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Thermodynamic and kinetic considerations: effect of β-cyclodextrin on methyl methacrylate dispersion polymerization

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Abstract

Effect of β-cyclodextrin (CD) on methyl methacrylate dispersion polymerization forming poly (methyl methacrylate) (PMMA) particles was investigated. The presence of CD showed obviously effects on the polymerization, so as to increase the rate of polymerization and the conversion of monomer, as well as decrease the particle size. These effects were evidenced by the more increase in the CD content. The change of free energy derived from thermodynamic investigation in the present of CD was lower than that in the absence of CD. Also the monomer reactivity in the presence of CD is actually higher than that in the absence of CD. The decrease of free energy would be thermodynamically responsible for the increase of MMA conversion. The increase of monomer reactivity may take charge of increasing the polymerization rate. The dependency of particle size on CD content may be thermodynamically responsible for the change of macromolecular conformations of stabilizer due to the interaction of CD and stabilizer.

Keywords: Thermodynamics and kinetics; Cyclodextrin; MMA polymerization

1. Introduction

β-Cyclodextrin (CD) is torus-shaped cyclic oligosaccharide consisting of seven α-1,4-linked D-glucopyranose units with an internal hydrophobic cavity. It is well known that this structure possesses remarkable ability to include many organic compounds [1–4]. Because of this unique behavior, CD and its derivatives have been studied extensively in many research fields such as drug delivery system [5], separation and absorption of materials [6,7], environmental protection devices [8] and functional catalysts [9] etc. Recently, it was found that CD could be used in polymer chemistry as well [10]. Ritter et al. [11] have shown that in nearly all cases of methacrylates polymerizations, the polymerizations in the presence of CD usually are in high monomer conversion. A polymerization with high conversion will be economical and suitable to large scale of applications, and thus is essentially necessary for practical operations. Meanwhile, they have also shown that [12] CD might produce significant effect on the particle size of resulted polymers. These interesting results have driven much endeavor to investigate the probable roles of CD in polymerization process, especially the intrinsic role. It is generally thought that the inclusion/complexation behavior of CD for monomer plays the most important roles in polymerization process. In currently accepted opinion [13, 14], the complexation may aid the transport of monomer to the loci of polymerization and correspondingly results in a higher monomer concentration at the loci of polymerization, which has the effect of increasing the rate of polymerization and monomer conversion. The change of particle size with CD may be as the results of interaction of CD and colloids, or CD and stabilizers/surfactants etc. [15]. Virtually, so far, these viewpoints are still qualitative, cannot summarize all phenomena, such as under a comparable condition, the particle size does not seemingly depend completely on CD [16]. Also the quantitative relation of both monomer conversions from two polymerizations cannot be well summarized [17]. It is thus clear that taking more considerations, especially the additional considerations, on this process is necessary.

Synthetic poly (methyl methacrylate) (PMMA) particles have met various desires in different aspects [18–20]. Amongst them, dispersion polymerization is in common use due to the relatively simple operation. In present study,

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methyl methacrylate (MMA) dispersion polymerization forming PMMA particles was used as template polymerization process. Based on the polymerization process, the effects of CD on the MMA conversion and particle size were investigated. The preliminary interpretations based on thermodynamics and kinetics were presented.

2. Experimental

2.1. Materials

MMA came from Bodi Chemical Co., Tianjing (China) was purified by distillation-reduced pressure before use. Polyvinyl pyrrolidone (PVP) (MW, 10,000–70,000) was obtained from Silong Chemical Co., Guangdong. Benzoyl peroxide (BPO) was purchased from the Chemical Factory of Hubei University. CD was obtained from the Kelong Chemical Factory, Sichuan. All other chemicals were commercially available products of reagent grade.

2.2. Synthesis of PMMA particles

PMMA particles were synthesized by dispersion polymerization. In water/methanol [1/7(w/w)] dispersion medium, based on MMA monomer, 2% (w/w) BPO as initiator and 1% (w/w) PVP as stabilizer were used in this polymerization. The polymerization was carried out on a 100 ml of three-necked flask fitted with a mechanical stirrer, nitrogen inlet and reflex condenser. The agitation speed was fixed at 250 rpm throughout the process. After deaerated with nitrogen gas, the polymerization was performed at 70 °C for 24 h. The resulted particles were separated by centrifugation, and washing with methanol and water for 3 times, respectively. In present article, the figures that follow CD (such as CD-1.25%, CD-6.25% and CD-18.75%) were the percentage content of CD (related to the monomer); Blank meant the polymerization in the absence of CD.

2.3. Determination of monomer conversions

Following the description as in Section 2.2, the conversions of monomer at various times (70 °C) were determined. Under the protection of nitrogen gas, a sample was taken out every hour from this polymerization system. These conversions were calculated by [21]:

$$x = \frac{m_{\mathrm{p}}}{m_{\mathrm{m}}} \times 100\%$$

Where, x is the conversion of monomer, m_{p} the mass of polymer produced in the given time, and m_{m} the mass of monomer containing in the sample. Each experiment was repeated at least for 3 times and the average value was given. The conversions of monomer at various temperatures were also determined following above descriptions. After polymerization for 24 h, the sample was taken out from these systems and then the conversion was determined.

2.4. Particle size analysis

The particle size was determined using a Malvern Master Sizer/E particle size analyzer (UK), which functions under the principle of laser diffraction. The size distribution curve displays the particle size along the *x*-axis and the percentage along the *y*-axis. From these data the average mean diameter of the particles was determined.

2.5. UV spectroscopy

With the same medium as the polymerization system, the UV spectra of samples were obtained from U-2010 spectrophotometer (Hitachi, Japan). The apparatus was equipped with statistical software for data treatment. At ambient temperature, the sample was putted into the quartz of vessel with the medium as referrer. The scanning range was 190–300 nm.

3. Results and discussion

3.1. Effect of CD on the conversion of MMA

The effect of CD on MMA conversion is shown in Figs. 1 and 2. As can be observed from Fig. 1, at various times, MMA conversions are higher in the presence of CD than that in the absence of CD. The enhancement on the conversion is evidenced by the increase in the CD concentration. They are also in similar enhancements at various temperatures (Fig. 2). The observation means that the rate of polymerization in the presence of CD is larger than that in the absence of CD. Clearly, CD plays an important role in increasing the rate of polymerization. Jeromin et al. [22] had confirmed that in a similar study the complexation of methacrylates to CD might significantly increase the monomer reactivity. The increase in the monomer reactivity may be responsible for the enhance-

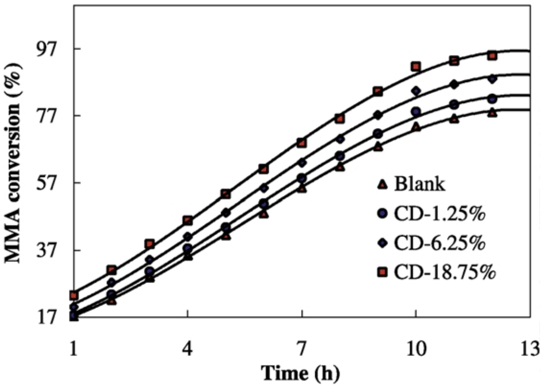

Fig. 1. Effect of CD on MMA conversion (70 °C).

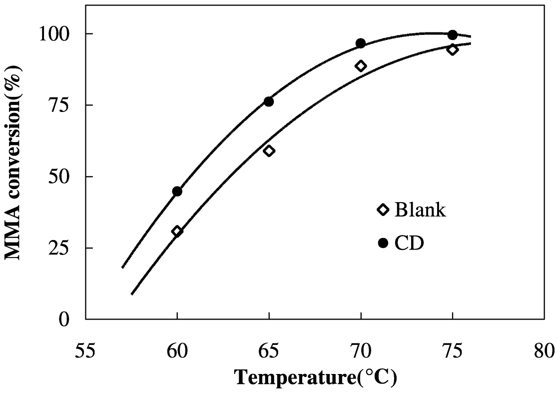

Fig. 2. Effect of CD on MMA conversion (CD, 6.25%. Time, 24 h).

ments of the rate of polymerization and MMA conversion. Rimmer et al. [23] indicated that in the polymerization process, CD might aid transport of the monomer to the loci of polymerization, which correspondingly increases the monomer concentration at the locus of polymerization and thus increases the rate of polymerization. The explanations to some extent well elucidate the phenomena of increasing the rate of polymerization and monomer conversion. Virtually, so far, the explanations are rather qualitative; quantitative aspect still needs more investigations. Also the explanations cannot summarize the effects of temperature and time on the polymerization process. Clearly, some additional information waits to be considered. Further investigation shows that the change of free energy in the presence of CD is lower than that in the absence of CD. Also the monomer reactivity with CD is actually higher than that without CD. The decrease in the change of free energy would be thermodynamically responsible for improving the monomer conversion. The increase in the monomer reactivity may take charge of increasing the polymerization rate. The more information will be shown in Sections 3.1.1 and 3.1.2.

3.1.1. Thermodynamic consideration

Marangoni et al. [24] have pointed out that thermodynamics is an efficient mean in investigating a chemical process. However, so far, few workers in polymer field have employed it to investigate the polymerization process. Virtually, thermodynamics can give much additional information involved by the polymerization process. With the initial state and the final state of reaction molecules in hands, one can expect to learn about the thermodynamic process involved by this polymerization. It has been well known that the extent to a chemical reaction is closely associated with the change of chemical potential in this reaction system. According to thermodynamic theory, the basic expression of chemical potential is:

$$\mu = \mu^{\phi} + RT \ln \frac{C}{C^{\phi}} \tag{1}$$

Here, μ and μ^{ϕ} are the actual chemical potential and standard chemical potential of reacting monomer molecules, respectively. C and C^{ϕ} are the corresponding monomer concentration. Apparently, according to above expression, the change in the concentration of monomer would result in the corresponding change of chemical potential. Up to the end of the polymerization, the final change of chemical potential will be [25]:

$$\Delta\mu = RT \ln \frac{C_1}{C_0} = RT \ln(1 - x) \tag{2}$$

Here, C_1 and C_0 are the final and the initial concentration of monomer, x the conversion of monomer. Now, based on thermodynamic relationship, we know:

$$\Delta\mu = \Delta\bar{H}_{\mathrm{m}} - T\Delta\bar{S}_{\mathrm{m}} \tag{3}$$

Connecting Eq. (2) with (3), one may obtain:

$$\ln(1 - x) = \frac{\Delta\bar{H}_{\mathrm{m}}}{RT} - \frac{\Delta\bar{S}_{\mathrm{m}}}{R} \tag{4}$$

This final expression is a universal relationship in chemical reaction [26,27]. Expectedly, the monomer conversion relies intrinsically on the changes of enthalpy and entropy of the reaction. Also, it can be seen that thermodynamics correlates monomer conversion and temperature. Compared to general viewpoint, thermodynamics apparently shows the advantage of quantification. As expressed in Eq. (4), the diagram [$\ln(1 - x)$ versus $1/T$] is normally expected to be a straight-line (Fig. 3). The changes of thermodynamic parameters derived from Fig. 3 are shown in Table 1. Adding CD into MMA polymerization on one hand increases the enthalpy 148.47 kJ mol^{-1}. On the other hand, the addition also increases the entropy 445.36 J mol^{-1} K^{-1}. It is noticeable, also most important that the addition of CD decreases the free energy of this system by -4.28 kJ mol^{-1}. The decrease in the free energy would thermodynamically tend to improve the monomer conversion. The increase of enthalpy may be responsible for the complexation of CD and monomer [28]. The increase of entropy may be ascribed to the change of zone concentration of monomer due to the complexation [13,14].

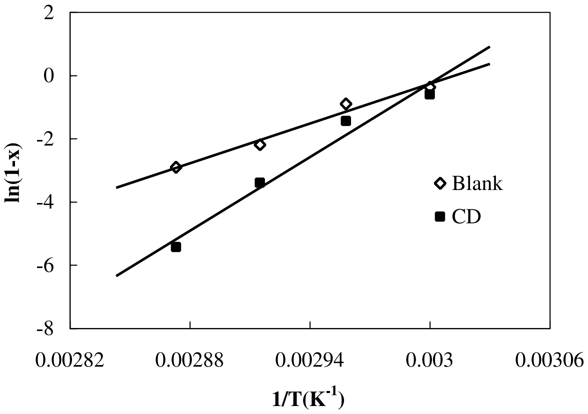

Fig. 3. Thermodynamic curves of both polymerization systems.

Table 1
Changes of thermodynamic parameters in both systems

Polymerization system	Changes of thermodynamic parameters		
	Enthalpy (kJ mol^{-1})	Entropy (J mol^{-1} K^{-1})	Free energy (kJ mol^{-1}, 70 °C)
Without CD	174.22	524.80	−5.78
With CD	322.69	970.16	−10.06
Effect of CD	148.47	445.36	−4.28

3.1.2. Kinetic consideration

Under a free radical polymerization condition, monomers and radical 'fragments' of initiator form preliminary free radicals (initiation) Subsequently, these preliminary free radicals combine with other monomers forming the longer chains of free radicals (propagation), and so go on iteratively to the end. Compared to the propagation, monomer consumption in initiation step is rather minor. Thus the magnitude of the monomer conversion rests mainly with monomer consumption in the propagation. According to kinetic theory, the basic expression of the rate of propagation is [29]:

$$\frac{dx}{dt} = k_p[M][M\cdot] \tag{5}$$

Here, $[M]$ and $[M\cdot]$ are the concentration of monomer and total concentration of various chain-length of radicals. According to the scenario of steady state, during the polymerization, the radical concentration might be taken account for as a fixed value, the initiation rate then approximately equals to the termination rate [29]. One may obtain following relationship with a simple treatment:

$$[M\cdot] = \left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}} \tag{6}$$

Here, f is the initiation efficiency of initiator, $[I]$, the concentration of initiator. k_d and k_t are the rate constants of initiation and termination. Replacing Eq. (6) into Eq. (5), one may obtain:

$$\frac{dx}{dt} = k_p\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}[M]$$

or

$$\frac{dx}{dt} = k_p[M]\left(\frac{v_i}{2k_t}\right)^{\frac{1}{2}} \tag{7}$$

Here v_i is the rate of initiation. Whether the polymerization contains CD or not, each has a similar relationship. Taking account for the effects of initiation and termination on the consumption of monomer is comparatively limited, one would expect k_p and $[M]$ to play main roles in determining the conversion. Connecting both similar relationships, one may obtain:

$$\frac{dx^{CD}}{dx^{B}} = \frac{k_p^{CD}[M]^{CD}}{k_p^{B}[M]^{B}} \tag{8}$$

Here, the superscripts CD and B mean the polymerizations with CD and without CD. Defining a new symbol A_r as follows:

$$A_r \equiv \frac{k_p^{CD}}{k_p^{B}} \tag{9}$$

Basing on general theory, we know A_r is a fixed value under a given temperature. Obviously, under comparable conditions, A_r may reflect the relative reactivity of monomer between polymerizations with CD and without CD. By a simple treatment, Eq. (4) can be rewritten into:

$$\frac{dx_{t_i}^{CD}}{(1-x_{t_i}^{CD})} = A_r\frac{dx_{t_i}^{B}}{(1-x_{t_i}^{B})} \tag{10}$$

Here, x_{t_i} is the monomer conversion of a given time. Via integration, following equation may be obtained:

$$\ln(1-x_{t_i}^{CD}) = A_r\ln(1-x_{t_i}^{B}) \tag{11}$$

Clearly, the conversions from both systems are closely associated with the reactivity of monomer. Also the conversions from both systems are actually correlative. A_r-value may be obtained from the diagram $[\ln(1-x^{CD})$ versus $\ln(1-x^{B})]$ (Fig. 4), and whose result is shown in Table 2. As can be observed from Table 2, CD produces significant effect on the monomer reactivity. 1.25%(w/w) content of CD induces 11.4% of increases in the monomer reactivity. The higher content of CD correspondingly results in higher MMA reactivity. The increase of MMA reactivity in the presence of CD may be responsible for the increase of polymerization rate of MMA. The similar observation is also found in an earlier literature [11].

3.2. Thermodynamic consideration for the effect of CD on particle size

Effect of CD on particle size of PMMA is shown in Fig.

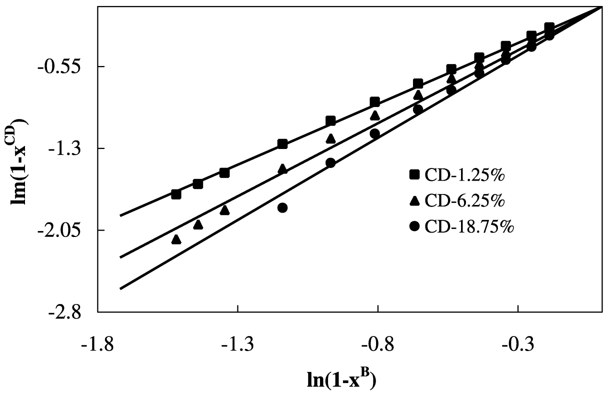

Fig. 4. Relation between $\ln(1-x^{CD})$ and $\ln(1-x^{B})$.

Table 2
Effect of CD on the monomer reactivity

CD content (%)	A_r
0	1
1.25	1.114
6.25	1.337
18.75	1.504

5. As is apparent, the particle size shows a clear dependency on CD content. PMMA particles, 9.493 μm in average diameter, are produced from the polymerization in absence of CD. However, with 1.25% of CD, the PMMA particles, 8.706 μm in the diameter, are produced from this process, and also the uniformity has a some extent of improvement. The higher content of CD will result in the smaller particles. This strongly indicates that CD plays an important role in decreasing the particle size. It has been well known that stabilization action is the basis of particles formation. The mechanism of stabilization with macromolecular stabilizer is usually thought of as entropic in origin. Grafting of monomers to the stabilizer plays an important role in this system. Clearly, if the macromolecule is to stabilize the colloid, the stabilizer must present enough entropy to overcome the very large amounts of enthalpy associated with the high surface area of a polymeric colloid [30]. As solvated segments of the macromolecular chain can exist in many random coil conformations, the required increase in the entropy of the surface can be supplied from the macromolecular chain that contains hydrophobic segments adsorbed to the particle surface and also segments that are soluble in the aqueous phase. With the stabilization mechanism in mind, one would not expect a rigid cyclic polymer such as CD to act as colloid stabilizer. Further investigation found from this case that in the absence of stabilizer, even 20% of CD could not lead to the formation of particles from this polymerization. The phenomena were also similar in the earlier report [31,32]. It would appear from this case that CD plays an assistant role in aiding stabilizing the colloid.

Fig. 6 gives the effect of CD on the UV spectra of PVP stabilizers. As can be observed, the presence of CD produces a certain degree of red shift. The red shift is evidenced by the further increase in the CD content. This indicates that there exists an interaction between PVP and CD. The same observation was also found in an earlier literature of Loftsson and his co-worker [33]. As afore-elucidated, the chain of macromolecule stabilizer may exist in many random coil conformations. The change in the conformations due to the interaction of CD and stabilizer may present more suitable conformation to overcome the increase of surface enthalpy.

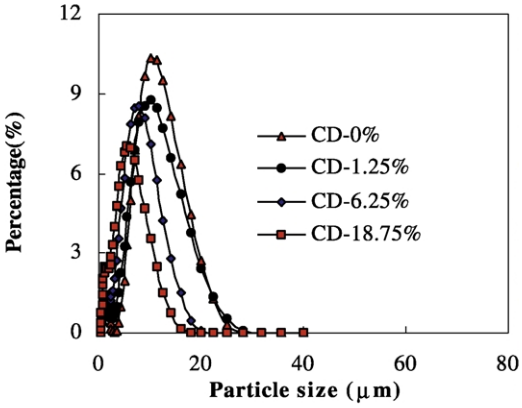

Fig. 5. Effect of CD on size-distribution of particles.

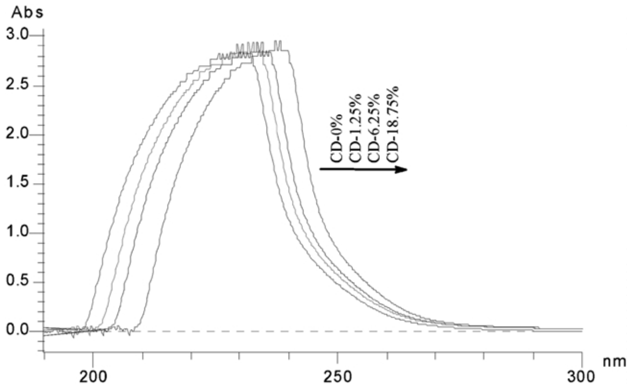

Fig. 6. Effect of CD on UV spectra of PVP.

4. Final remarks

This research presents the preliminarily thermodynamic and kinetic considerations on the effect of CD on MMA dispersion polymerization forming particles. The polymerization in the presence of CD is in higher monomer conversion than that in the absence of CD. Also the particles formed from the polymerization with CD are smaller than that without CD. These effects of CD are evidenced by the more increase in the CD content. The complexation/inclusion mechanism of CD and monomer to some extent well interprets the increases of polymerization rate and monomer conversion. Virtually, the explanation is still qualitative; quantitative aspect needs more investigations. Also the explanations cannot summarize the effects of temperature and time on the polymerization process. So, here we take additional considerations on the polymerization process. Thermodynamic investigation shows that the change of free energy from the polymerization with CD is lower than that without CD. Also the monomer reactivity in the presence of CD is actually higher than that in the absence of CD. The decrease of free energy would be thermodynamically responsible for the increase of MMA conversion. The increase of monomer reactivity may take charge of increasing the polymerization rate. The particle size shows an obvious dependency on the CD content. This may be thermodynamically responsible for the change of macromolecular conformations of stabilizer due to the interaction of CD and stabilizer. It is also necessary to point out that the interpretation is somewhat tentative; further work is necessary and is currently underway. Other aspects that, have not, as yet, been addressed in the article, are also expected to be significant.

References

[1] Henriques ES, Bastos M, Geraldes CC, Ramos MJ. J Chem Thermodyn 2003;35:1717.

[2] Wei YL, Ding LH, Dong C, Niu WP, Shuang SM. Spectrochim Acta, Part A: Mol Biomol Spectrosc 2003;59:2697.

[3] Li JF, Wei WX, Ding LH, Dong C. Spectrochim Acta, Part A: Mol Biomol Spectrosc 2003;59:2759.

[4] Liu Y, Li L, Zhang HY, Liang P, Wang H. Carbohydr Res 2003;338: 1751.

[5] Debunne A, Vervaet C, Remon JP. Eur J Pharm Biopharm 2002;54: 343.

[6] Bai DM, Zhao XM, Hu ZD. Chin J Anal Chem 2001;29:413.

[7] Crini G. Bioresource Technol 2003;90:193.

[8] Massey KA, Van Engelen DL, Warner IM. Talanta 1995;42:1457.

[9] Shiraishi Y, Tomita H, Fujiki K, Hirai H. React Funct Polym 1998;36: 99.

[10] Wang YJ, Zhang ZP, He BL. Prog Chem 2000;12:318.

[11] Ritter H, Tabatabai M. Prog Polym Sci 2002;27:1713.

[12] Ritter H, Schwarz-Barac S, Stein P. Macromolecules 2003;36:318.

[13] Madison PH, Long TE. Biomacromolecules 2000;1:615.

[14] Bernhardt S, Glockner P, Theis A, Ritter H. Macromolecules 2001;34: 1647.

[15] Storsberg J, van Aert H, van Roost C, Ritter H. Macromolecules 2003; 36:50.

[16] Rimmer S, Mohammed Ramli AN, Lefèvre S. Polymer 1996;37:4135.

[17] Glöckner P, Ritter H. Macromol Rapid Commun 1999;20:602.

[18] Park JY, Shim JJ. J Supercrit Fluids 2003;27:297.

[19] Ye Q, Ge XW, Zhang ZC. Radiat Phys Chem 2003;66:11.

[20] Bulmus V, Ayhan H, Piskin E. Chem Engng J 1997;65:71.

[21] Zhai MH, Zhang WM, Shen EH, Fu Z, Zhang F. Acta Phys Chem Sinica 1999;15:747.

[22] Jeromin J, Ritter H. Macromol Rapid Commun 1998;19:377.

[23] Rimmer S, Tattersall PI. Polymer 1999;40:5729.

[24] Marangoni G, Tremaine PJ. Chem Thermodyn 2001;33:1619.

[25] Fu XC, Shen WX, Yao TY. Physicochemistry, 4th ed. Beijing: Chin. High Edu. Press; 1998. p. 786.

[26] Luo LT, Li SJ, Deng GFJ. Rare Earths 2003;21:494.

[27] Li SJ, Luo LT. Chin J Nanchang Univ (Nat Sci) 2001;25:290.

[28] Glockner P, Metz N, Ritter H. Macromolecules 2000;33:4288.

[29] Feng XD, Tang AQ, Qian RY, Hen BL, Yu TY, Lin SA. Chemistry and physics of polymer. Guangzhou: Chin. Zhongshan Univ. Press; 1984. p. 55.

[30] Rimmer S, Tattersall PI. Polymer 1999;40:6673.

[31] Schmölzer S, Hoffmann H. Colloids Surf A: Physicochem Eng Asp 2003;213:157.

[32] Retna Raj C, Ramaraj R. Electrochim Acta 1998;44:279.

[33] Loftsson T, Fririksdóttir H. Inter J Pharm 1998;163:115.