpolymerization polymer. Temperature, 45 °C; current density, 7.08×10^{-2} mA/cm^2; $[Sn^{+2}]_i$, 1.61×10^{-3} M; reaction time, 6 h; agitation rate, 100 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

TA]$_i$ ratio from 1.00 through 2.00 to 5.00, increases the optimum pH_i value from 1.75 through 2.50 to 3.25.

Effect of Initiator Concentration

The results show that increasing the concentration of initiators from 0.20×10^{-3} to 1.61×10^{-3}M increases the MW_0 from 2.52×10^4 to 7.25×10^5 g/mol, and the MW_∞ from 2.44×10^4 to 9.12×10^5 g/mol, as shown in Figure 10. The results also show that the effect of initial redox initiator concentration on the postpolymerization polymer is less obvious compared with other factors. An explanation for this result may be that the active initiator concentrations are similar to each other after electrolysis, which induces the same effect on the postpolymerization.

Effect of Monomer Concentration

In general, increasing the concentration of monomer increases the MW_0 and MW_∞, as shown in Figure 11. For example, increasing the monomer concentration from 0.48 to 0.73 M increases the MW_0 and MW_∞ from 4.90×10^4 and 5.20×10^4g/mol, respectively, to 2.45×10^5 and 3.39×10^5 g/mol, respectively. In contrast, increasing the monomer concentration from 0.73 to 0.98 M increases the MW_0 and MW_∞ from 2.45×10^5 and 3.39×10^5g7sol;mol, respectively, to 7.25×10^5 and 9.12×10^5g/mol, respectively. Apparently, the

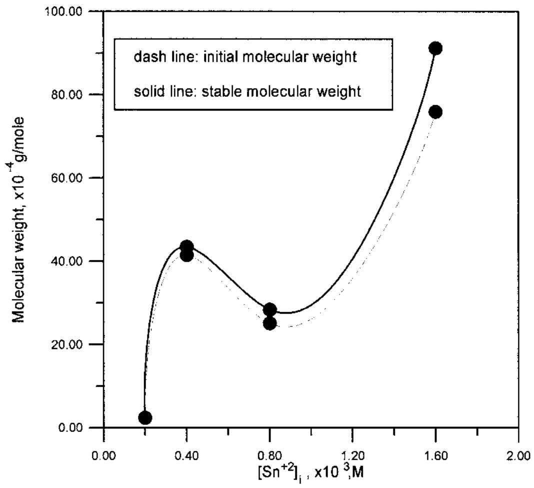

Figure 10 Effect of $[Sn^{+2}]_i$ of electropolymerization on both the MW_0 and MW_∞ of the postpolymerization polymer. Temperature, 45 °C; current density, 7.08×10^{-2} mA/cm^2; pH_i, 2.50; $[Sn^{+2}]_i$/$[EDTA]_i$,1.00; reaction time, 6 h; agitation rate, 100 rpm; $[DMAEM\text{-}MC]_i$, 0.98 M.

effect of monomer concentration on both the MW_0 and MW_∞ is similar and the MW_∞ is >20% MW_0. Consequently, the initial monomer concentration is a minor factor for the molecular weight of the postpolymerization polymer.

CONCLUSIONS

The Sn^{+2}/EDTA initiator system has very obvious postpolymerization, which is quite different from

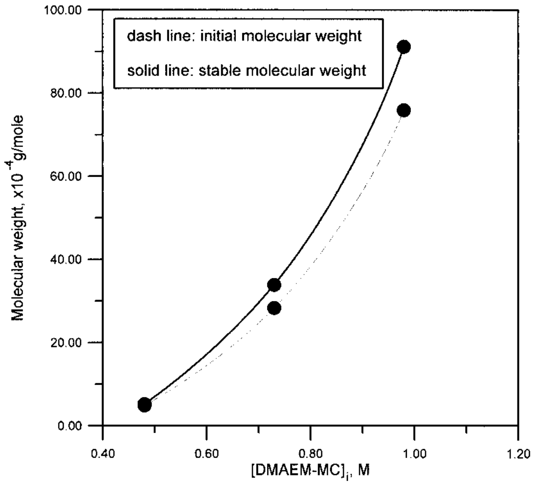

Figure 11 Effect of $[DMAEM\text{-}MC]_i$ of electropolymerization on both the MW_0 and MW_∞ of the postpolymerization polymer. Temperature, 45 °C; current density, 7.08×10^{-2} mA/cm^2; pH_i, 2.50; $[Sn^{+2}]_i$,1.61×10^{-3} M; $[Sn^{+2}]_i$/$[EDTA]_i$,1.00; reaction time, 6 h; agitation rate,100 rpm.

other electropolymerization systems. This characteristic may have positive effect on the fabrication of sensor and SPE because the doping of Sn^{+2}/Sn^{+4} increases the conductivity of polymer. Furthermore, the increase of polymer molecular weight of postpolymerization promotes the mechanical properties of polymer film.

The major factors affecting the molecular weight of the postpolymerization polymer are current density, pH_i, and $[Sn^{+2}]_i$ /[EDTA]$_i$ ratio. In contrast, original polymerization temperature, monomer concentration, initial initiator concentration are minor factors.

The results show that increasing the current density decreases the MW_∞. At 7.00 pH_i, the highest MW_∞ appears at a $[Sn^{+2}]_i$ /[EDTA]$_i$ ratio of 1, and the MW_∞ can be as high as 1.12×10^7 g/mol. Within the range 1.75–4.00 pH_i, the optimum $[Sn^{+2}]_i$ /[EDTA]$_i$ ratio for obtaining the highest MW_∞ increases with the increase of pH_i, and the highest MW_∞ of 8.27×10^6 g/mol appears at a pH_i of 1.75 and a $[Sn^{+2}]_i$ /[EDTA]$_i$ ratio of 1.

The results also reveal that increasing the original reaction temperature, initial initiator concentration, and initial monomer concentration increase the molecular weight of the postpolymerization polymer.

The support of the National Science Council of the Republic of China (NSC 85-2214-E-006-013), National Cheng-Kung University, and Kun-Shan University of Technology are acknowledged.

REFERENCES

1. Tomii, N.; Isono, K.; Hasegawa, T. Jpn. Pat. 09-78486 (1997).
2. Sugiyama, T. Jpn. Pat. 09-188991 (1997).
3. Elliott, D. L.; Hunter, W. E.; Falcione, R. J. U.S. Pat. 5647956 (1997).
4. Sandstrom, E. R.; Shanton, K. J.; Hartjes, T. P.; Swoboda, D. P. Eup. Pat. 786553 (1997).
5. Nagarajan, R. Wong, S. J. B. Eur. Pat. 805234 (1997).
6. Schwoyer, William L. K. Polyelectrolytes for Water and Wastewater Treatment; CRC Press: Boca Raton, FL, 1986; pp 16–25.
7. Parker, S.; Kulicke, W. M.; Bohm, N.; Kotz, J.; Jaeger, W. Angew Makromol Chem 1997, 250, 15.
8. Chen, J. C.; Chen, F.; Gerald, G. C. J.; Vasconcellos, S. R. U.S. Pat. 5643462 (1997).
9. Chen, J. C.; Chen, F.; Walterick, G. C., Jr. U.S. Pat. 5684109 (1997).
10. Chen, H. L.; Farinato, R.; Hawkins,P. PCT Int. Appl. WO. Pat. 97-18167 (1997).
11. Kitchener, J. A. Br Polym J 1972, 4, 217.
12. Hoffmann, F.; Cinatl, J. J.; Kabickova, H.; Cinatl, J.; Kreuter, J.; Stieneker, F. Int J Pharm 1997, 157, 189.
13. Oshlack, B.; Pedi, F. J.; Chasin, M. U.S. Pat. 5580578 (1996).
14. Dietrich, R.; Sachs, G.; Ney, N.; Benedikt, G. PCT Int. Appl., WO. Pat. 97-02020 (1997).
15. Mori, A.; Iijima, J.; Shirai, T.; Okumura, F. Jpn. Pat. 07-330585 (1995).
16. Jaeger, W.; Zimmermann, A.; Hahn, M.; Hildebrandt, V.; Reichert, K. H. PCT Int. Appl., WO. Pat. 97-30094 (1997).
17. Takeda, H. U.S. Pat. 5587415 (1996).
18. Okajima, N. Jpn. Pat. 08-325399 (1996).
19. Hirata, M.; Yamanaka, K.; Adachi, S. Jpn. Pat. 08-159998 (1996).
20. Yokota, A. Jpn. Pat. 07-270364 (1995).
21. Nanba, N.; Tezuka, S. Jpn. Pat. 07-270363 (1995).
22. Takahashi, K.; Noda, K. Jpn. Pat. 06-68907 (1994).
23. Takahashi, K.; Akashi, H.; Noda, K.; Tanaka, K. Jpn. Pat. 07-118480 (1995).
24. Takahashi, K.; Akashi, H.; Noda, K.; Tanaka, K. U.S. Pat. 5643490 (1997).
25. Nayak, P. L.; Lenka, S. J. J Macromol Sci, Macromol Chem 1980, C19(1), 83.
26. Shapoval, G. S.; Lipatova, T. E. " Electrochemical Initiation of Polymerization" [in Russian], Naukova Dumka, Kiev, 1977.
27. Bezuglyi, V. D.; Alekseeva, T. A. Electrochemistry of Polymer [in Russian], Osnova, Kharkov 1990.
28. Lin, T. Y.; Chou, T. C. J Electrochem Soc 1997, 144(3), 835.
29. Lund, H.; Baizei, M. M. Organic Electrochemistry: An Introduction and Guide, 3rd edition, Marcel Dekker: New York, 1990; p1348.
30. Mallon, H. J.; Utschick, H.; Unseld, W. Acta Polym 1991, 42(12), 627.
31. Decker, C.; Moussa, K. J Polym Sci, Part A: Polym Chem 1987, 25(2), 739.
32. Kopietz, M.; Lechner, M. D.; Steinmeier, D. G. Eur Polym J 1984, 20(7), 667.
33. Nikitin, Anatoolig N. Macromol Theory Simul 1996, 5(5),957.
34. Bol′shakov, A. I.; Kiryukhin, D. P.; Barkalov, I. M. Vysokomol Soedin, Ser B 1989, 31(3), 219.
35. Muidinov, M. R.; Dzhardimalieva, G. I.; Selenova, B. S.; Pomogailo, A. D.; Barkalov, I. M. Izv Akad Nauk SSSR, Ser Khim 1988, 11, 2507.
36. Shklyarova, E. I.; Korolev, B. A.; Stroganov, L. B.; Golubev, V. B.; Zubov, V. P.; Kabanov, V. A. Vysokomol Soedin, Ser B 1980, 22(5), 372.
37. Shklyarova, E. I.; Golubev, V. B.; Zubov, V. P.; Kabanov, V. A. Vysokomol Soedin, Ser A 1980, 22(5), 1001.
38. Sarkar, Arun K.; Dolit, Santi R. J Polym Sci, Polym Chem Ed 1980, 18(2), 691.
39. Shukla, Ram Ji; Sinha, A. K. Asian J Chem 1993, 5(1), 150.