

# Curing of DGEBA Epoxy Resin by Low Generation Amino-Group-Terminated Dendrimers

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Received 8 February 2005; accepted 29 June 2005

DOI 10.1002/app.24688

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Low generation amino-group-terminated poly(ester-amine) dendrimers PEA1.0 ( $\text{NH}_2$ )<sub>3</sub> and PEA1.5 ( $\text{NH}_2$ )<sub>8</sub>, and poly(amido-amine) dendrimer PAMAM1.0 ( $\text{NH}_2$ )<sub>4</sub> were used as diglycidyl ether of bisphenol A (DGEBA) epoxy resin hardeners. Thermal behavior and curing kinetics of dendrimer/DGEBA systems were investigated by means of differential scanning calorimetry (DSC). Compared with ethylene diamine (EDA)/DGEBA system, the dendrimer/DGEBA systems gradually liberated heat in two stages during the curing process, and the total heat

liberated was less. Apparent activation energy and curing reaction rate constants for dendrimer and EDA/DGEBA systems were estimated. Thermal stabilities and mechanical properties of cured thermosetting systems were examined as well. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3902–3906, 2006

**Key words:** dendritic; epoxy resin hardeners; thermal behavior; kinetics; mechanical properties

## INTRODUCTION

Epoxy resin is one of the most important thermosetting materials because of its superior physicochemical properties: good mechanical strength, excellent adhesion to a variety of surfaces, durability under harsh environmental conditions, excellent electrical properties, and hydrolytic stability. Epoxy resin hardeners and curing technologies have great influence on the properties of cured epoxy resins. There are many reports on curing of different epoxide systems, but the hardeners mainly belong to conventional small molecules, such as 1,2-diamine cyclohexane,<sup>1</sup> maleic anhydride,<sup>2</sup> methyl-tetrahydrophthalic anhydride,<sup>3</sup> etc., among which aliphatic polyamino-hardeners can cure their epoxide systems at room temperature, but they are highly poisonous and their curing systems have short pot life. Polycarboxylic acids and anhydrides pose difficulty in formulating high solid coatings because most of them have high melting point, low solubility in organic solvents, and poor compatibility with coexisting ingredients.<sup>4</sup> Therefore, research on novel epoxide curing agents has been attracting great attention. Recently, Kim and Lee<sup>5</sup> used linear phenol resins as hardeners and investigated the contributions

of the network structure to the cure kinetics of epoxy resin systems. Okazaki et al.<sup>6</sup> cured epoxy resin by hyperbranched polyamidoamine-modified ultrafine silica.

Dendrimers are molecules with a well-defined primary structure based on a hyperbranched, fractal-like motif emanating from a central core. As a new class of macromolecules, they are identified as promising candidate materials for a wide variety of applications that include energy-harvesting, drug delivery, surfactant, catalyst, and nanocomposite.<sup>7–9</sup> Low generation amino-group-terminated poly(ester-amine) dendrimers PEA1.0 ( $\text{NH}_2$ )<sub>3</sub> and PEA1.5 ( $\text{NH}_2$ )<sub>8</sub>, and poly(amido-amine) dendrimer PAMAM1.0 ( $\text{NH}_2$ )<sub>4</sub> were used as epoxy resin hardeners in our previous studies.<sup>10,11</sup> They were less volatile, less poisonous, and well compatible with epoxide. In comparison with ethylene diamine (EDA)/diglycidyl ether of bisphenol A (DGEBA) system, dendrimer/DGEBA systems had long pot life, long gel time, and quick curing speed.

In this article, thermal behavior and kinetics of dendrimer/DGEBA systems in the curing process were investigated by DSC; the thermal stabilities and mechanical properties of the cured dendrimer/DGEBA systems were also examined.

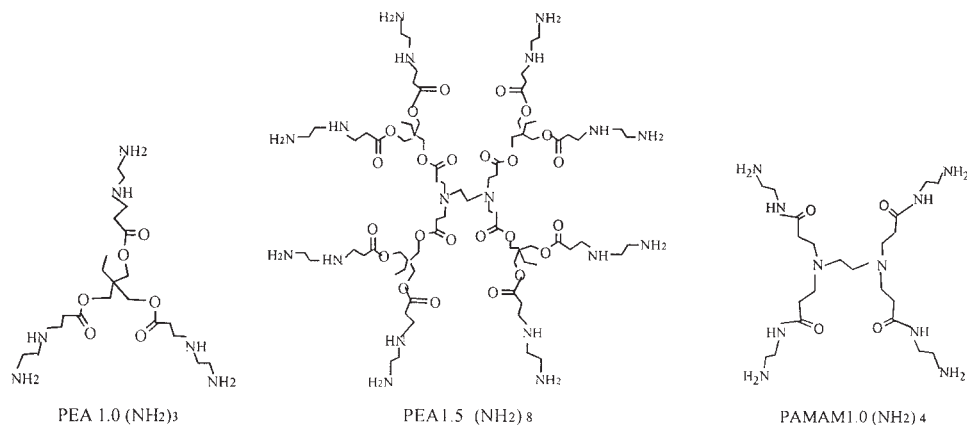
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Contract grant sponsor: Suzhou University (The Excellent Youth Teacher Fund); contract grant number: R2317144.

## EXPERIMENTAL

### Materials

Low generation amino-group-terminated poly(ester-amine) dendrimers PEA1.0 ( $\text{NH}_2$ )<sub>3</sub> and PEA1.5 ( $\text{NH}_2$ )<sub>8</sub>,



**Figure 1** Structures of low generation dendrimers.

and poly(amido-amine) dendrimer PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub> were synthesized as described in Refs. 10, 11, and 12 respectively. Their structures are shown in Figure 1. Diglycidyl ether of bisphenol A epoxy resin (DGEBA, 6101, epoxide no.: 0.41–0.47) was purchased from the Adhesion Agent Company of Suzhou (China). Ethylene diamine (EDA) was supplied by the Third Reagent Company of Shanghai (China).

### DSC and TGA analysis

DGEBA and hardener were carefully and homogeneously mixed at the stoichiometric ratio (1 : 1) of epoxy group and hydrogen atom in amino groups in an ice-water bath. DSC and TGA analysis were done on a SDT 2960 simultaneous DSC–TGA instrument (TA Company) using N<sub>2</sub> as the purge gas. The weight of the samples was ~8 mg. Nonisothermal curing was carried out from 20 to 400°C at the rates of 5, 10, 15, and 20 K/min.

### Mechanical property test

The mixtures of DGEBA and hardener with the same composition as that for DSC and TGA analysis were cured at 50°C for 5 h and 95°C for 1 h in a rectangle mold, then cooled to room temperature and no-notch specimens (120 × 15 × 1.5 mm<sup>3</sup>) were obtained. Mechanical properties were tested on an Instron 1122 universal test machine (maximum measurement, 5000 N; Instron, UK) with a 2-mm/min cross-head speed and 100 mm distance between two cross heads, at ambient condition (25°C). Five specimens were tested and the results were averaged to obtain a mean value.

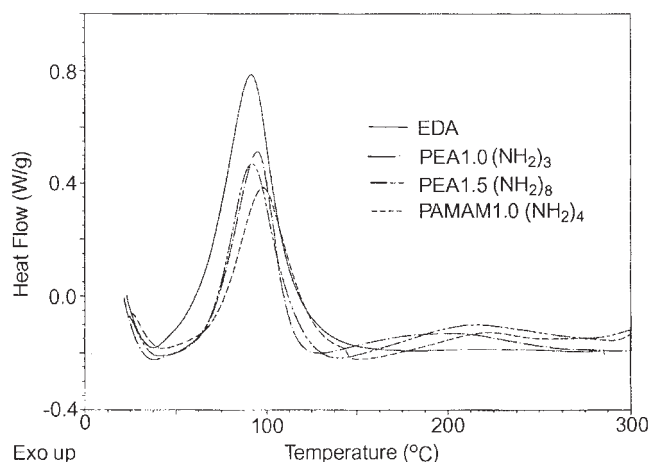
## RESULTS AND DISCUSSION

### The thermal behavior of dendrimer/DGEBA systems in the curing process

The DSC thermograms of PEA1.0 (NH<sub>2</sub>)<sub>3</sub>, PEA1.5 (NH<sub>2</sub>)<sub>8</sub>, PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>, and EDA/DGEBA sys-

tems at 5 K/min under a N<sub>2</sub> atmosphere are represented in Figure 2. The top exothermic peak ( $T_p$ ) and the reaction heat ( $\Delta H$ ), which came from integration of the area of the peak and the baseline, are listed in Table I.

Obviously, EDA/DGEBA system had only one exothermic peak, and dendrimer/DGEBA systems had two. The reason is that there are primary amino-hydrogen and secondary amino-hydrogen in the structure of dendrimers. In the course of curing reaction, the peripheral primary amino-hydrogen reacts first, giving the first exothermic peak and forming crosslinking networks which make the reaction of secondary amino-hydrogen difficult because of steric hindrance. Consequently, the corresponding second exothermic peak appeared with higher top temperature and a wider peak formed when compared with the first one. The results of DSC analysis showed that the dendrimer/DGEBA systems gradually liberated heat in two stages during the curing process, and the total heat liberated was less than that of EDA/epoxide system.



**Figure 2** The dynamic DSC scans of different epoxide systems run at 5 K/min.

**TABLE I**  
The Results of DSC Scans of Different Epoxide Systems

Hardener	$T_p$ (K)	$\Delta H$ (J/g)
EDA	364.6	433.1
PEA1.0 (NH <sub>2</sub> ) <sub>3</sub>	368.1	474.6
PEA1.5 (NH <sub>2</sub> ) <sub>8</sub>	365.1	479.6
PAMAM1.0 (NH <sub>2</sub> ) <sub>4</sub>	371.2	483.6

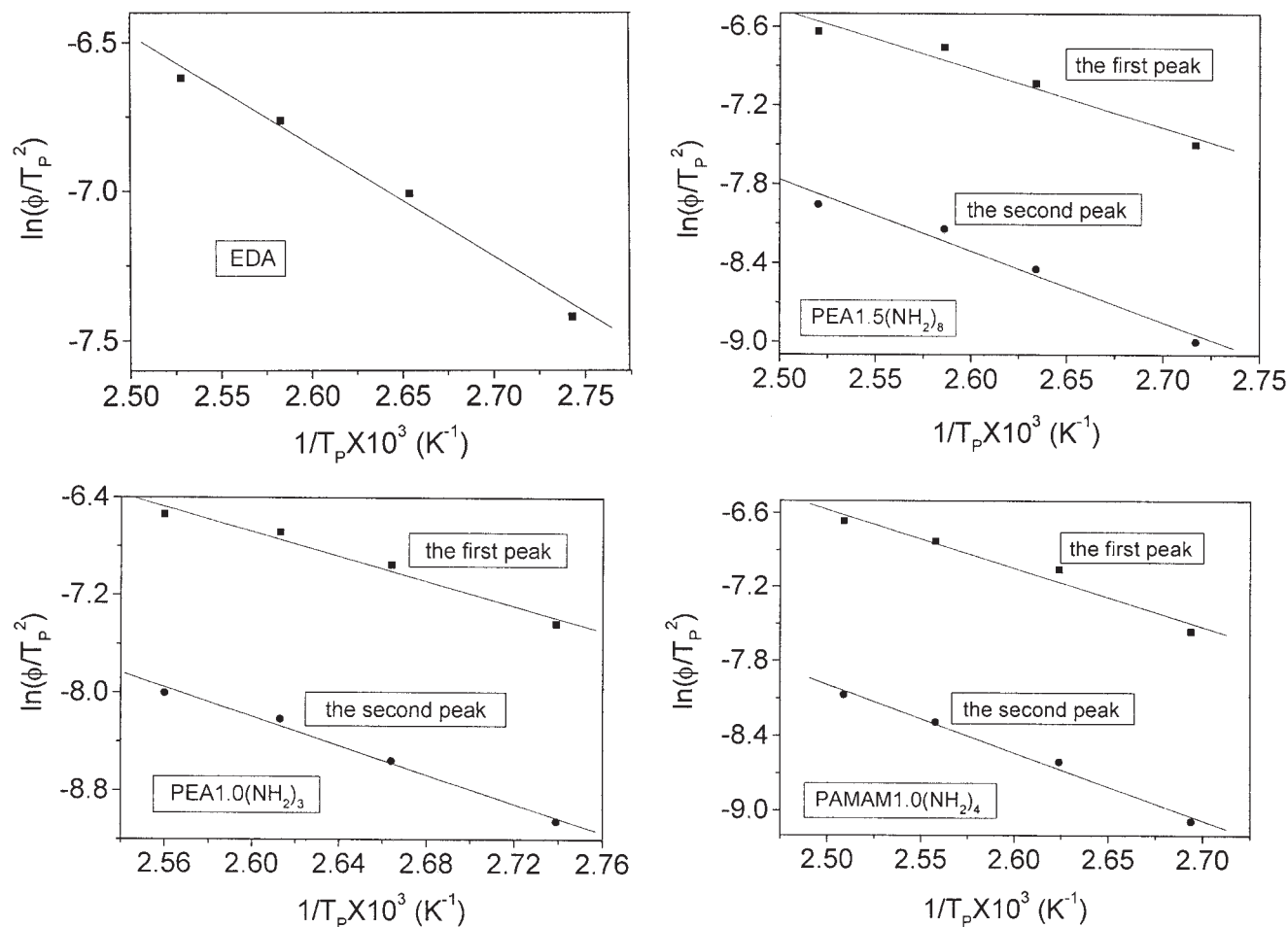
The heating rate, 5 K/min.

### Curing kinetics of dendrimer/DGEBA systems

Apparent activation energy of curing reaction of dendrimer/DGEBA systems

Curing kinetics of dendrimer/DGEBA systems was studied by DSC analysis and Kissinger's<sup>13</sup> method. According to Kissinger's method, the relationship between the top temperature of the exothermic peak and the heating rate during the nonisothermal curing process of epoxide systems is shown in eq. (1):

$$d \ln\left(\frac{\phi}{T_p^2}\right) / d\left(\frac{1}{T_p}\right) = -\frac{\Delta E}{R} \quad (1)$$



**Figure 3**  $\ln(\phi/T_p^2) - (1/T_p)$  graphs.

Here,  $\phi$  is the heating rate (K/min),  $T_p$  is the peak temperature (K),  $R$  is the universal gas constant ( $R = 8.314 \text{ J/mol} \cdot \text{K}$ ),  $\Delta E$  is the apparent activation energy (J/mol) of curing reaction. The straight linear fittings of  $\ln(\phi/T_p^2)$  versus the inverse of the peak temperature ( $1/T_p$ ) are shown in Figure 3. From the slope of the lines,  $\Delta E$  can be obtained.<sup>14</sup>

Furthermore, frequency factor ( $A$ ) can be estimated by eq. (2) (Ref. <sup>14</sup>):

$$A \approx \frac{\phi \Delta E \exp(\Delta E/RT_p)}{RT_p^2} \quad (2)$$

Selected kinetics parameters of epoxide curing reactions are listed in Table II.

Corresponding to the DSC thermograms of epoxide systems with different hardeners, the dendrimer/DGEBA systems exhibited two activation energies  $\Delta E_1$  and  $\Delta E_2$ , and two frequency factors  $A_1$  and  $A_2$ . The activation energy and the frequency factor of dendrimer/DGEBA systems were higher than those of EDA/DGEBA system, indicating that the curing reac-

**TABLE II**  
Kinetics Parameters of Epoxide Curing Reactions

Hardener	$\Delta E$ (kJ mol <sup>-1</sup> )		$A$ (10 <sup>-4</sup> s <sup>-1</sup> )	
	$\Delta E_1$	$\Delta E_2$	$A_1$	$A_2$
EDA	30.91		0.5015	
PEA1.0 (NH <sub>2</sub> ) <sub>3</sub>	37.28	45.16	4.234	1.509
PEA1.5 (NH <sub>2</sub> ) <sub>8</sub>	42.28	49.75	27.45	4.078
PAMAM1.0 (NH <sub>2</sub> ) <sub>4</sub>	39.53	45.41	8.228	1.093

tion of the dendrimer/DGEBA systems was more difficult than that of EDA/DGEBA system; however, the curing reaction rate constants of dendrimer/DGEBA systems increased faster than that of EDA/DGEBA system, which is discussed in the following paragraph.

Curing reaction rate constants of dendrimer/DGEBA systems

The curing reaction rate constant  $k$  of different epoxide systems can be expressed by the Arrhenius eq. (3) (Ref. 3):

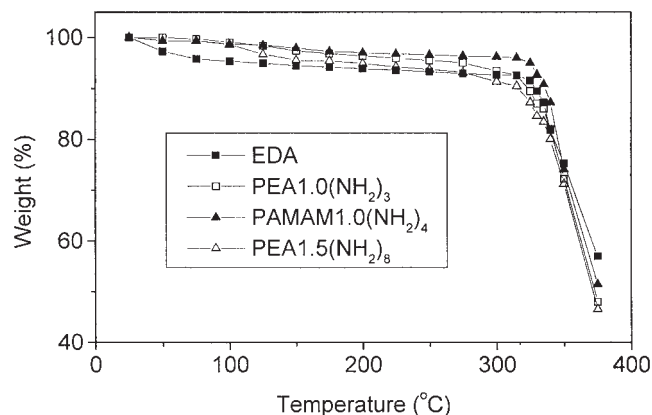
$$k = A \exp(-\Delta E/RT) \quad (3)$$

The  $k$  at different temperatures ( $T$ ) can be calculated using the values  $\Delta E$  and  $A$  given in Table II. The results are shown in Table III.

The data in Table III show that the curing reaction rate constants  $k_1$  and  $k_2$  of PEA1.0 (NH<sub>2</sub>)<sub>3</sub>, PEA1.5 (NH<sub>2</sub>)<sub>8</sub>, and PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>/DGEBA systems

**TABLE III**  
Curing Reaction Rate Constants of Different Epoxide Systems

Hardener	Temperature (K)	$k_1$ (10 <sup>3</sup> s <sup>-1</sup> )	$k_2$ (10 <sup>3</sup> s <sup>-1</sup> )
EDA	293.2		15.6
	323.2		50.6
	368.2		206
	393.2		392
	423.2		767
PEA1.0 (NH <sub>2</sub> ) <sub>3</sub>	293.2	9.96	0.136
	323.2	39.8	0.757
	368.2	217	5.91
	393.2	471	15.1
	423.2	1057	40.2
PEA1.5 (NH <sub>2</sub> ) <sub>8</sub>	293.2	8.02	0.0556
	323.2	40.1	0.370
	368.2	275	3.56
	393.2	662	10.0
	423.2	1655	29.4
PAMAM1.0 (NH <sub>2</sub> ) <sub>4</sub>	293.2	7.44	0.0886
	323.2	33.5	0.500
	368.2	202	3.94
	393.2	460	10.1
	423.2	1085	27.1



**Figure 4** TGA curves of epoxide systems with different hardeners.

were lower than those of EDA/DGEBA system below 50°C, complying with the fact that the pot life and gel time of dendrimer/DGEBA systems were longer than those of EDA/epoxide system.<sup>10,11</sup> However, they increased very fast when the temperature was raised. When the temperature rose from 20 to 150°C, the  $k$  of EDA/DGEBA system increased by 48 times, while the  $k_1$  and  $k_2$  of PEA1.0 (NH<sub>2</sub>)<sub>3</sub>, PEA1.5 (NH<sub>2</sub>)<sub>8</sub>, and PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>/DGEBA systems increased by 105 and 295, 205 and 528, and 145 and 305 times, respectively, conforming to the fact that the curing speed of dendrimer/DGEBA systems was faster than that of EDA/DGEBA system, when cured at 95, 120, and 150°C.<sup>10,11</sup>

#### Thermal stabilities of cured dendrimer/DGEBA systems

From the thermogravimetric analysis (TGA) (Fig. 4), it can be found that the thermogravimetric behavior of epoxide systems with PEA1.0 (NH<sub>2</sub>)<sub>3</sub>, PEA1.5 (NH<sub>2</sub>)<sub>8</sub>, PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>, and EDA as hardeners were similar on the whole, but the weight loss of EDA/epoxide system was more than that of dendrimer/epoxide systems when the temperature rose from 20 to 100°C, indicating that the EDA volatilized continuously. The order of the stabilities of the cured systems expressed by hardeners was PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub> > PEA1.0 (NH<sub>2</sub>)<sub>3</sub> ≈ EDA > PEA1.5 (NH<sub>2</sub>)<sub>8</sub> according to the temperature at which the cured thermosetting systems began to seriously degrade.

#### Mechanical properties of cured dendrimer/DGEBA systems

Mechanical properties of PEA1.0 (NH<sub>2</sub>)<sub>3</sub>, PEA1.5 (NH<sub>2</sub>)<sub>8</sub>, PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>, and EDA/epoxide systems are shown in Table IV. The tensile strength of dendrimer/DGEBA systems was higher than that of

**TABLE IV**  
**Mechanical Properties of Different Epoxide Systems**

Cured system	Tensile strength (MPa)	Extension at break (%)
EDA/DGEBA	39.2	2.3
PEA1.0 (NH <sub>2</sub> ) <sub>3</sub> /DGEBA	41.5	1.8
PEA1.5 (NH <sub>2</sub> ) <sub>8</sub> /DGEBA	42.1	1.5
PAMAM1.0 (NH <sub>2</sub> ) <sub>4</sub> /DGEBA	45.2	2.4

EDA/DGEBA system. From this it can be interpreted that the degree of crosslinking of a thermosetting system affects its mechanical properties. The high degree of crosslinking of dendrimer/DGEBA systems leads to the high tensile strength. However, it slightly lowers the extension at break of PEA1.0 (NH<sub>2</sub>)<sub>3</sub> and PEA1.5 (NH<sub>2</sub>)<sub>8</sub>/DGEBA systems. It is worth noticing that the tensile strength and extension at break of PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>/DGEBA system increase at the same time, which may be dependent on its amide skeleton.

### CONCLUSIONS

Low generation amino-group-terminated poly(ester-amine) dendrimers PEA1.0 (NH<sub>2</sub>)<sub>3</sub> and PEA1.5 (NH<sub>2</sub>)<sub>8</sub>, and PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub> were effective epoxy resin hardeners. The dendrimer/DGEBA systems showed unique thermal behavior; that is, they gradually liberated heat in two stages during the curing process, and the total heat liberated was less than that of EDA/DGEBA system. Curing kinetics study by DSC found that the apparent activation energy of dendrimer/DGEBA systems was higher than that of EDA/DGEBA system, and the curing reaction rate constants for the front systems were lower than that of

the one behind when the curing temperature was below 50°C, but they increased faster than that of the one behind when temperature rose, which conformed to the fact that dendrimer/epoxide systems exhibited long pot life, long gelation time, and fast curing speed.<sup>10,11</sup> The thermal stability of the cured thermosetting systems explained by hardeners was PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub> > PEA1.0 (NH<sub>2</sub>)<sub>3</sub> ≈ EDA > PEA1.5 (NH<sub>2</sub>)<sub>8</sub>. The tensile strength of poly(ester-amine) dendrimer/DGEBA systems was higher than that of EDA/DGEBA system and their extension at break was slightly lower than that of EDA/DGEBA system, while the tensile strength and the extension at break of PAMAM1.0 (NH<sub>2</sub>)<sub>4</sub>/DGEBA system were higher than those of EDA/DGEBA system.

### References

1. Fraga, F.; Burgo, S.; Rodriguez, N. *J Appl Polym Sci* 2001, 82, 3366.
2. Kagathara, V. M.; Parsania, P. H. *Polym Test* 2002, 21, 181.
3. Calabrese, L.; Valenza, A. *Eur Polym Mater* 2003, 39, 1355.
4. Toshio, Y.; Masahiro, I. *Prog Org Coat* 2000, 40, 267.
5. Kim, W. G.; Lee, J. Y. *Polymer* 2002, 43, 5713.
6. Okazaki, M.; Murota, M.; Kawaguchi, Y.; Tsubokawa, N. *J Appl Polym Sci* 2001, 80, 573.
7. Zheng, J.; Stevenson, M. S.; Hikida, R. S.; Van Patten, P. G. *J Phys Chem B* 2002, 106, 1252.
8. Fréchet, J. M. J. *J Polym Sci Part A: Polym Chem* 2003, 41, 3713.
9. Paleos, C. M.; Tsiourvas, D.; Sideratou, Z.; Tziveleka, L. *Biomacromolecules* 2004, 5, 524.
10. Xu, D. M.; Zhang, K. D.; Ning, C. H.; Zhu, X. L. *Chem Res Appl* 2004, 16, 320.
11. Xu, D. M.; Zhang, K. D.; Xu, Y.; Zhu, X. L. *Chin Appl Chem* 2004, 21, 708.
12. Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew Chem Int Ed Engl* 1990, 29, 138.
13. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
14. Cui, Z. C.; Lö, C. L.; Yang, B.; Su, X. P.; Yang, H.; Huo, C. S. *Acta Polym Sin* 2002, 2, 149.