# Radiation-Induced Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Poly($\gamma$-methyl-L-glutamate) Membrane in Ethanol Solution

**YUE-E FANG, XIA ZHAO**

Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

*Received 19 April 1997; accepted 6 October 1997*

**ABSTRACT:** The radiation-induced graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto poly($\gamma$-methyl-L-glutamate) membranes was investigated in ethanol. The effects of dose, dose rate, concentration of HEMA, and temperature on the degree of grafting were studied. The initial rate of grafting copolymerization shows the following functional relationship equation: $dG_0/dt = k[M]_0\dot{D}^{0.56}$. The average values of the apparent constants at 27 and 37°C for the initial rates of grafting are $k_1 = 51$ and $k_2 = 91$ $G\%h^{-0.44}$ $kGy^{-0.56}$ $mol^{-1}$ L, respectively. The apparent activation energy of grafting copolymerization is $E = 10.7$ kcal/mol. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1575–1580, 1998

**Key words:** radiation-induced; dose rate; PMLG-*g*-HEMA; initial rate of grafting; apparent activation energy

## INTRODUCTION

Synthetic polypeptides are extremely interesting polymers because of the close relationship they bear to proteins. Synthetic polypeptides have been used widely in material applications for synthetic skin analogs, absorbable sutures, and biocompatible materials. The biocompatibility of polymeric materials is very important in medical applications.

Amudeswari and colleagues[1] reported that the graft copolymerization of 2-hydroxyethyl methacrylate (HEMA), in combination with hydrophobic monomers, onto soluble collagen was employed in the synthesis of hydrogels. Elias and associates[2] studied the crosslinking of poly($\alpha$-amino acids). Shi and coworkers[3] reported on the preparation and permeability of a block copolymer membrane from poly($\gamma$-methyl-L-glutamate) (PMLG) and polyester. He and associates[4] studied permeation of anticancer drugs through synthesized polypeptide membranes. Shi and colleagues[5] reported on the kinetics of radiation-induced graft copolymerization of HEMA onto PMLG membranes. Although biocompatibility of PMLG membrane is excellent, its hydrophilicity is not good. To develop PMLG membrane suitable for medical applications, we studied the radiation-induced graft copolymerization of HEMA onto PMLG membranes in ethanol solution. This study has not been found in recent papers.

## EXPERIMENTAL

### Preparation of PMLG and Membrane

The PMLG was prepared by polymerization of $\gamma$-methyl-L-glutamate-*N*-carboxy-2-amino acid an-

*Correspondence to:* Y.-E. Fang.

Journal of Applied Polymer Science, Vol. 68, 1575–1580 (1998)
 CCC 0021-8995/98/101575-06

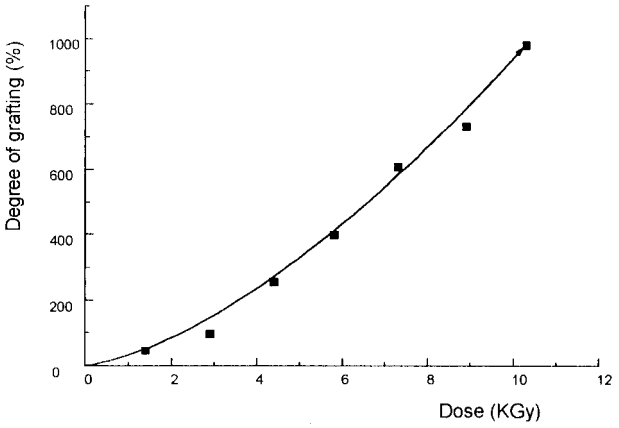


**Figure 1** Effect of radiation dose on degree of grafting in ethanol. Grafting conditions: HEMA concentration, 1.454 mol/L; grafting temperature, 19°C; membrane thickness, 38 $\mu$m; dose rate, 4.4 kGy/h.

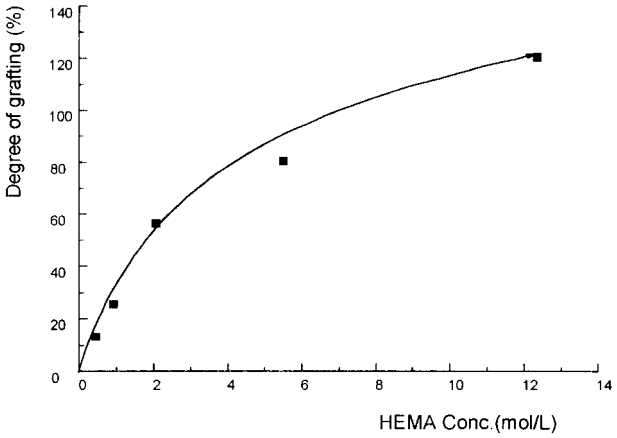


**Figure 3** Effect of HEMA concentration on degree of grafting in ethanol. Grafting conditions: grafting temperature, 20°C; membrane thickness, 40 $\mu$m; dose rate, 4.4 kGy/h; dose, 1.47 kGy.

hydride (MLG-NCA) which was initiated by triethylamine in 1,2-dichloroethane at room temperature for 24 h.

The reaction mixture was poured into hot water and PMLG was precipitated. The PMLG was recrystallized two or three times in 1,2-dichloroethane. Molecular weight of PMLG with $M_n = 1.5 \times 10^5$ was determined by gel permeation chromatography.

The PMLG membranes were cast from 5–8 wt % 1,2-dichloroethane solutions on a glass plate by evaporating the solvent in air at room temperature for 48 h in a dust-free laminar flow hood.

## Grafting Procedure

The PMLG membranes were cut, washed with ethanol, and dried at 60°C under vacuum (10 mmHg) for 7 h; the initial weight, $W_0$, was then measured.

Ethanol was chosen as solvent. The samples were immersed in the HEMA monomer solution in glass reaction vessels, bubbled with $N_2$ gas (99.9%) for 20 min to remove $O_2$, then irradiated in a 60,000 Ci cobalt-60 source.

The grafted membranes were extracted with ethanol at 60°C for several hours to remove monomer and poly-HEMA, then dried, and the dry

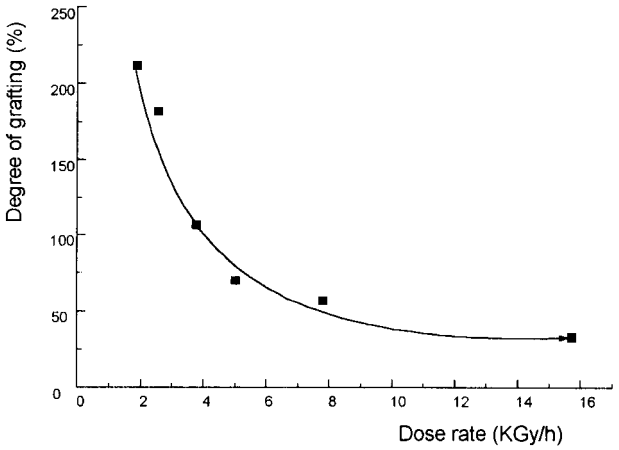


**Figure 2** Effect of dose rate on degree of grafting in ethanol. Grafting conditions: HEMA concentration, 1.454 mol/L; grafting temperature, 21°C; membrane thickness, 39 $\mu$m; grafting dose, 3 kGy.

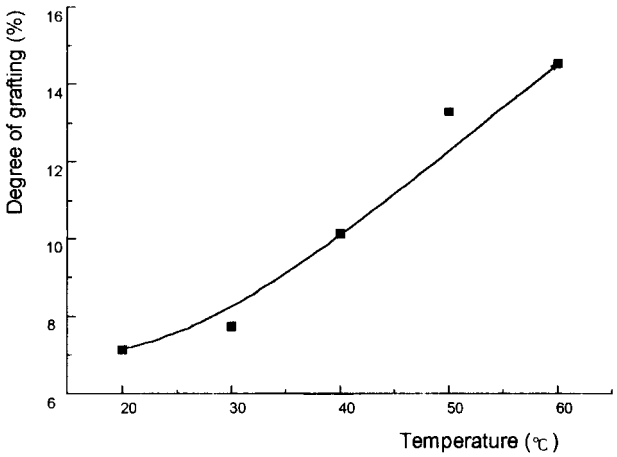


**Figure 4** Effect of grafting temperature on degree of grafting in ethanol. Grafting conditions: HEMA concentration, 0.915 mol/L; membrane thickness, 35 $\mu$m; dose rate, 4.4 kGy/h; dose, 1.1 kGy.

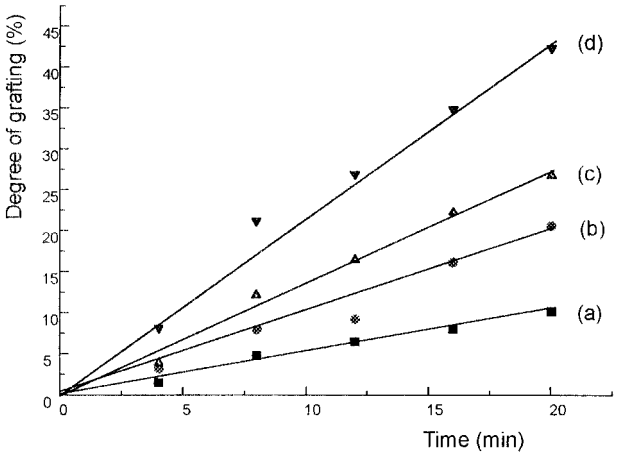


**Figure 5** Rate of grafting at varying HEMA concentrations in ethanol for PMLG membrane. HEMA concentrations (mol/L): (a) 0.412; (b) 0.823; (c) 1.235; (d) 1.646. Dose rate, 1.862 kGy/h; membrane thickness, 38 $\mu$m, grafting temperature, 27°C.

grafted membranes ($W_g$) were weighed. The degree of grafting ($G\%$) was obtained according to the following equation:

$$G(\%) = (W_g - W_0)/W_0 \times 100$$

### Characterization

The spectra of the PMLG and the PMLG-*g*-HEMA polymers were measured with a Nicolet 170 SX Fourier Transform Infrared Photoacoustic Spectroscope (PA-FTIR). The morphologies of the polymer membranes were observed with a Hitachi X-650 Scanning Electron Microscope (SEM).

## RESULTS AND DISCUSSION

### Influence of Dose

Figure 1 shows the effect of dose on the direct graft of HEMA onto PMLG membranes in ethanol solution. The grafting was carried out in the dose range of 1.4 to 10.3 kGy; other conditions were kept constant. From Figure 1, it can be observed that the degree of grafting increases gradually with increasing dose. Ethanol has two major effects on the grafting reaction: (1) homopolymers of HEMA and grafted polymer chains were dissolved in ethanol, and (2) the PMLG membrane is swelled in ethanol.[6] These two effects lead both to greater monomer concentration within the grafting regions and to greater monomer availability within the surrounding solution. Therefore it is apparent that ethanol permits attainment of much higher grafting levels as dose increases. The curve in Figure 1 is typical of a reaction becoming monomer diffusion-controlled.

**Table I Initial Rate and Apparent Rate Constant of Graft Copolymerization of 27°C for 1.862 kGy/h**

| Initial Concentration $[M]_0$ (mol/L) | Initial Rate of Grafting $dG_0/dt$ ($G\%$/h) | Apparent Rate Constant $k_1$ ($G\%h^{-0.44}$ $kGy^{-0.56}$ $mol^{-1}$ L) |
|---|---|---|
| 0.412 | 28.80 | 49 |
| 0.823 | 60.00 | 51 |
| 1.235 | 83.40 | 48 |
| 1.646 | 131.70 | 57 |
| | | (*Average value* 51) |

### Effect of Dose Rate

Figure 2 indicates the effect of dose rate on degree of grafting. It can be seen that the dose rate increases with decreasing degree of grafting. At higher rates, short grafted branches were formed during the copolymerization. At lower dose rates, HEMA diffused into the surface zone of the PMLG

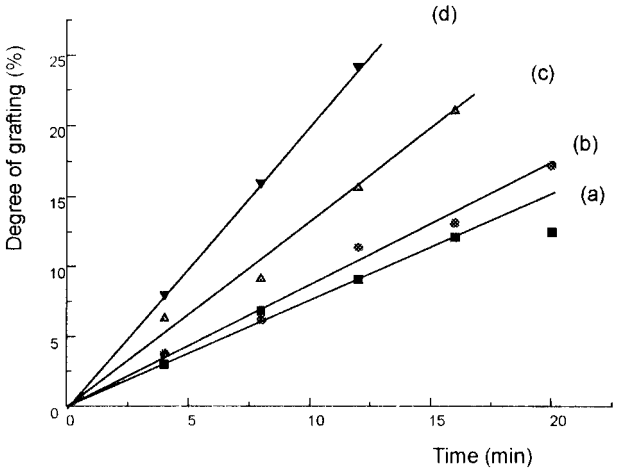


**Figure 6** Degree of grafting at different dose rates in ethanol for PMLG membrane. Dose rate (kGy/h): (a) 1.340; (b) 1.862; (c) 3.567; (d) 7.300; HEMA concentration, 0.412 mol/L; membrane thickness, 35 $\mu$m; grafting temperature, 37°C.

**Table II Initial Rate and Apparent Rate Constant of Graft Copolymerization at 37°C for $[M]_0$ = 0.412 mol/L**

| Dose Rate $\dot{D}$ (kGy/h) | Initial Rate of Grafting $dG_0/dt$ ($G$%/h) | Apparent Rate Constant $k_2$ ($G\%h^{-0.44}$ $kGy^{-0.56}$ $mol^{-1}$ L) |
|---|---|---|
| 1.340 | 44.4 | 91 |
| 1.862 | 52.8 | 90 |
| 3.567 | 77.4 | 92 |
| 7.300 | 113.4 | 90 |
| | | (*Average value* 91) |

membrane and longer grafted branches were formed, resulting in a larger degree of grafting.

### Effect of HEMA Concentration

Figure 3 shows that the degree of grafting increases with increasing HEMA concentration. This result suggests that the degree of grafting is dependent not only on the amount of trapped radicals but also on the diffusibility of HEMA into PMLG membrane. The diffusibility of HEMA through the grafted layer of a PMLG membrane seems to be enhanced at higher monomer concentrations, which leads to the increase in degree of grafting.

### Effect of Temperature

Figure 4 indicates the degree of grafting with the grafting temperature curve for grafting of HEMA onto PMLG membranes. From Figure 4, it can be seen that the degree of grafting increases with grafting temperature. Below 30°C the degree of grafting is rather small and increases slowly with temperature, but from 30°C up it rises much faster. This may be due to the lower temperature; HEMA molecules could not diffuse into the PMLG membranes easily, so a grafting reaction took place mainly at the membrane surface. At higher temperatures the PMLG chain can move to some extent; thus diffusion of HEMA molecules into the membranes occurs. The higher the temperature, the easier the diffusion, so the larger degree of grafting.

### Kinetics of Grafting Copolymerization

#### *Rate of Grafting*

Figure 5 indicates the initial rates of grafting ($dG_0/dt$) at varying concentrations of HEMA for PMLG membranes. The results show that the initial rates are linear with time. As is clear from these results, the initial rates of grafting increases with increasing concentrations of HEMA for PMLG membranes. The initial rates of grafting, $dG_0/dt$, obtained graphically, are shown in Table I.

#### *Dose Rate*

Figure 6 shows the initial rate of grafting at different dose rates for grafting of HEMA onto PMLG membranes. The results show that initial rates are linear with time and that the initial rate of grafting increases with dose rate.

The initial rates of grafting, $dG_0/dt$, obtained graphically, are shown in Table II. According to the data in Table I, Figure 7 shows that a plot of $\ln dG_0/dt$ against $\ln[M]_0$ provides a linear relationship with a stop of 1; that is, $dG_0/dt$ varies with the initial HEMA concentration ($[M]_0$). This result is expressed by the following relationship:

$$dG_0/dt \propto [M]_0 \quad (1)$$

Figure 8 shows the ln–ln plot of $dG_0/dt$ against the dose rate obtained with data in Table II. The linear relationships with a slope of 0.56 in Figure 8 are obtained, i.e., $dG_0/dt$ varies as $\dot{D}^{0.56}$, such as

$$dG_0/dt \propto \dot{D}^{0.56} \quad (2)$$

It is found from eqs. (1) and (2) that the initial rate of grafting is proportional to the $[M]_0$ and

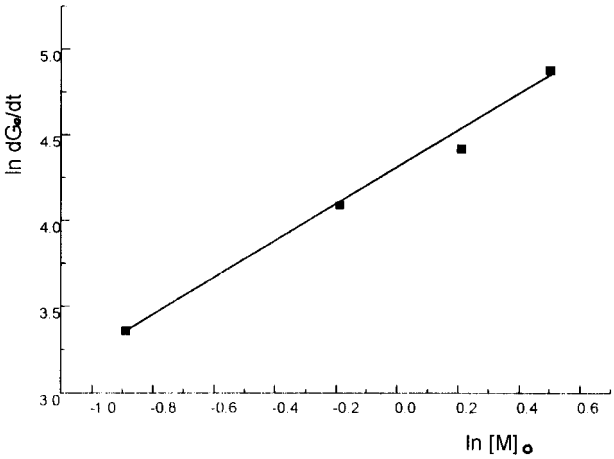


**Figure 7** Effect of HEMA concentration on initial rate of grafting.

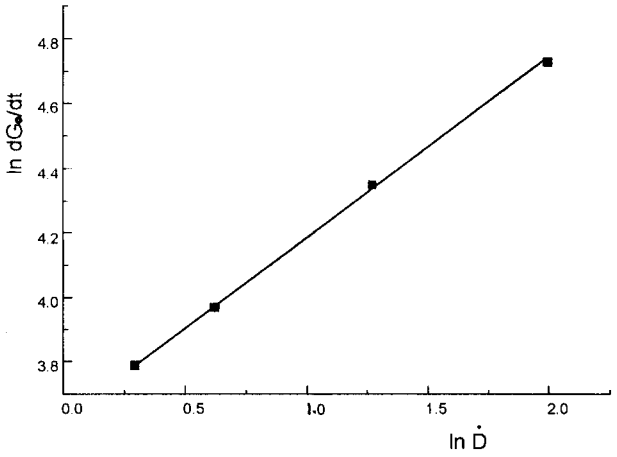


**Figure 8** Effect of dose rate on initial rate of grafting.

$\dot{D}^{0.56}$. Combination of eqs. (1) and (2) yields, for radiation graft of HEMA onto PMLG membranes:

$$dG_0/dt = k[M]_0\dot{D}^{0.56} \quad (3)$$

where $k$ is the apparent constant of the initial rate of graft copolymerization.

According to the data in Tables I and II, $k_1$ and $k_2$ values were calculated by eq. (3). These values are listed in Tables I and II, respectively.

### *Apparent Activation Energy*

Integrating Arrhenius equation

$$d \ln k/dT = E/RT^2 \quad (4)$$

where $E$ is the Arrhenius activation energy, $T$ the temperature (K), and $R$ the gas constant, yields

$$\ln k = -E/RT + C \quad (5)$$

where $C$ is an indefinite integral constant. The average values of $k_1$ and $k_2$ in Tables I and II were obtained at the grafting temperatures of 27 and 37°C, respectively. Therefore,

$$\ln(k_2/k_1) = E(T_2 - T_1)/RT_1T_2$$
$$\ln(91/51) = E \times 10/1.987 \times 300 \times 310$$

that is, $E = 10.7$ kcal/mol, the apparent activation energy of the initial rate for grafting copolymerization of HEMA onto PMLG membrane.

### Structure and Morphology of PMLG-*g*-HEMA Membrane

PA-FTIR spectra of PMLG and PMLG-*g*-HEMA membranes are shown in Figure 9. The band at 3300 $cm^{-1}$ is due to N—H stretching vibration in the amide CONH in the PMLG chain. When the PA-FTIR spectra in Figure 9(a–c) are compared, it is seen that in the spectra of (b) and (c) one new absorption appears at 3500 $cm^{-1}$, due to O—H stretching vibration of the grafted poly(2-hydroxyethyl methacrylate) chains with pendant $—CH_2CH_2OH$. These absorption peaks increase with increasing degree of grafting. This result proves that HEMA is grafted onto the PMLG matrix membrane.

Figure 10 shows the morphologies of PMLG and PMLG-*g*-HEMA membranes observed by SEM. When the micrographs in Figure 10(a,b) are compared, it is seen Figure 10(b) had a microphase-separated structure of the constituent chains. The bright portions of the graft are the island phases dispersed in the dark PMLG matrix (sea phase) [Fig. 10(b)].

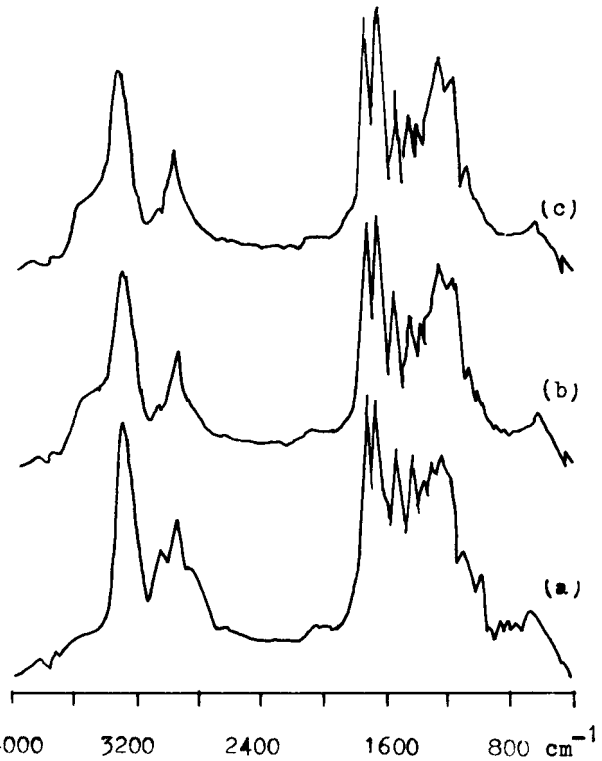


**Figure 9** PA-FTIR spectra of PMLG and PMLG-*g*-HEMA membranes: (a) 0% grafting; (b) 45% grafting; (c) 93% grafting.

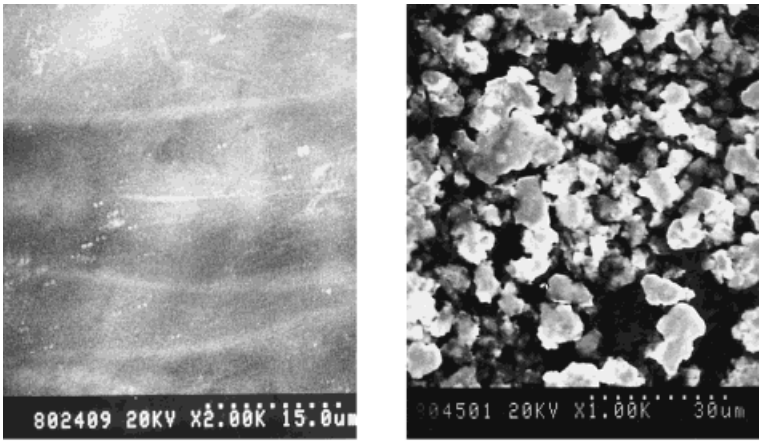


**Figure 10** Scanning electron micrographs of PMLG and PMLG-*g*-HEMA membranes: (a) 0% grafting; (b) 45% grafting.

## CONCLUSIONS

1. The PMLG was prepared by polymerization of MLG-NCA which was initiated with triethylamine in 1,2-dichloroethane at room temperature for 24 h.
2. PMLG-*g*-HEMA membranes were prepared by direct grafting by means of cobalt-60 $\gamma$ radiation of HEMA onto PMLG membranes.
3. The influences of concentration of HEMA and dose rate on grafting rate were investigated. The initial rate of grafting fitted the following equation: $dG_0/dt = k[M]_0\dot{D}^{0.56}$.
4. The average values of the apparent constants of the initial rates of grafting at 27 and 37°C are $k_1 = 51$ and $k_2 = 91$ $G\%\mathrm{h}^{-0.44}$ $\mathrm{kGy}^{-0.56}$ $\mathrm{mol}^{-1}$ L, respectively.
5. The apparent activation energy of graft copolymerization is $E = 10.7$ kcal/mol.

## REFERENCES

1. S. Amudeswari, C. Rami, and K. Thomas Joseph, *J. Appl. Polym. Sci.,* **32,** 4939 (1986).
2. H. G. Elias, M. B. El-Sabbah, W. M. Lopis, and J. Semen, *J. Macromol. Sci., Chem.,* **A16**(2), 529 (1981).
3. T. Y. Shi, J. Zheng, Y. E. Fang, and H. Y. Wang, *Water Treatment,* **6,** 85 (1991).
4. W. D. He, Y. E. Fang, T. Y. Shi, *J. Biomed. Eng.,* **12**(3), 187 (1995) (in Chinese).
5. T. Y. Shi, Y. E. Fang, X. Zhao, F. Shi, *J. China Univ. Sci. Technol.,* **25,** 65 (1995) (in Chinese).
6. Y. Fujimoto, *Poly(amino acid): Application and Prospect,* K. Kotansha Scientific, Tokyo, Japan, 1974, p. 142.