

Novel Methods for Synthesis of High-Impact Polystyrene with Bimodal Distribution of Rubber Particle Size

Daishuang Li,¹ Jing Peng,¹ Maolin Zhai,¹ Jinliang Qiao,^{1,2} Xiaohong Zhang,² Genshuan Wei¹

¹Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

²SINOPEC, Beijing Research Institute of Chemical Industry, Beijing 100013, People's Republic of China

Received 9 April 2005; accepted 31 March 2006

DOI 10.1002/app.24624

Published online 2 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: By using *in situ* prepolymerization and radiation curing, high-impact polystyrene (HIPS) with a bimodal distribution of the size of the rubber particles (bimodal HIPS) was synthesized in the presence of ultrafine full-vulcanized powdered styrene-butadiene rubber (UFPSBR) and polybutadiene rubber (BR). TEM photographs indicated that UFPSBR was dispersed uniformly as a single particle with a diameter of about 100 nm. On the other hand, bimodal HIPS with different rubber particle size distributions could also be obtained

by blending HIPS and UFPSBR grafting styrene (UFPSBR-g-St) with different grafting yields. The bimodal HIPS with the smallest rubber particle size, at about 100 nm, could be prepared by blending the monomodal HIPS containing big rubber particles with polystyrene/UFPSBR. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2071–2075, 2008

Key words: Polystyrene; morphology; radiation; synthesis; nanoparticles

INTRODUCTION

HIPS is basically a blend of polystyrene (PS) and a graft copolymer of butadiene and styrene that owes its high toughness to the unique “salami” domains of BR, which contains many PS subdomains. The influence of particle morphology on the mechanical properties of HIPS has been extensively reported in the literature.^{1–4}

It is well known that the optimum diameter of rubber particles in high-impact polystyrene (HIPS) with a monomodal distribution of rubber particle size (monomodal HIPS) is 1–2 μm .^{5,6} However, a few studies showed that better impact toughness could be obtained in bimodal HIPS than in monomodal HIPS with the same rubber content.^{7–10} Okamoto's results revealed that long extended crazes induced from the large particles overlapped with the minute crazes from small rubber particles in the vicinity of the large particles, leading to higher impact strength.¹⁰

Okamoto also suggested that the greater the difference in the sizes of the particles that constitute bimodal HIPS, the higher was the impact strength of Izod.¹⁰ Therefore, decreasing the size of small particles in bimodal HIPS could lead to improvement in impact strength, although it

is not easy to disperse very small rubber particles in a PS matrix very well, especially those nanometer sized particles. Our previous study reported that ultrafine full-vulcanized particles powdered rubber (UFPR), prepared with gamma irradiation and spray drying, could be easily dispersed in plastics and had shown great applicability for use in toughening plastics.^{11–17} The size of the dispersed phase could be precontrolled, and the particle size of UFPR depended on the particle size of the rubber latex used. Therefore, it is possible to produce nanometer-sized UFPR if rubber latex with nanometer-sized particles could be synthesized.

In the present work, some novel methods for preparing bimodal HIPS were introduced in which the smallest rubber particle was about 100 nm. The morphology of these bimodal HIPS was observed by TEM to show the dispersion of UFPSBR.

EXPERIMENTAL

Materials

Styrene-butadiene rubber latex (SBRL-50) with a particle size of about 100 nm and an 85% gel fraction; polybutadiene rubber (BR 9000); and commercially available PS (688C) and HIPS (492J) were supplied by Yanshan Petrochemical Corporation (Beijing, China). SBR-g-St grafting copolymer was synthesized in our lab using gamma irradiation.¹⁸ UFPSBR (VP-101), prepared from SBRL-50 by irradiation crosslinking and spray drying, was supplied by SINOPEC, Beijing

Correspondence to: G. S. Wei (gswei@pku.edu.cn).

Contract grant sponsor: National High Technology Research and Development Program of China (863 program); contract grant number: 2002AA302510.

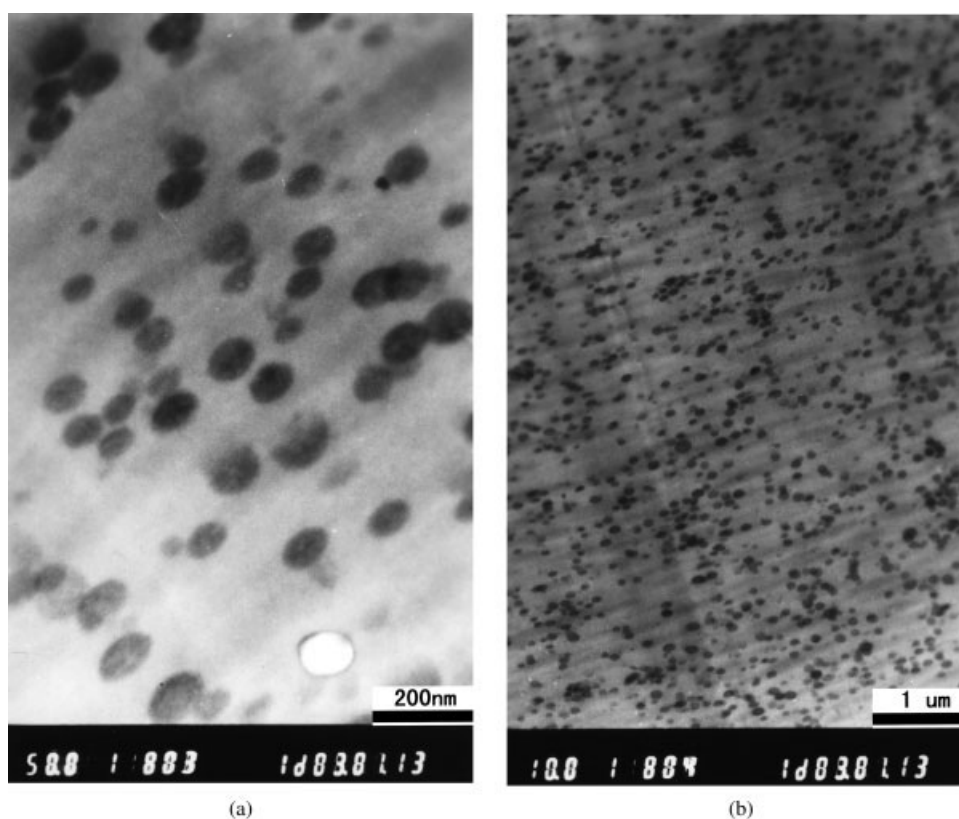


Figure 1 TEM photographs of monomodal HIPS (PS/UFPSBR).

Research Institute of Chemical Industry, Beijing, China. Prior to use, styrene was first washed with 10 wt % NaOH solution to remove inhibitor and then distilled under vacuum. Antioxidant 1010 was used as received.

Synthesis of monomodal and bimodal HIPS with UFPSBR

Both monomodal and bimodal HIPS were prepared via two-stage polymerization. First, styrene was prepolymerized in a glass reactor with benzoyl peroxide (BPO) as an initiator at 80°C–85°C in the presence of UFPSBR (for monomodal HIPS) or the BR and UFPSBR (for bimodal HIPS). For the latter, the stirring speed was about 200 rpm before phase reversion and 90 rpm after phase reversion. Then the prepolymer syrup was taken out of the reactor and further polymerized to a solid state under gamma irradiation at room temperature.

The polymer received was shattered in a plastic cracker (SP-160A, Nanhui Tanzhi Light Industry Mechanical Corporation, China) and then melt-extruded in a twin-screw extruder (SJSH-30, Nanjing, China) at 170°C–190°C with 0.5 wt % antioxidant 1010 at a speed of 100 rpm.

Preparation of UFPSBR-g-St

To prepare UFPSBR-g-St,¹⁸ SBRL-50 was diluted with water to a certain content of dry rubber. The required

amount of styrene was added to the latex, stirred for at least 2 h to disperse well, and then irradiated under γ -rays from a ⁶⁰Co source (Institute of Applied Chemistry, PKU, Beijing, China) at room temperature. Finally the SBR-g-St powdered rubber was obtained by spray-drying the SBR-g-St latex received.

Preparation of bimodal HIPS by blending method

PS and UFPSBR or UFPSBR-g-St were blended with 0.5 wt % antioxidant 1010 by a twin-screw extruder. The temperature for blending was 170°C–190°C, and the speed of the twin screw was 120 rpm.

TEM measurement

The samples were ultramicrotomed to form sections with a thickness of about 100 nm and stained with OsO₄. The morphology of the specimens was observed by TEM (JEOL JEM-100CX, Japan).

RESULTS AND DISCUSSION

Monomodal HIPS was synthesized when styrene was *in-situ* polymerized in the presence of UFPSBR. Then the resulting polymer was passed through extrusion process. The microstructure of the received polymer samples are shown in Figure 1, which indicated that

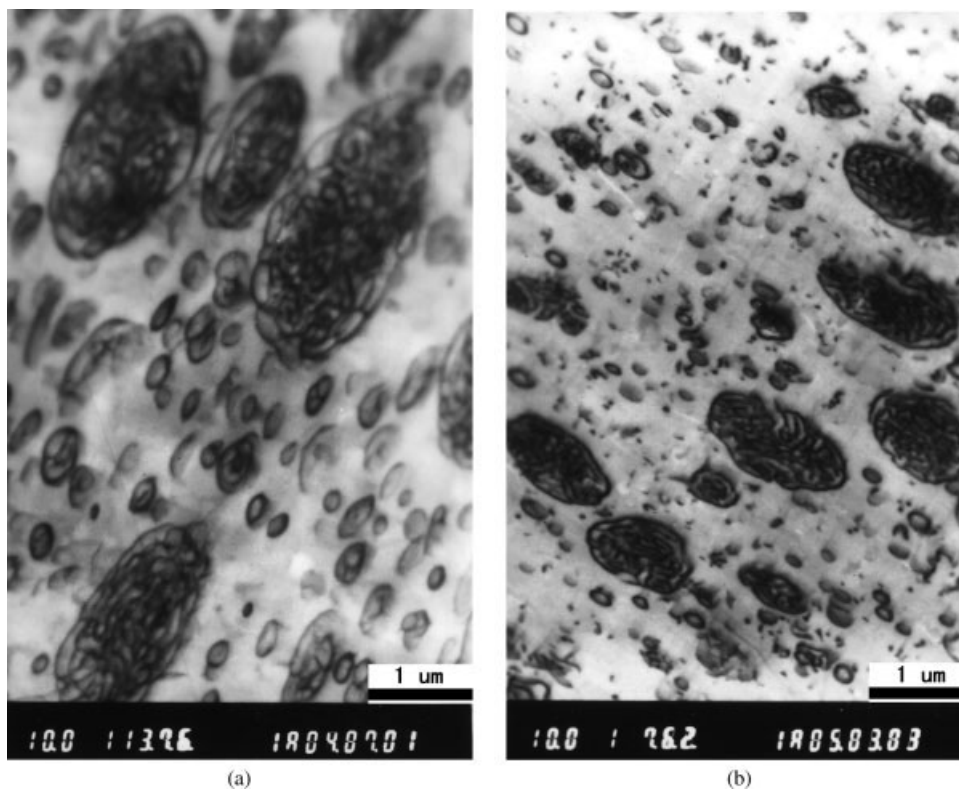


Figure 2 TEM photographs of bimodal HIPS (PS/BR/UFPSBR).

the UFPSBR was dispersed uniformly in PS. The dispersed phase size was about 100 nm. Because of the high crosslinking density of UFPSBR, UFPSBR par-

ticles were difficult to entangle each other. Consequently, the UFPSBR particles could be dispersed easily in styrene monomer under stirring. During poly-

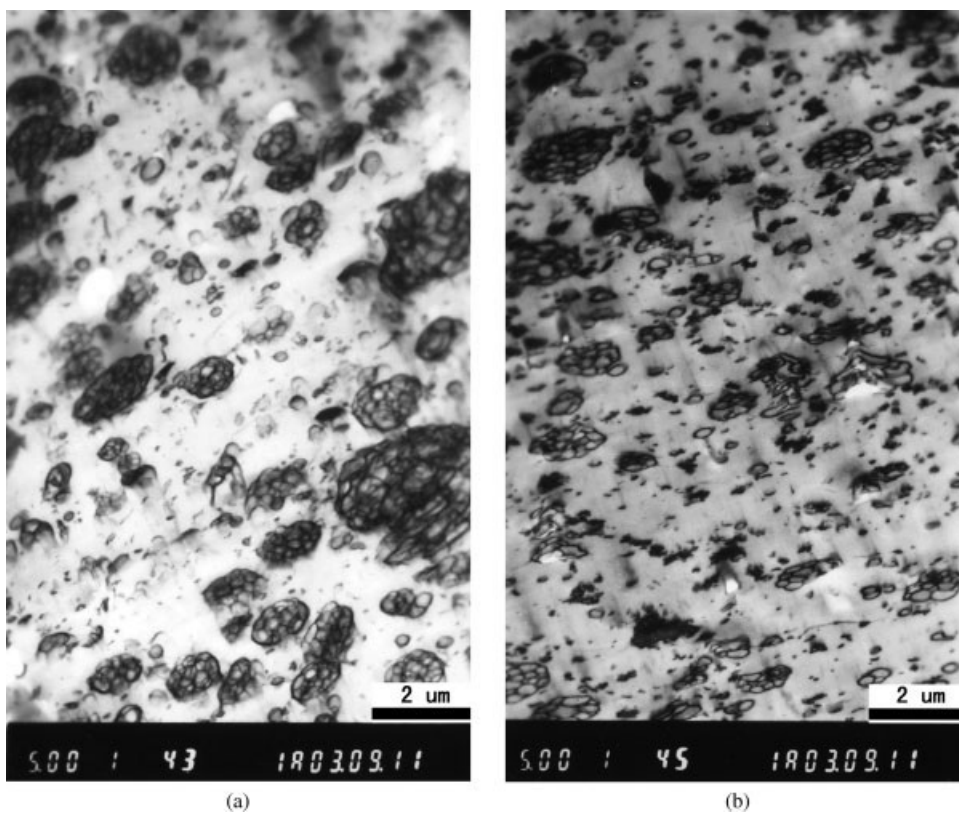


Figure 3 TEM photographs of (a) HIPS and (b) HIPS/UFPSBR blend.

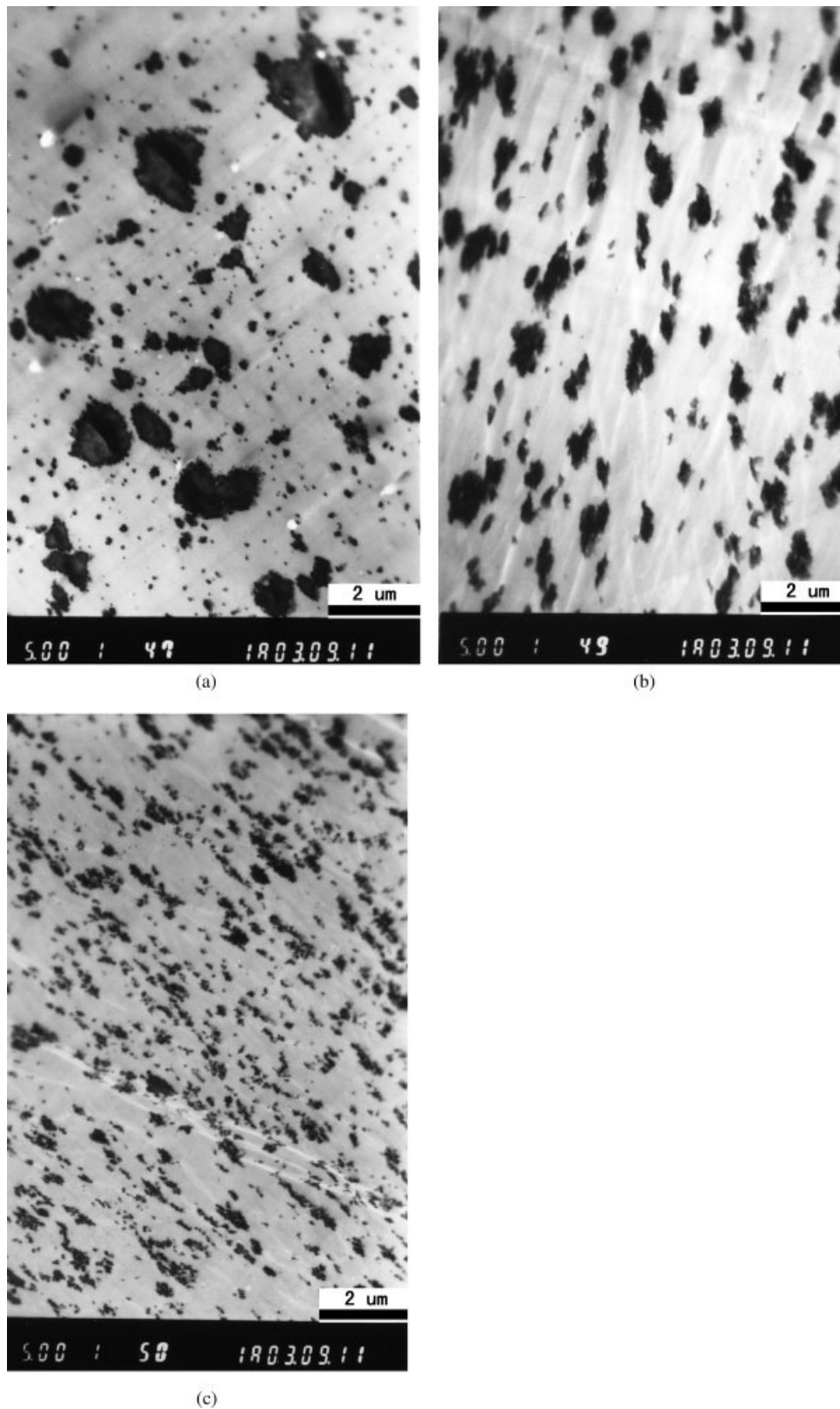


Figure 4 TEM photographs of PS/UFPSBR-g-St blends with different grafting yields: (a) 0, (b) 8%, (c) 32%.

merization grafting between styrene and UFPSBR might occur. The reasons mentioned above would lead to good dispersion of UFPSBR in PS by *in situ* polymerization.

The TEM photographs (Fig. 1) clearly revealed that the UFPSBR particles that were 100 nm in size were well dispersed in the PS matrix as individual particles. Therefore, if we blended this polymer and other

monomodal HIPS with big rubber particles, bimodal HIPS could be obtained. On the other hand, bimodal HIPS could be directly synthesized by the *in situ* polymerization of styrene in the presence of UFPSBR and BR simultaneously. The TEM photographs of the bimodal HIPS (PS/BR/UFPSBR) samples (Fig. 2) also clearly demonstrated the existence of the nanoscale-dispersed UFPSBR particles and “salami” structure with an average size of 1.5 μm that belonged to BR.

Lavengood prepared bimodal HIPS by blending two HIPS having 0.6- and 2.5- μm BR particles, respectively.⁷ The sizes of the BR particles in HIPS used in Hobbs's experiment were 0.48 and 0.81 μm .⁸ The smallest BR particle in Okamoto's experiment was 200 nm.¹⁰ Obviously, in the bimodal HIPS prepared in the present work, the difference between the big and small particles was much larger than those reported previously. Higher impact strength could be expected in this bimodal HIPS compared to those prepared by others because of the existence of the smaller particles.

Some studies have reported that bimodal HIPS could be prepared by blending two monomodal HIPS with different size distributions.⁷⁻¹⁰ In our work, it was found that if UFPSBR was blended with HIPS directly, a bimodal HIPS could be prepared as well. However, most of the UFPSBR particles aggregated on a micron scale in the PS rather than as single particles. The average sizes of BR and UFPSBR were about 2.5 and 1.5 μm , respectively [Fig. 3(b)].

It was found that increasing grafting yield of UFPSBR with styrene could improve the compatibility and decrease the microdomains size. Thus, if we blended HIPS and the UFPSBR-*g*-St with different grafting yields, different size distributions of bimodal HIPS could be obtained. Because of the complicated background of the TEM photographs of HIPS, UFPSBR-*g*-St was blended with PS, and the morphology of the blends was observed for convenient observation, as shown in Figure 4, which indicated that the dispersed size of UFPSBR-*g*-St decreased with increasing grafting yield.

The dispersed sizes of the UFPSBR-*g*-St shown in Figure 4(a-c) were about 1.5, 0.5, and 0.2 μm , respectively. The difference between the TEM photographs shown in Figures 1 and 4 was a result of the different synthesis methods. For the former, the UFPSBR was first swelled sufficiently by styrene monomer and

then grafted with styrene when styrene was polymerized. Therefore, the UFPSBR particles were more compatible with that PS matrix than that in the blend.

CONCLUSIONS

Via two-stage polymerization of styrene monomer in the presence of UFPSBR and BR, bimodal HIPS, with small particles about 100 nm, could be synthesized. It is a very convenient way to prepare bimodal HIPS, in which the small particles were dispersed uniformly in the PS matrix on a nanoscale. Moreover, bimodal HIPS could be obtained through blending monomodal HIPS with big rubber particles with monomodal HIPS that contained nanoscale-dispersed UFPSBR or UFPSBR-*g*-St with different grafting yields, leading to bimodal HIPS with different size distributions.

References

1. Agganval, S. L.; Livigni, R. A. *Poly Eng Sci* 1977, 17, 498.
2. Anzaldi, S.; Bonifaci, L.; Malaguti, E.; Vighi, M. G.; Ravanetti, P. *J Mater Sci Lett* 1994, 13, 1555.
3. Cigna, G.; Matarrese, S.; Biglione, G. F. *J Appl Polym Sci* 1976, 20, 2285.
4. Katime, A.; Quintana, J.; Price, C. *Mater Lett* 1995, 22, 297.
5. Bucknall, C. B. *Toughened Plastics*. Applied Science Publishers Ltd. London: 1977.
6. Cignal, G.; Lomellini, P. *J Appl Polym Sci* 1989, 37, 1527.
7. Lavengood, R. E., U.S. Pat. 4,214,056 (1980).
8. Hobbs, S. Y. *Polym Eng Sci* 1986, 26, 74.
9. Wrotecki, C.; de Charentenay, F. X. *Yield Frac Polym* 1988, 7, 51.
10. Okamoto, Y.; Miyagi, H.; Kakugo, M. *Macromol* 1991, 24, 5639.
11. Qiao, J.; Wei, G.; Zhang, X.; Zhang, S.; Gao, J.; Zhang, W.; Liu, Y.; Li, J.; Zhang, F.; Zhai, R.; Shao, J.; Yan, K.; Yin, H. U.S. Pat. 6,423,760 (2002).
12. Zhang, M.; Liu, Y.; Zhang, X.; Gao, J.; Huang, F.; Song, Z.; Wei, G.; Qiao, J. *Polymer* 2002, 43, 5133.
13. Liu, Y.; Zhang, X.; Wei, G.; Gao, J.; Huang, F.; Zhang, M.; Guo, M.; Qiao, J. *Chin J Polym Sci* 2002, 20, 93.
14. Huang, F.; Liu, Y.; Zhang, X.; Wei, G.; Gao, J.; Song, Z.; Zhang, M.; Qiao, J. *Macromol Rapid Commun* 2002, 23, 786.
15. Peng, J.; Qiao, J.; Zhang, S.; Wei, G. *Macromol Mater Eng* 2002, 287, 867.
16. Peng, J.; Zhang, X.; Qiao, J.; Wei, G. *J Appl Polym Sci* 2002, 86, 3040.
17. Zhang, X.; Wei, G.; Liu, Y.; Gao, J.; Zhu, Y.; Song, Z.; Huang, F.; Zhang, M.; Qiao, J. *Macromol Symp* 2003, 193, 261.
18. Li, D.; Peng, J.; Zhang, X.; Qiao, J.; Li, J.; Wei, G. *Chin J Polym Sci*, 2005, 23, 261.