

The Preparation and Characterization of Crosslinked Polytriazoles with Different Network Grids

Xiaofei Wang, Liqiang Wan, Yanpeng E, Farong Huang, Lei Du

Key Laboratory for Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Received 14 June 2010; accepted 9 August 2010

DOI 10.1002/app.33157

Published online 14 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Crosslinked structures of a resin had a great influence on its properties. Studying the effect of a crosslinked network on resin properties will benefit to design and prepare a new resin with good performances. A series of alkyne group-capped oligomers were designed and well characterized. The corresponding crosslinked polytriazoles with different network grids were obtained when multifunctional azide monomer was used as a crosslinking agent. The glass transition temperature (T_g) of the crosslinked polytriazoles was measured

by Differential Scanning Calorimetry. The results showed networks with a small grid size would exhibit high T_g s. The relationship between T_g and the size of the network grids of the crosslinked polytriazoles was discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 419–424, 2011

Key words: alkyne group-capped oligomers; crosslinked polytriazoles; glass transition temperature; size of the network grid

INTRODUCTION

Polytriazole (PTA) resins, as a novel kind of thermosetting resins, were prepared from multifunctional alkyne and azide monomers. By thermal Huisgen 1,3-dipolar cycloaddition reaction of the two monomers at a low temperature, PTA resins could be prepared without releasing low molecular weight byproducts. The researches showed PTA resins possessed excellent processability, mechanical and heat-resistance properties.^{1–6}

As well known, the crosslinked structures of a resin had a great influence on its properties.^{7–10} Investigation on the effect of the molecular structure and crosslinking character of a crosslinked network on properties would give an effective guide for the design and preparation of a new crosslinkable resin. For PTA resins, a kind of new developing thermosetting resins, the relationship between structures and properties was required to be established. In our last work,¹¹ the effect of structures on the properties of a PTA resin was investigated. Herein, we further discussed the influence of crosslinked structures on

properties of PTA resins with different network grids. First, a series of alkyne group-capped oligomers with different molecular weight were synthesized from the monomers, 1,4-diazidomethyl benzene (Scheme 1, a) and dipropargyl ethers of bisphenol A (Scheme 1, c), by changing the molar ratio of azide monomer to alkyne monomer and well characterized. Second, the monomer, trifunctional azide 1,3,5-tris(azidomethyl)-2,4,6-trimethyl-benzene (Scheme 1, b) was used as a crosslinking agent and mixed with the oligomers to make a series of crosslinkable resins, and then crosslinked PTA resins were prepared and characterized. Finally, the relationship between the size of the network grids and properties of the crosslinked PTA resins was investigated.

EXPERIMENTAL

Materials

1,4-Diazidomethyl benzene (a), 1,3,5-tris(azidomethyl)-2,4,6-trimethyl-benzene (b), and bispropargyl ethers of bisphenol A (c) were synthesized in our laboratory.^{1,3,4} Dimethylformamide (DMF) was used as received from Sinopharm Chemical Reagent Co. (Shanghai, China).

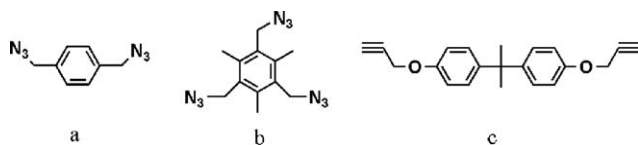
Characterization

Proton nuclear magnetic resonance (¹H-NMR) spectra were obtained on a BRUKER AVANCE 500 (500 Mz) instrument, and tetramethylsilane (TMS) was

Correspondence to: F. Huang (fhuanglab@ecust.edu.cn).

Contract grant sponsor: National High Technology Research and Development Program of China; contract grant number: 2002AA305103.

Contract grant sponsor: National Basic Research Program of China; contract grant number: 5131101.



Scheme 1 Multifunctional azide and alkyne monomers.

used as an internal standard. Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet 550 instrument (TA). The thermal measurement of the PTA resins was characterized with a Diamond Differential Scanning Calorimetry (PE) analyzer under nitrogen at the heating rate of 20°C/min. The size of the network grids of the crosslinked PTA resins was measured by the swelling test and the equilibrium swelling ratio was used as a characterization parameter.

Synthesis of oligomers capped with alkyne groups (OAs)

The alkyne group-capped oligomers (OAs) were synthesized by the catalyst-free thermal cycloaddition of diazide (a) and dialkyne (c) with a molar ratio $[a]/[c] < 1$ (see Scheme 2 and Table I). In a typical synthesis of OA-1, a (0.94 g, 5 mmol), c (3.04 g, 10 mmol), and DMF (1.71 g, 1.80 mL) were added into a flask equipped with a magnetic stirrer, a thermometer, and a condenser. The obtained mixture was stirred to form a solution, then heated to 80°C and kept at this temperature for 18 h. The solution was poured onto a glass plate and spread over the plate. Then the plate was placed into a vacuum stove at 80°C and maintained for 12 h. After the solvent was removed, a light yellow solid was obtained. The other OAs were prepared in similar procedures. The OAs were characterized by FTIR and ¹H-NMR analyses.

Preparation of the crosslinked polytriazole resins (PTAs) with different network grids

The PTAs with different network grids were prepared from various OAs and the trifunctional azide, 1,3,5-tris(azidomethyl)-2,4,6-trimethylbenzene (b), and the molar ratio of the groups ($[\text{alkyne}]/[\text{azide}]$) was 1/1. In a typical synthesis, OA-1 (1.19 g, 1.5 mmol), b (0.29 g, 1 mmol), and DMF (1.48 g, 1.57

mL) were added into a flask equipped with a magnetic stirrer. The mixture was stirred at room temperature until a clear solution occurred. Then the clear solution was poured on a glass plate and spread over the plate. The plate was placed into a vacuum stove to remove the solvent and a light yellow film was obtained. The film was further cured in an oven according to the reported curing procedure of the PTA resins: 70°C/12 h + 110°C/2 h + 150°C/2 h + 180°C/2 h + 200°C/2 h to afford the dark brown crosslinked product PTA-1.³⁻⁶ The other PTAs were obtained from b and different OAs in the same manner as PTA-1.

Swelling test of the crosslinked PTAs

Swelling test of the obtained crosslinked PTAs was conducted in DMF at room temperature. The PTA film sample (1.00 × 1.00 cm²) was immersed in DMF for 14 d which was long enough for all the crosslinked PTAs at swelling equilibrium stage at room temperature, then lifted from DMF, and wiped up the surface. The mass of the crosslinked PTA at swelling equilibrium stage was measured, and equilibrium swelling ratio of the PTA could be expressed as:

$$Q_e = m_e/m_i \quad (1)$$

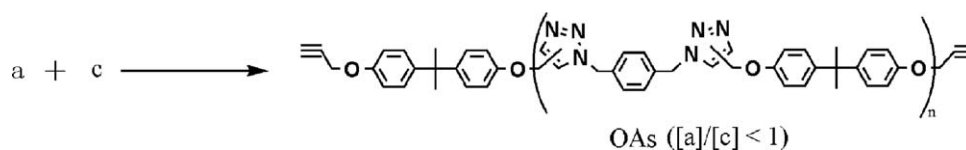
where m_e and m_i were the mass of crosslinked PTA at swelling equilibrium stage and initial stage, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of oligomers (OAs)

The catalyst-free thermal 1,3-dipolar cycloaddition of 1,4-diazidomethyl benzene (a) and bispropargyl ethers of bisphenol A (c) was utilized to synthesize the linear oligomers. A series of alkyne group-capped oligomers (OAs) were obtained by changing the molar ratio of monomer a to c ($[a]/[c] < 1$). The OAs were all light yellow solids, and soluble in non-proton strong polar solvents such as DMF, DMAc. Structures of the OAs were characterized by ¹H-NMR (DMSO-*d*₆) and FTIR spectroscopy.

Figure 1 showed the typical ¹H-NMR spectrum of OA-1. As shown in Figure 1, the new characteristic



Scheme 2 Synthesis of the alkyne group-capped oligomers (OAs).

TABLE I
Analysis Results of the Oligomers

Monomer ([a]/[c])	Oligomer	M_n^a	M_n^b	
			(1)	(2)
1/2	OA-1	796	834	835
2/3	OA-2	1288	—	—
4/5	OA-3	2272	—	—
6/7	OA-4	3256	3306	3322
9/10	OA-5	4732	—	—
19/20	OA-6	9652	9582	9619
29/30	OA-7	14572	—	—

^a The designed M_n of the OAs, which was calculated by the equation $M_n = \frac{188r+304}{1-r}$, where r was the molar ratio of monomers a to c .

^b The M_n of the OAs was calculated from the $^1\text{H-NMR}$ analyses. (1) $M_n = 492 \frac{h'+h}{d} + 304$; (2) $M_n = 492 \frac{i'+j}{d} + 304$; where h' , h , and d represented the integration intensity of the relative protons (see Fig. 1).

signals of triazole protons (C—H) at 8.24 ppm (i) and 7.85 ppm (i'), benzyl protons (—CH₂—) at 5.62 ppm (j') and 5.58 ppm(j) and methylene (—CH₂—) derived from the propargyl groups at 5.16 ppm (h') and 5.06 ppm(h) were observed. The azidomethyl protons signal (—CH₂—) of the monomer a at 4.47 ppm (f) disappeared in the spectrum of OA-1, implying there were not azide groups in the structure. On the other hand, there were the signals of monomer c at 4.75 ppm (d) and 3.54 ppm (e), which illustrated OA-1 was terminated with propargyl group. All results were consistent to the structure of OA-1. In addition, it was found that there were about 61% 1,4-isomer of triazole rings in OA-1 molecular chains by calculating the ratio of area of the

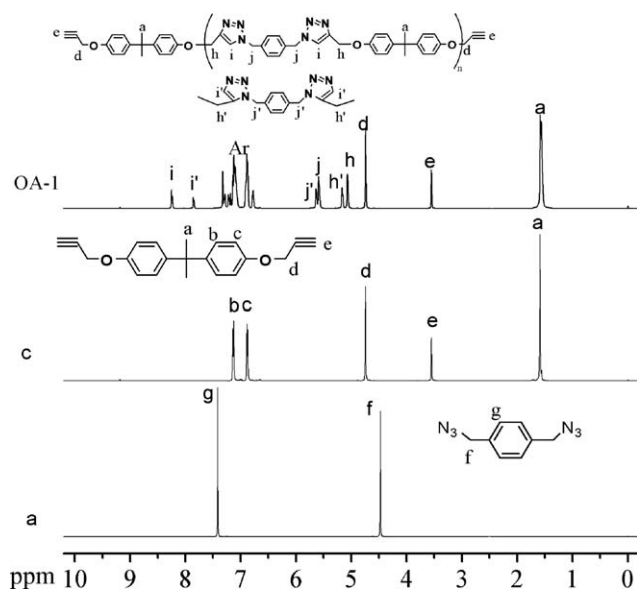


Figure 1 $^1\text{H-NMR}$ (DMSO- d_6) spectra of a , c , and OA-1.

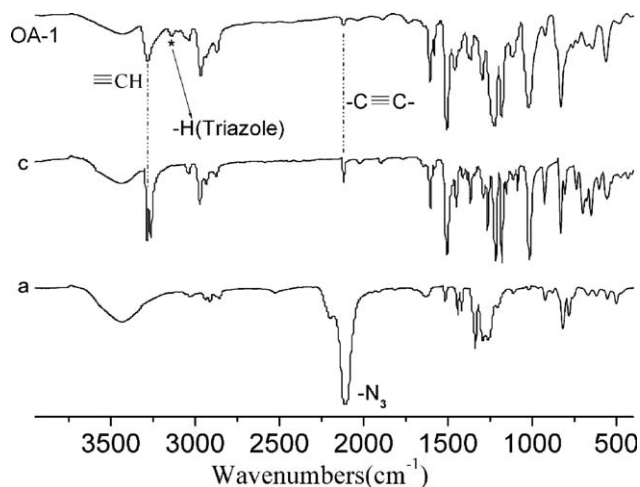


Figure 2 Typical FTIR spectra of a , c , and OA-1.

peak (i) assigned to 1,4-isomer to that (i') to 1,5-isomer. The pairs of peak (j) and peak (j'), peak (h) and peak (h') also demonstrated the distribution of the isomers.

Figure 2 showed the typical FTIR spectrum of OA-1. As shown in Figure 2, the characteristic absorption at 3140 cm^{-1} attributed to the hydrogen on the triazole ring was observed. This indicated there were triazole rings in the structure of OA-1. The absorptions attributed to propargyl groups were found at 3280 cm^{-1} ($\equiv\text{C-H}$) and 2120 cm^{-1} ($-\text{C}\equiv\text{C}-$), and that of azide groups was not observed, which meant the OA-1 was alkyne group-capped.

Molecular weights of the OAs were evaluated from $^1\text{H-NMR}$ analyses, and the analysis results were tabulated in Table I. As shown in Table I, the measured molecular weights of the OAs were in accord with the designed molecular weights. This indicated that the OAs were well prepared.

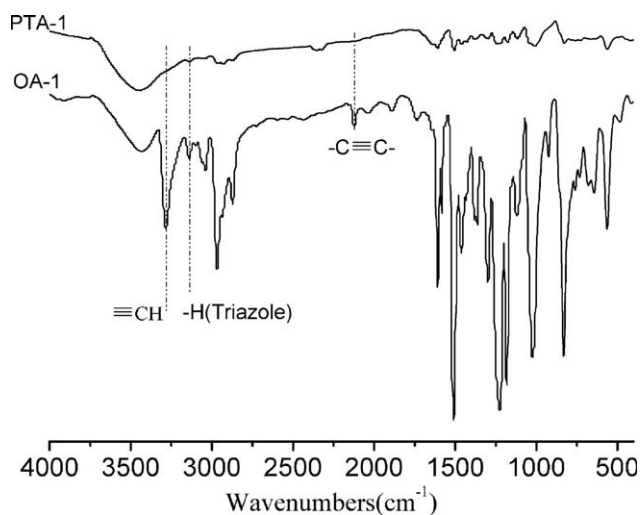


Figure 3 Typical IR spectra of OA-1 and crosslinked PTA-1.

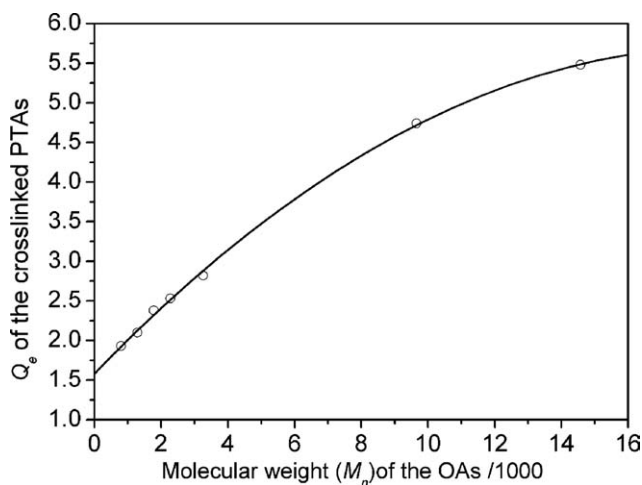


Figure 4 Relationship between equilibrium swelling ratios of the crosslinked PTAs and molecular weights of the OAs.

Characterization of the crosslinked PTAs with different network grids

The crosslinked PTAs with different network grids were prepared from various OAs and 1,3,5-tris(azidomethyl)-2,4,6-trimethyl-benzene (b). The polymer films were made by a spread method, and dark brown crosslinked PTAs were obtained after the films cured through the curing procedure.

Figure 3 showed a typical IR spectrum of crosslinked PTA-1. As shown in Figure 3, the absorptions attributed to the propargyl groups at 3280 cm^{-1} ($\equiv\text{C}-\text{H}$) and 2120 cm^{-1} ($-\text{C}\equiv\text{C}-$) disappeared in the spectrum of PTA-1, indicating the crosslinking reaction between propargyl and azide groups was complete.

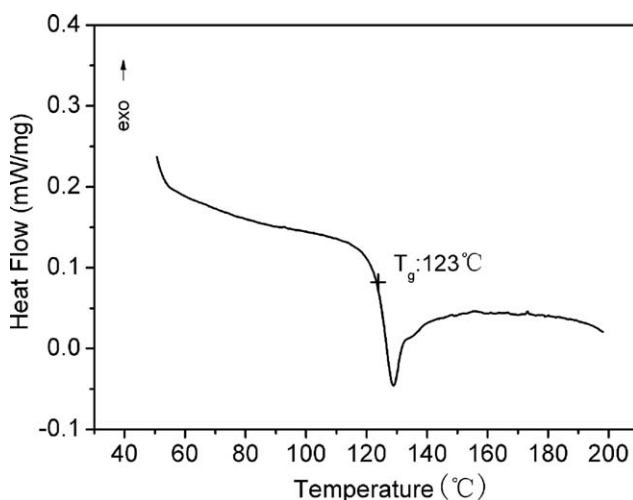


Figure 5 A typical DSC curve of the crosslinked PTA-7.

TABLE II
DSC Analysis Results of the Crosslinked PTAs

Oligomer	Polytriazole	$T_g/^\circ\text{C}$
OA-1	PTA-1	141
OA-2	PTA-2	140
OA-3	PTA-3	134
OA-4	PTA-4	128
OA-5	PTA-5	128
OA-6	PTA-6	121
OA-7	PTA-7	123

The networks of the crosslinked PTAs were confirmed by the swelling test in DMF at room temperature. Figure 4 showed the relationship between equilibrium swelling ratios (Q_e) of the PTAs and molecular weights (M_n) of the OAs. As shown in Figure 4, Q_e of the crosslinked PTAs increased with M_n of the OAs. This indicated that crosslinked PTAs with different network grids were obtained.

Thermal properties of the crosslinked PTAs were characterized by DSC under nitrogen at a heating rate of $20^\circ\text{C}/\text{min}$. Figure 5 showed a typical DSC curve which was attributed to the PTA-7. As shown in Figure 5, an obvious glass transition was observed. The glass transition temperature of PTA-7 arrived at 123°C . The DSC analysis results of all crosslinked PTAs were tabulated in Table II.

Effect of the size of network grids on glass transition temperatures (T_g s) of crosslinked PTAs

The network size of the crosslinked PTA (M_n of the OAs) would have a significant influence on its T_g .

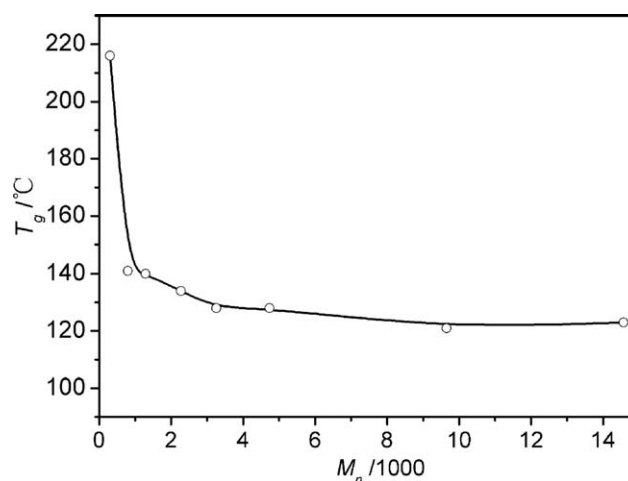


Figure 6 T_g of the crosslinked PTAs changed with M_n of the OAs. (As special cases, the T_g of crosslinked PTA based on b + c was also shown in this figure.)

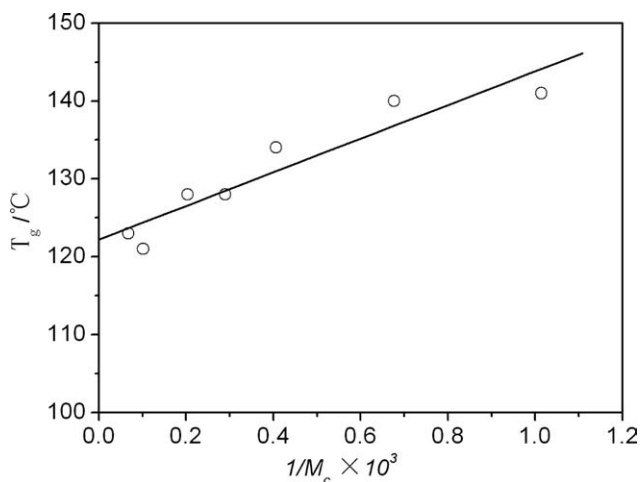


Figure 7 T_g of the crosslinked PTAs as a function of the crosslinking density.

Figure 6 showed the change of T_g of the crosslinked PTAs with M_n of the OAs. As shown in Figure 6, an initially rapid and then slow decreasing curve was observed. The critical point of the curve was found at ca. 2000, which showed a critical molecular weight of the OAs. If $M_n < 2000$, the size of the network grids had a significant influence on the T_g ; while $M_n > 2000$, the influence was not obvious.

In general, the increasement of crosslinking density of a network would result in enhancement of thermal properties. However, there were also differences among networks from different raw materials. We chose the molecular weight of two adjacent crosslinking sites as a crosslinking density. Based on the theory of glass transition,¹² T_g can often be expressed as a function of crosslinking density by the following relationship:

$$T_g = T_{g\infty} + k/M_c \quad (2)$$

where T_g was the glass transition temperature of the crosslinked PTA, $T_{g\infty}$ the glass transition temperature of the oligomers OAs with a nearly infinite high molecular weight, k a constant associated with the average functionality of crosslinking system, and M_c the molecular weight between two adjacent crosslinking sites. For the studied PTAs system, M_c can be calculated by the following equation:

$$M_c = M_n + M' \quad (3)$$

where M_n was the molecular weight of OAs and M' the revised value determined by the crosslinking monomer. Here, the value of M' was obtained from the equation:

$$M' = 2M_a/n \quad (4)$$

where M_a was the molecular weight and n its functionality degree of the crosslinking monomer. Therefore, M' for the crosslinked PTAs made from the OAs and b were 190.

The relationship between T_g and $1/M_c$ of the crosslinked PTAs was shown in Figure 7. As shown in Figure 7, T_g increased linearly with $1/M_c$, and the linear correlation coefficient r was 0.94. From the slope and intercept of the fitted line, values of k and $T_{g\infty}$ were obtained as 21,600 and 122, respectively. Thus, the relationship between T_g and crosslinking density for the crosslinked PTAs could be given by

$$T_g = 122 + 21600/M_c \quad (5)$$

The value of $T_{g\infty}$ was a little larger than the measured value 94 by Dynamic Mechanical Analysis of the linear polytriazole.¹³ The reasons were that: (1) the measured linear PTA was with a limited molecular weight; (2) DMA was usually carried out under a much lower heating rate than DSC. Therefore, the obtained value of $T_{g\infty}$ was credible. The relationship between T_g and M_n of OAs could be expressed as follows:

$$T_g = 122 + 21600/(M_n + 190) \quad (6)$$

CONCLUSIONS

A series of alkyne group-capped oligomers (OAs) and crosslinked PTAs with different network grids were well synthesized from a, b, c by the cycloaddition reaction of propargyl and azide groups and characterized. The size of the network grids had an effective influence on T_g s of PTAs: small network grids of PTAs would result in a high T_g . The relationship between T_g s of the PTAs and M_n of the OAs was described as $T_g = 122 + 21600/(M_n + 190)$.

References

- Hu, Y. H.; Luo, Y. H.; Wan, L. Q.; Qi, H. M.; Huang, F. R.; Du, L. *Acta Polym Sin* 2005, 4, 560.
- Luo, Y. H.; Hu, Y. H.; Wan, L. Q.; Xue, L.; Zhou, W.; Huang, F. R.; Shen, X. N.; Qi, H. M.; Du, L.; Chen, X. B. *Chem J Chin U* 2006, 27, 170.
- Wan, L. Q.; Luo, Y. H.; Xue, L.; Tian, J. J.; Hu, Y. H.; Qi, H. M.; Shen, X. N.; Huang, F. R.; Du, L.; Chen, X. B. *J Appl Polym Sci* 2007, 104, 1038.
- Tian, J. J.; Wan, L. Q.; Huang, J. Z.; Hu, Y. H.; Huang, F. R.; Du, L. *Polym Adv Technol* 2007, 18, 556.

5. Tian, J. J.; Wan, L. Q.; Huang, J. Z.; Hu, Y. H.; Huang, F. R.; Du, L. *Polym Bull* 2008, 60, 457.
6. Wang, X. F.; Zhao, Z. F.; Tian, J. J.; Wan, L. Q.; Hu, Y. H.; Huang, F. R.; Du, L. *Polym J* 2009, 41, 498.
7. Shibayama, K.; Suzuki, Y. *J Polym Sci Part A: Polym Chem* 1965, 3, 2637.
8. Lau, C. H.; Hodd, K. A. *Br Polym J* 1986, 18, 316.
9. Hsieh, T. T.; Hsieh, K. H.; Simon, G. P.; Tiu, C.; Hsu, H. P. *J Polym Res* 1998, 5, 153.
10. Li, Z. F.; Yang, G. H.; Xu, C. M. *J Polym Sci Part A: Polym Chem* 2004, 42, 1126.
11. Tian, J. J.; Wang, X. F.; Wan, L. Q.; Hu, Y. H.; Huang, F. R.; Du, L. *High Perform Polym* 2010, 22, 198.
12. Han, Z. W.; Zhang, D. Z.; Yang, Q. X.; Wang, B. F. In *Textbook of Polymer Science*; East China University of Science and Technology Press: Shanghai, 2001; pp 240–242.
13. Wan, L. Q.; Tian, J. J.; Huang, J. Z.; Hu, Y. H.; Huang, F. R.; Du, L. *J Macromol Sci Part A: Pure Appl Chem* 2007, 44, 175.