

SIMULTANEOUS MEASUREMENT OF FREE RADICAL DECAY IN POLYMERIZATION OF MMA INITIATED BY AIBN USING ESR AND ITS KINETIC MODEL*

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Abstract The kinetics of free radical decay in the polymerization of MMA initiated by AIBN was studied by means of ESR spectroscopy. It was found that the curves of radical decay are strongly associated with the reaction temperature, the initiator concentration and the solvent. In the case of the radical polymerization carried out at high temperature or in solution, the radical concentration first reached a maximum, then declined monotonously with reaction time. It was also found that the greater the amount of initiator or the higher the temperature, the more rapidly the radicals decay. When the bulk polymerization was implemented at a relatively low temperature, the curves of radical decay became more complicated, i.e., the radical concentration rapidly rose to a maximum, then dropped to a minimum, finally increased again with reaction time. Taking into account the diffusion effect, a semi-empirical equation is suggested to describe the kinetics of propagating radical decay.

Keywords Radical polymerization, Decay, MMA, ESR, Modeling

INTRODUCTION

Free radical polymerizations are characterized by the presence of an auto-acceleration in the polymerization rate as the reaction proceeds^[1]. It would normally be expected that a reaction rate falls with time, because the monomer concentration and the initiator concentration decrease with time^[2]. However, the exact opposite is observed in many polymerizations where the rate of polymerization increases with conversion^[2]. As the polymer concentration increases, the macromolecular chains become overlapped and entangled with one another. This causes a significant reduction in termination rate, which often referred to as the Trommsdorff or gel effect^[3].

Electron spin resonance (ESR) spectroscopy was introduced to the study of free radical polymerization kinetics by Fischer^[4]. The stationary concentration of macroradicals in free radical polymerization was measured simultaneously by several authors^[3, 5-10] using ESR spectrometer. In this work, we report on the use of an on-line ESR to measure the radical concentration in the polymerization of methyl methacrylate (MMA) initiated by 2,2'-azobisisobutyronitrile (AIBN) under different conditions, and discuss the influence of viscosity on the decay curve of the propagating radical concentration. In the case of high temperature or solution polymerization, the viscosity increases rather slowly with the monomer conversion, and the diffusion of radicals is affected slightly by the monomer conversion and the decay of radical concentration is also affected slightly. Alternatively, for the bulk polymerization performed at lower temperature, the kinetic behavior of the reaction system is associated with the high viscosity, which results in a complicated curve of radical decay. Besides, we tried to develop a comprehensive kinetic model for describing the polymerization process over the entire course of reaction, while taking account of the influence of diffusion behavior of the propagating radicals on the polymerization.

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EXPERIMENTAL

Commercial MMA was washed with an aqueous solution of 5% NaOH and with deionized water, then it was dried successively with anhydrous sodium sulfate and 0.4 nm molecular sieves and fractionated under reduced pressure. AIBN was recrystallized from ethanol.

ESR spectra were recorded on a Varian Model E-112 spectrometer (X-band). Sample cooling and temperature control were accomplished by connecting a quartz Dewar pipe to a Dewar flask. The inside temperature of the Dewar pipe was monitored with a thermocouple. The glass ESR sample tube containing MMA and AIBN was bubbled with high purity N_2 gas to remove the oxygen. Then the tube was sealed. Typical conditions for acquisition of ESR spectral data were as follows: field intensity 3270 G, sweep width 5×100 G, amplitude modulation 2.0×1 G, gain 2.5×10000 , microwave frequency 100 kHz, microwave power 10 mW, time constant 0.25 s, phase 180° .

RESULTS AND DISCUSSION

ESR Spectra During Polymerization of MMA

The ESR spectra at various reaction times for the bulk polymerization of MMA are shown in Fig. 1. A weak 13-line spectrum, which was attributed to the MMA radicals in liquid state^[3, 6, 8, 10], was observed at the initial stage of polymerization. It was composed of five outer lines and eight inner lines, the relative intensity of which is approximately 1:4:6:4:1 and 1:1:3:3:3:3:1:1, respectively. As the polymerization proceeded, this 13-line spectrum quickly changed into a kind of strong 5 + 4 line spectrum (1:2:3:4:5:5:4:3:2:1), which was attributed to the MMA radicals in the solid state^[3, 10]. Since the steric configurations of the PMMA radicals are not fixed in one conformations but are distributed among several possible superposed conformations because of the steric complexity of polymer molecules in the amorphous state^[11], the change from the weak 13-line to the strong 9-line or even 7-line spectrum is related to the transformation of PMMA radical conformation. This transformation will certainly lead to the change of radical activity and the reaction rate constant of termination.

Taking the height of the central and the adjacent peaks obtained during polymerization of MMA as the apparent propagating radical concentration^[6, 8, 9], which was plotted against the reaction time, we studied the decay curve of the propagating radical concentration under different polymerization conditions.

Influence of Initial Concentration of Initiator

The polymerization of MMA was carried out at 98°C with different initiator/monomer molar ratio from 0.0037 to 0.0148. The apparent propagating radical concentration was measured, and the decay curves of PMMA radicals were given in Fig. 2. It was found that the radical concentration rose to its maximum within a short time, and then dropped monotonously. We also found that the greater the amount of the initiator, the more rapidly the radical decayed. When the initiator concentration was as low as given in the curve (shown by Δ) of Fig. 2, the apparent propagating radical concentration decreased so slowly and smoothly that it seems to be more or less in a steady state throughout the process of polymerization, except during the initial period of the reaction.

Temperature Effect on the Decay Curves of PMMA Radicals

The bulk polymerization of MMA was implemented at various temperatures with the same concentration of initiator. As shown as in Fig. 3, the decay curves of PMMA radicals at various temperatures varied both in shape and intensity. Since higher temperature leads to lower viscosity of a polymerization system and easier diffusion of the propagating radicals, the normal radical-to-radical termination is expected, which results in a monotonous decay curve of the radicals. When the temperature dropped to 64°C , the quickly increasing viscosity of the system made the propagating radicals wrapped up and difficult to move. This brought about a decrease of the apparent rate constant of termination^[10], so that the radical concentration increased once again after the minimum value. It was also found that the higher the temperature, the more rapidly the radical decayed. Figure 4 gives the similar plots of radical concentration against reaction time, with the molar ratio of AIBN to MMA changing from 0.0148 to 0.0074. In general, the decay curve of the free radical depends on two factors. First, in accordance with

the normal chemical kinetic law, the radical concentration should drop from the maximum. Second, the viscosity of the system should affect the movement of the polymer chain radicals and cause a decrease of the radical activity and the apparent rate constant of termination, which results in an increase of the radical concentration during a certain period of reaction time.

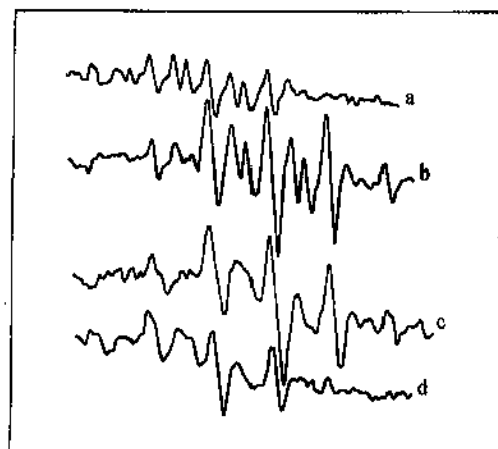


Fig. 1 ESR spectra obtained at different polymerization times (bulk polymerization)
Weight of AIBN: 0.1012 g; amount of MMA: 5.1 mL;
polymerization temperature: $64 \pm 0.1^\circ\text{C}$; reaction time:
(a) 49 min, (b) 52 min, (c) 60 min and (d) 68 min

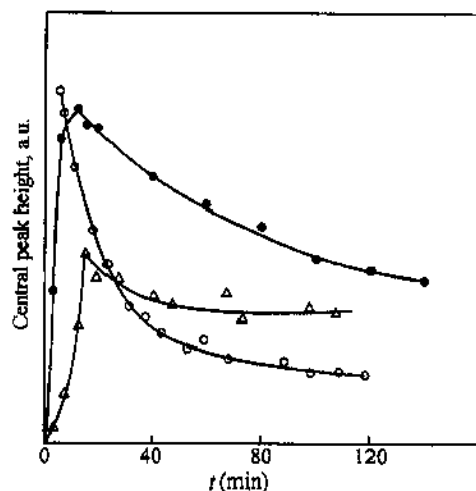


Fig. 2 The influence of initiator concentration on the decay curves of PMMA radicals
Temperature: $98 \pm 0.1^\circ\text{C}$
Molar ratio of AIBN to MMA: O 0.0148,
● 0.0074, Δ 0.0037

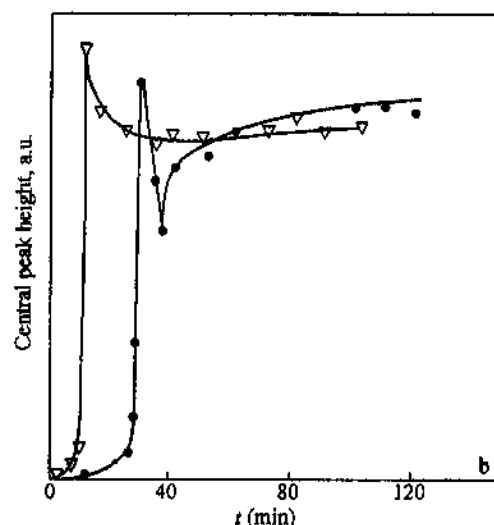
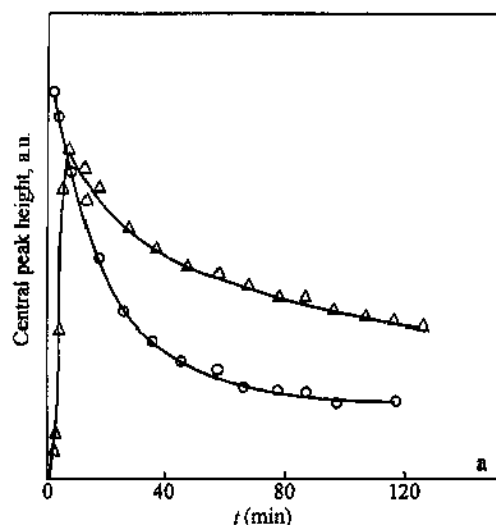


Fig. 3 The temperature effect on the decay curves of PMMA radicals
Molar ratio of AIBN to MMA: 0.0148
Temperature: O $98 \pm 0.1^\circ\text{C}$, Δ $87 \pm 0.1^\circ\text{C}$, ▽ $77 \pm 0.1^\circ\text{C}$, ● $64 \pm 0.1^\circ\text{C}$

Solvent Effect on the Decay Curves of PMMA Radicals

From the above discussion we know that the viscosity of polymerization system plays an important role in the process of chain radical termination. The addition of a solvent to the polymerization system or a elevation in

temperature has a similar effect on the diffusion behavior of radicals. Comparing the curve in Fig. 3 (shown by $\bullet$, no solvent) with that in Fig. 5 (shown by $\circ$, with benzene as solvent), it is evident that the solvent reduced the upward trend of the radical concentration after it reached the maximum. Thus the decay curves with only one peak for the polymerization of MMA in benzene at 64°C were observed in Fig. 5. Also from Fig. 5 it is known that the greater the amount of solvent added, the quicker the radical concentration diminishes.

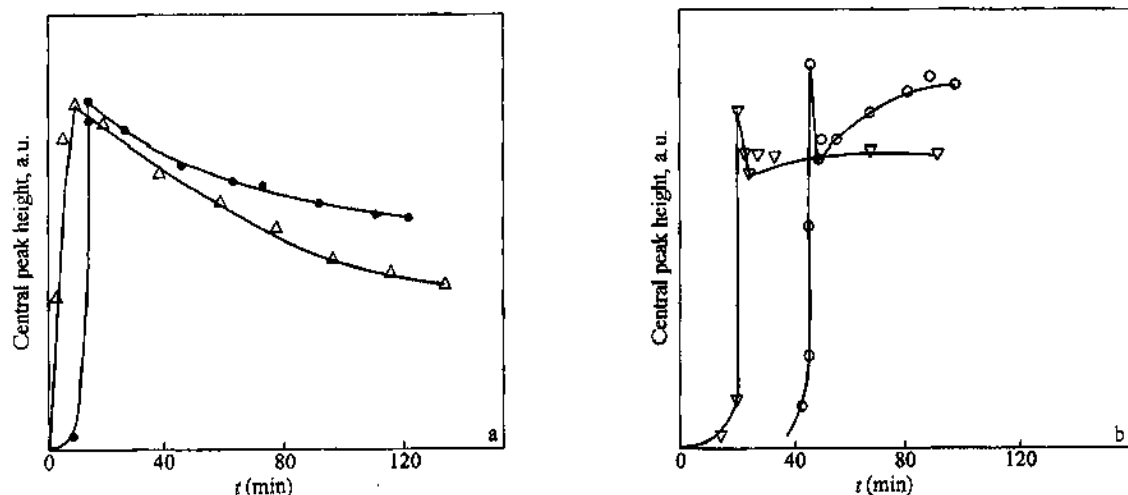


Fig. 4 The effect of temperature on the decay curves of PMMA radicals
Molar ratio of AIBN to MMA: 0.0074
Temperature: $\triangle 98 \pm 0.1^\circ\text{C}$, $\bullet 87 \pm 0.1^\circ\text{C}$, $\nabla 77 \pm 0.1^\circ\text{C}$, $\circ 64 \pm 0.1^\circ\text{C}$

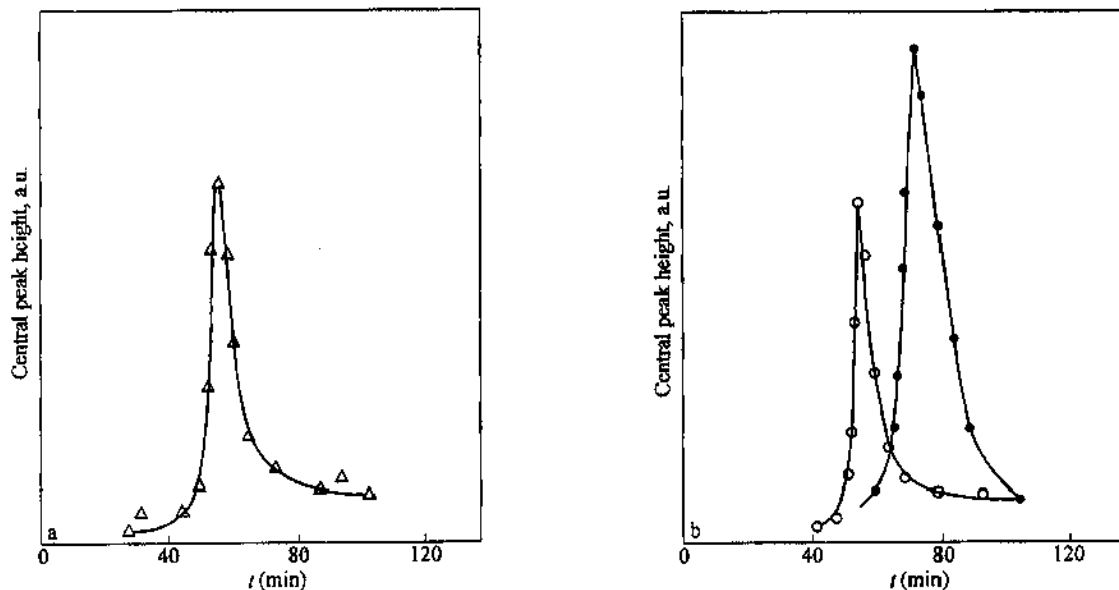


Fig. 5 The effect of solvent on the thermal-initiating system
Temperature: $64 \pm 0.1^\circ\text{C}$; molar ratio of AIBN to MMA: 0.0148;
volume ratio of MMA to benzene: $\triangle 5:1$, $\circ 4:1$, $\bullet 3:1$

Kinetic Model for Radical Decay

In the preceding section, it has been concluded that both the normal chemical kinetic rule and the diffusion influence upon the decay process of PMMA radicals should be taken into account. From the experimental data given in this work, we have tried to establish a kinetic model for the free radical decay of bulk polymerization as

follows. For the convenience of discussion, the normal kinetics of free radical polymerization without viscosity effect is considered beforehand, of which the kinetic differential equations are as follows:

$$dI/dt = -k_d I \quad (1)$$

$$dR_0/dt = 2fk_d I - [k_p M + (k_{tc} + k_{td}) \sum R_n] R_0 \quad (2)$$

$$dR_n/dt = k_p M R_{n-1} - [k_p M + (k_{tc} + k_{td}) \sum R_n] R_n \quad (3)$$

$$dN_n/dt = (k_{td} + 0.5k_{tc}) R_n \sum R_n \quad (4)$$

$$d \sum R_n/dt = 2fk_d I - (k_{tc} + k_{td}) (\sum R_n)^2 \quad (5)$$

$$dM/dt = -k_p M \sum R_n \quad (6)$$

where k_d is the rate constant of the initiator dissociation, R_0 represents the concentration of primary radicals, f is the efficiency of the initiation, M and I represent respectively the concentrations of monomer and initiator, k_p is the rate constant for propagation, k_{tc} and k_{td} are the rate constants for termination by coupling and disproportionation, respectively, R_n and N_n denote the respective concentrations of chain radicals with n monomeric units and inactive n -mers. The initial conditions of Eqs. (1)–(6) are as follows:

$$I|_{t=0} = I_0, M|_{t=0} = M_0, R_n|_{t=0} = N_n|_{t=0} = 0$$

Obviously the rate constants of termination k_{td} and k_{tc} keep constant when the effect of viscosity is negligible during the process of polymerization. From Eq. (1), we obtain:

$$I = I_0 \exp(-k_d t) \quad (7)$$

Combining Eq. (7) with Eq. (5) results in:

$$d \sum R_n/dt = 2fk_d I_0 \exp(-k_d t) - (k_{tc} + k_{td}) (\sum R_n)^2 \quad (8)$$

With the aid of a computer, it is easy to find the numerical solution for Eq. (8), and the results are given in Figs. 6, 7 and 8. Comparing Figs. 6–8 with Fig. 2, it is found that the kinetic model without consideration of diffusion effect is appropriate for the free radical polymerization of MMA at high temperature.

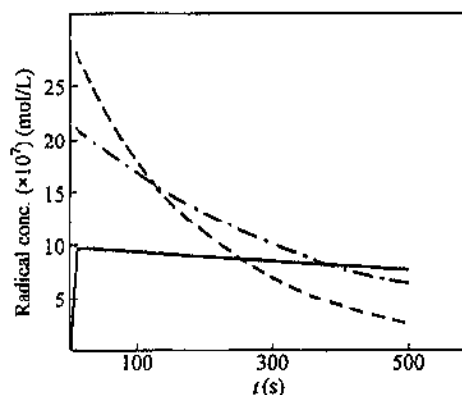


Fig. 6 Radical decay versus reaction time, calculated from the polymerization without viscosity effect

$I_0 = 0.01$, $k_t = 1.1 \times 10^6$; (---) $k_d = 10^{-2}$, (-.-) $k_d = 5 \times 10^{-3}$; (—) $k_d = 10^{-3}$

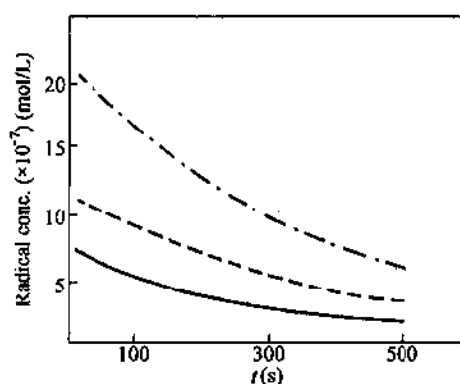


Fig. 7 Radical decay versus reaction time, calculated from the polymerization without viscosity effect

$k_d = 5 \times 10^{-3}$, $k_t = 1.1 \times 10^6$; (-.-) $I_0 = 0.01$, (---) $I_0 = 0.003$, (—) $I_0 = 0.001$

Alternatively, if the polymerization temperature is relatively low, the effect of viscosity should be taken into account, and the apparent rate constants of termination are symbolized by k'_{td} and k'_{tc} , which vary with the reaction time. If a revision factor is introduced into the rate constants of termination:

$$(k'_{td} + k'_{tc}) = (k_{td} + k_{tc}) a \exp(-bt) \quad (9)$$

where k_{td} and k_{tc} are respectively identical with those in Eq. (8), then the semi-empirical kinetic differential equation adapted to propagating radicals is

$$d \Sigma R_p / dt = 2fk_d I_0 \exp(-k_d t) - (k_{tc} + k_{td}) a \exp(-bt) (\Sigma R_p)^2 \quad (10)$$

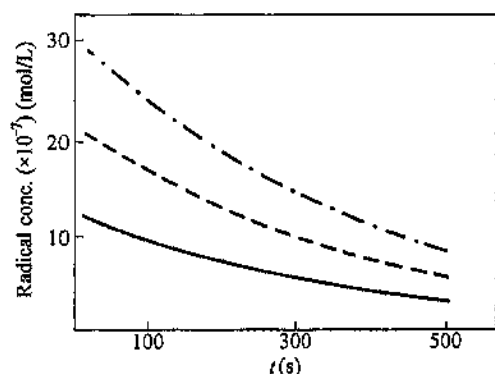


Fig. 8 Radical decay versus reaction time, calculated from the polymerization without viscosity effect $I_0 = 0.01$, $k_d = 5 \times 10^{-3}$; (---) $k_t = 1.1 \times 10^6$, (—) $k_t = 3.3 \times 10^6$, (- · -) $k_t = 5.5 \times 10^5$

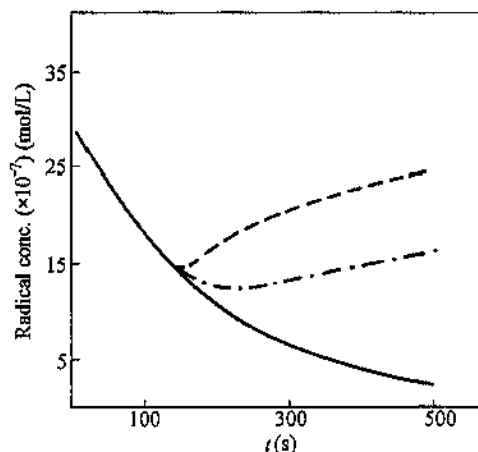


Fig. 9 Radical decay versus reaction time, calculated from the semiempirical equation for the polymerization with diffusion effect $I_0 = 0.01$, $k_d = 2 \times 10^{-3}$, $k_t = 1.1 \times 10^6$; (---) $a = 2$, $b = 0.006$, (- · -) $a = 3$, $b = 0.006$; (—) $a = 1$, $b = 0$

Equation (10) can also be easily solved numerically. The results obtained are shown in Fig. 9. Comparing Fig. 9 with Figs. 3 and 4, it is found that the semi-empirical model described by Eq. (10) conforms qualitatively to the experimental data of free radical decay in the polymerization governed by both normal kinetic factor and diffusion property. In light of Eq. (10), we shall study the kinetics of the whole process of free radical polymerization in detail, and the results will be reported elsewhere.

REFERENCES

- 1 North, A. M., "The Influence of Chain Structure on the Free Radical Termination Reaction", Chapter 5 in "Reactivity, Mechanism and Structure in Polymer Chemistry", Ed. by Jenkins, A. D. and Ledwith, A., Wiley-Interscience, New York, 1974
- 2 Odian, G. "Principles of Polymerization", third edition, Wiley, New York, 1991, p.286
- 3 Zhu, S., Tian, Y. and Hamielec, A.E., *Macromolecules*, 1990, 23: 1144
- 4 Fischer, H., *Adv. Polym. Sci.*, 1968, 5: 463
- 5 Bresler, S.E., Kazbekov, E.N. and Shadrin, V.N., *Makromol. Chem.*, 1974, 175: 2875
- 6 Tian, Y., Zeng, Y.G., Wang, G.B., Qiu, Z.W. and Shen, J.C., *Chem. J Chinese Univ.*, 1987, 8(9): 851
- 7 Kamachi, M., Kuwae, Y., Kohno, M. and Nozakura, S., *Polym. J.*, 1985, 17: 541
- 8 Shen, J.C., Tian, Y., Wang, G.B. and Yan, M.L., *Science in China (Series B)*, 1990, 33(2): 113
- 9 Carswell, T.G., Hill, D.J.T., Hunter, D.S., Pomery, P.J., O'Donnell, J.H. and Winzor, C.L., *Eur. Polym. J.*, 1990, 26(4): 541
- 10 Shen, J.C., Tian, Y., Wang, G.B. and Yan, M.L., *Makromol. Chem.*, 1991, 192: 2669
- 11 Sohma, J., Komatsu, T. and Kashiwabara, H., *Polym. Letters*, 1965, 3: 287