

# Polymerization of Methyl Methacrylate With a Thermal Iniferter: Diethyl 2,3-Dicyano-2,3-di(*p*-tolyl)succinate

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**ABSTRACT:** A hexa-substituted ethane type compound, diethyl-2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), was successfully synthesized and used for initiation of methyl methacrylate (MMA) polymerization. The reaction demonstrated the characteristics of a "living" polymerization; i.e., both the yield and the molecular weight of the resulting polymers increased linearly with increasing reaction time, the molecular-weight distribution of PMMA obtained was  $\sim 1.60$  and almost unaffected by the conversion, and the resultant polymer can be chain extended by adding fresh MMA. End group analysis of the resultant PMMA confirmed that DCDTS behaves as a thermal iniferter for MMA polymerization. A block copolymer was prepared from the resultant PMMA, which contains a hexa-substituted C—C bond functional end group. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2566–2572, 2001

**Key words:** "living" radical polymerization; thermal iniferter; diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS); methyl methacrylate

## INTRODUCTION

Radical polymerization can produce a wide variety of polymeric materials, but the fine structures of the polymers, such as the molecular weight, molecular weight distribution, and end groups, are difficult to control due to termination of the propagating radicals by irreversible coupling or disproportionation. "Living"/controlled radical polymerization is a technique which provides much better control. Recently, several systems based on reversible termination of propagating radicals have been found, such as iniferter,<sup>1</sup> nitroxide-mediated stable free radical polymerization

(SFRP),<sup>2</sup> atom transfer radical polymerization (ATRP),<sup>3,4</sup> and reversible addition fragmentation chain transfer (RAFT).<sup>5</sup> These techniques have made the synthesis of well-controlled polymers possible. Among these systems, the iniferter technique is a useful and convenient method for synthesis of vinyl polymers in a homogeneous system under mild reaction conditions, although the molecular weight and the polydispersity index are not well controlled. So far, many photoiniferters and thermal iniferters have been prepared and used for vinyl monomer polymerization to synthesize block, graft, star, and telechelic polymers, as well as macromonomers.<sup>6–19</sup>

As reported in the literature, photoiniferters are mainly *N,N*-diethyldithiocarbamyl-containing compounds.<sup>6–12</sup> Thermal iniferters, aside from phenylazotriphenylmethane,<sup>13</sup> are usually

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symmetrical di- or tetraphenyl-substituted ethane derivatives, where the other substituents are  $-\text{CN}$ ,  $-\text{OC}_6\text{H}_5$ ,  $-\text{OSi}(\text{CH}_3)_3$ ,  $-\text{CO}_2\text{CH}_3$ , and  $-\text{CO}_2\text{CH}_2\text{CH}_3$ .<sup>14–19</sup> These thermal iniferters are mainly used for the polymerization of methyl methacrylate (MMA). In this article, we introduce diethyl-2,3-dicyano-2,3-di(*p*-tolyl) succinate (DCDTS) as a thermal iniferter for the polymerization of MMA, and a mechanism for the polymerization is proposed based on end group analysis of the resulting PMMA. In addition, chain extension and block copolymerization of the resulting PMMA have been investigated.

## EXPERIMENTAL

### Materials

*p*-Methylbenzyl cyanide from Acros Company was used as received. Diethyl-carbonate and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled before use. MMA, styrene, solvents, and other reagents were purified by usual methods.

### Preparation of DCDTS Thermal Iniferter

DCDTS was synthesized by a process similar to the preparation of diethyl 2,3-dicyano-2,3-diphenylsuccinate reported previously.<sup>14</sup> Ethyl  $\alpha$ -cyanotolylacetate was prepared first by the reaction of *p*-methylbenzyl cyanide and diethyl carbonate in toluene, bp: 145°C/2000Pa; then DCDTS was synthesized by an oxidative coupling reaction of ethyl  $\alpha$ -cyanotolylacetate with a Cu(II)-TMEDA- $\text{O}_2$  system in chloroform. In a 250-mL three-necked flask equipped with a magnetic stirring bar, an oxygen burette and a reflux condenser were placed 9.0 g (44.3 mmol) of ethyl  $\alpha$ -cyanotolylacetate in 150 mL of chloroform, 5.0 g (50.5 mmol) of CuCl and 6.0 mL (50.5 mmol) TMEDA (as catalyst), and 7.0 g of  $\text{MgSO}_4$  (to remove water). At 50°C, the whole system was then flushed and filled with oxygen; the reaction was completed within 30 min. The reaction mixture was filtered from  $\text{MgSO}_4$  and washed with 40 mL of 2 M HCl and three times with 40 mL of water. After the usual workup, a yellow syrup was obtained, which was recrystallized once from methanol and four times from carbon tetrachloride to yield white crystalline purified DCDTS in 64.2% yield (5.75 g), mp: 118.7–119.5°C. IR(KBr): 825, 1512, 2868  $\text{cm}^{-1}$  ( $-\text{C}_6\text{H}_4-$ ), 1156, 1234  $\text{cm}^{-1}$  (C—O—C), 1750  $\text{cm}^{-1}$  (C=O), 2257  $\text{cm}^{-1}$  ( $-\text{CN}$ );

$^1\text{H}$ -nuclear magnetic resonance (NMR) ( $\delta$ , ppm, in  $\text{CDCl}_3$ , 400 MHz): 1.19–1.52 [6H,  $-\text{OCH}_2\text{CH}_3$ ], 2.34 [6H,  $\text{CH}_3\text{C}_6\text{H}_4-$ ], 4.23–4.41 [4H,  $-\text{OCH}_2\text{CH}_3$ ], 6.94–7.28 [8H,  $\text{CH}_3\text{C}_6\text{H}_4-$ ].

Elemental analysis for  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4$ :

Calcd (%): C 72.27 H 5.98 N 6.73

Found (%): C 72.25 H 5.88 N 6.64

### Polymerization

Polymerization of MMA with DCDTS thermal iniferter was carried out in sealed glass tubes. After polymerization for a given time, the contents of the tubes were dissolved in tetrahydrofuran (THF) and then poured into a large amount of methanol. The polymers were reprecipitated from a benzene solution with methanol as the precipitant and then dried. Block copolymers were prepared from the copolymerization of St with MMA prepolymer by a similar procedure. Separation of the mixture of homopolymers and block copolymer was carried out by solvent extraction. PMMA was extracted with 95% ethanol and PSt with cyclohexane.

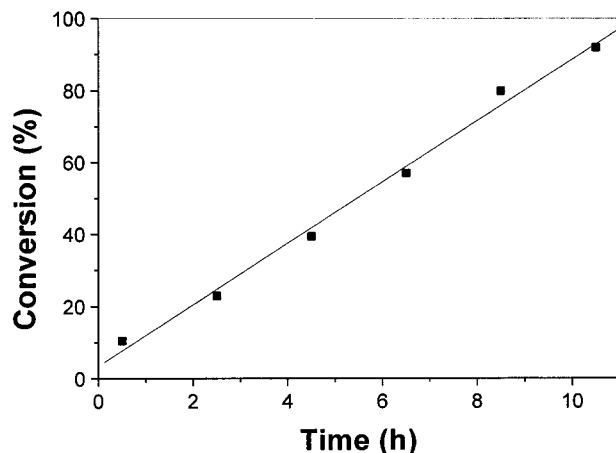
### Characterization

Molecular-weight and molecular-weight distribution data of the polymers were determined by gel permeation chromatography (GPC) using THF as the eluent at 1.0 mL/min at 35°C through three Waters  $\mu$ -Styragel columns (HT2+HT3+HT4) in series and a Waters 515 RI detector. The column system was calibrated with polystyrene standards. The data were analyzed on a Waters Millennium 32 system. Infrared (IR) and  $^1\text{H}$ -NMR spectra were recorded on a Nicolet IR 750 spectrometer and a Bruker ARX 400 spectrometer, respectively. Glass-transition temperatures ( $T_g$ ) were determined with a TA DSC-2010 differential scanning calorimeter (DSC) at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

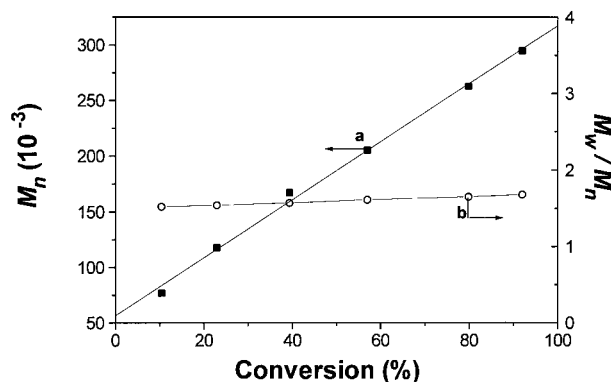
### “Living” Polymerization Characteristics of MMA With DCDTS as a Thermal Iniferter

The analytical data for the polymerizations at 50°C are compiled in Figures 1 and 2. Figure 1 shows a conversion >90% was obtained after 10.5 h, and the monomer conversion increase with



**Figure 1** Time-conversion relationship for bulk polymerization of MMA with DCDTS at 50°C; [MMA] = 9.4 mol L<sup>-1</sup>, [DCDTS] = 9.4 × 10<sup>-2</sup> mol L<sup>-1</sup>.

the increasing reaction time. In Figure 2, curve a shows that  $M_n$  increases linearly with conversion; the resultant polymer had a high molecular weight, and the  $M_n$  is 294,700 at 92% conversion. These results demonstrate the “living” nature of MMA polymerization with the DCDTS thermal iniferter. However, the polydispersity indexes of the resulting PMMA are not well controlled with the values at ~1.60. It can also be seen in Figure 2 that the linear relation of  $M_n$  and conversion does not pass through the origin. The deviation may be due to reversible equilibrium of the propagating radicals and the dormant species being not yet set up during the initial period of the polymerization, during which time normal irreversible termination occurred. After this period



**Figure 2** Conversion- $M_n$  (a) and conversion-MWD (b) relationships for bulk polymerization of MMA with DCDTS at 50°C; [MMA] = 9.4 mol L<sup>-1</sup>, [DCDTS] = 9.4 × 10<sup>-2</sup> mol L<sup>-1</sup>.

**Table I** Effect of Temperature on the Polymerization of MMA With DCDTS\*

Temp (°C)	Conversion (%)	$M_n$ (10 <sup>-3</sup> )	$M_w/M_n$
40	5.98	124.9	1.65
50	18.75	106.5	1.61
60	30.46	76.9	1.55
70	42.93	55.4	1.49
80	56.78	32.8	1.46

MMA, methyl methacrylate; DCDTS, diethyl 2,3-dicyanodi(p-tolyl)succinate.

\* Conditions: [MMA] = 9.4 mol L<sup>-1</sup>, [DCDTS] = 9.4 × 10<sup>-2</sup> mol L<sup>-1</sup>,  $t$  = 2 h.

(conversion <10% generally), the reversible equilibrium was set up, and the polymerization proceeded by a “living” process. Thus, the polymerization is a pseudoliving process.

MMA polymerization with DCDTS thermal iniferter can be carried out at different temperatures. The data for the effect of temperature on polymer molecular weight and conversion are compiled in Table I. The data show that within the same reaction time interval (2 h), conversion increased from 5.98% to 56.78% with increasing temperature from 40 to 80°C, while the molecular weight decreased remarkably from 124,900 to 32,800. This indicates that the polymerization follows the principle of conventional radical polymerization, i.e., the polymerization carried out at lower temperature, lower monomer conversion and higher molecular weight is obtained.

The effect of iniferter concentration on the polymerization is also studied. The results are compiled in Table II, which shows that in all iniferter concentrations used, the molecular weight increases with conversion. Within the same reac-

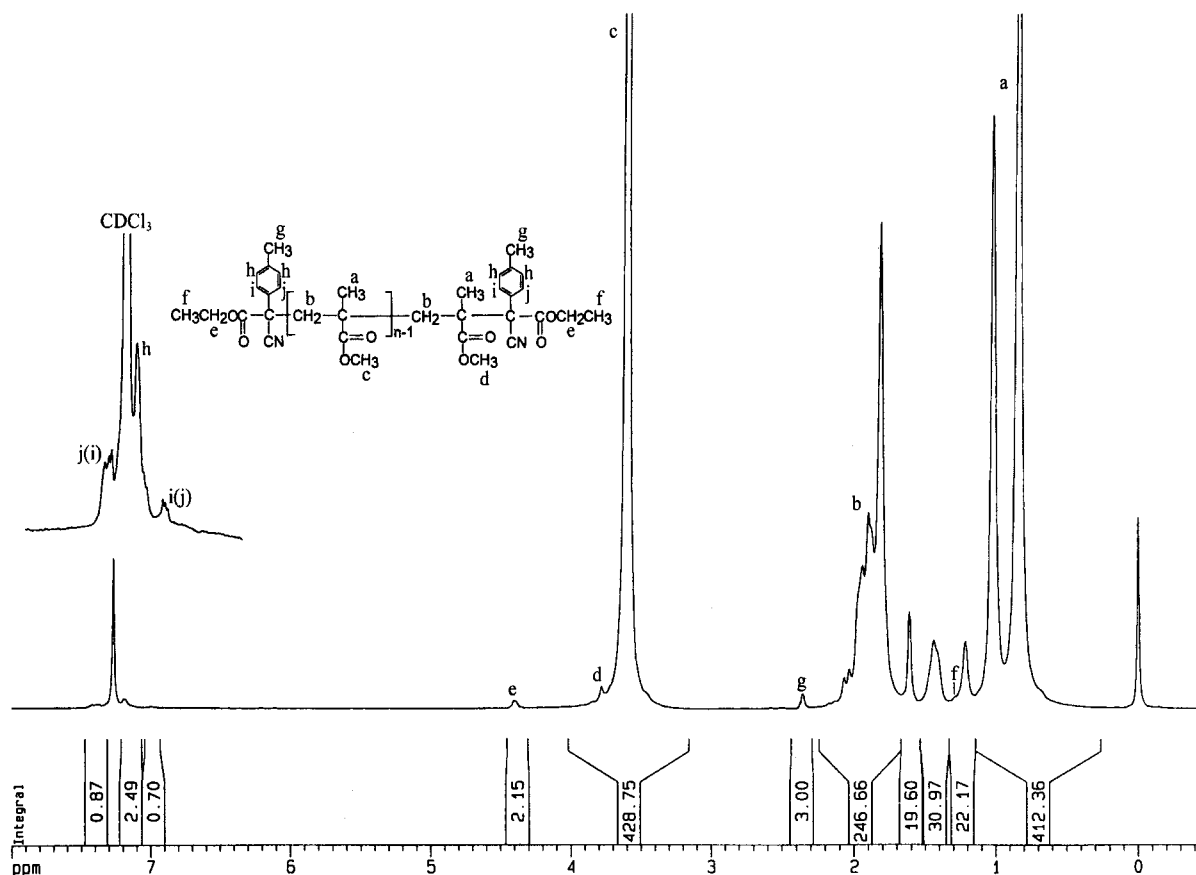
**Table II** Effect of DCDTS Concentration on the Polymerization of MMA\*

[DCDTS]/[MMA]	Time (h)	Conversion (%)	$M_n$ (10 <sup>-3</sup> )	MWD
1/100	2.5	22.91	117.7	1.54
	4.5	39.35	167.1	1.57
1/500	2.5	6.67	272.8	1.48
	4.5	10.90	354.2	1.51
1/1000	2.5	4.43	317.8	1.53
	4.5	8.48	396.5	1.56

MMA, methyl methacrylate; DCDTS, diethyl 2,3-dicyanodi(p-tolyl)succinate.

\* Conditions: [MMA] = 9.4 mol L<sup>-1</sup>.





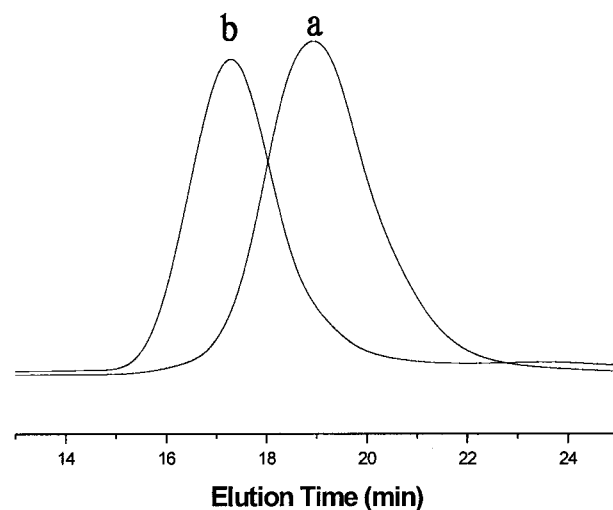
**Figure 3**  $^1\text{H-NMR}$  spectrum of DCDTS-PMMA (in  $\text{CDCl}_3$ , 4.00 MHz).

the carboxy-cyano-tolyl-methyl end group. The NMR data suggest that the end group of the polymer contains fragments of DCDTS, but the data cannot distinguish the fragments of the  $\alpha$ -end from those of the  $\omega$ -end. The result of end-group analysis implies that the polymerization proceeds by a reversible deactivation process.

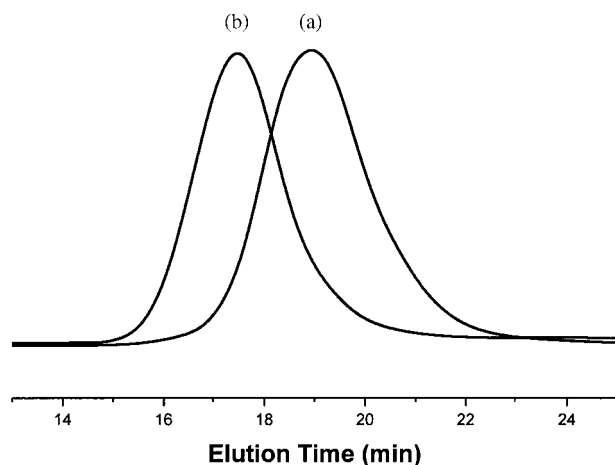
#### Chain Extension and Block Copolymerization

The PMMA obtained with an  $\omega$  hexa-substituted C—C bond end group (stamped DCDTS-PMMA) can be used as a thermal macroiniferter for chain extension with additional MMA or formation of a block copolymer by reaction with another monomer. A chain extension polymerization of PMMA was carried out in bulk at  $70^\circ\text{C}$  in the presence of DCDTS-PMMA with  $M_n = 32,800$  and  $M_w/M_n = 1.46$ , and a conversion of 65% was achieved after polymerization for 3 h. The  $M_n$  of the chain-extended PMMA was increased to 102,500 and the polydispersity index increased slightly to 1.49. The increase in molecular weight can be clearly seen in the GPC chromatograms as shown in Figure 4.

Block copolymers were also prepared by the same method. Figure 5 displays the GPC chromatograms for DCDTS-PMMA and PMMA-*b*-



**Figure 4** GPC chromatograms of PMMA before and after chain extension reaction at  $70^\circ\text{C}$ . (a) DCDTS-PMMA; (b) chain extended product.



**Figure 5** GPC chromatograms of PMMA before and after copolymerization with St at 70°C. (a) DCDTS-PMMA; (b) PMMA-*b*-PSt.

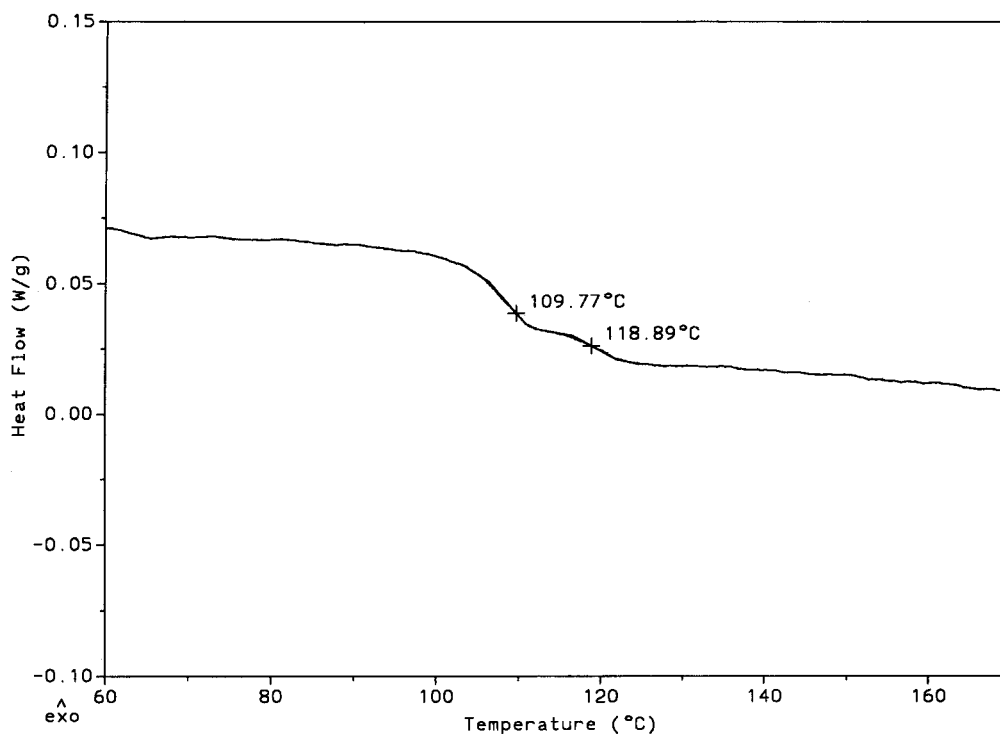
PSt. The data show no additional peak and the molecular weight increased from 32,800 to 91,600, confirming that a block copolymer had been formed. Formation of a PMMA-*b*-PSt copolymer was also confirmed by IR and DSC analyses. The IR spectrum of PMMA-*b*-PSt has the characteristic adsorption peaks of PMMA at 1731  $\text{cm}^{-1}$  (C=O), 1150  $\text{cm}^{-1}$  (C—O—C) and PSt at 700

$\text{cm}^{-1}$ , 1600  $\text{cm}^{-1}$ , and 3082  $\text{cm}^{-1}$  ( $-\text{C}_6\text{H}_5$ ), respectively. The DSC trace for PMMA-*b*-PSt is shown in Figure 6; two clear  $T_g$  transitions were seen at 119 and 109°C. In a comparative experiment, the  $T_g$  values of PMMA and PSt were determined to be 126 and 95°C, respectively.

The chain extension reaction and block copolymerization reveal that the hexa-substituted C—C bond in the end group of DCDTS-PMMA can thermally dissociate; these data support a conclusion that the polymerization of MMA with DCDTS thermal iniferter is a “living” polymerization process.

## CONCLUSIONS

A hexa-substituted ethane type compound, diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), was synthesized and used as a thermal iniferter for MMA polymerization, which demonstrates the characteristics of a “living” process. The PMMA obtained bearing a hexa-substituted C—C bond functional end group can be used as a macroiniferter, which can further extend with additional MMA or initiate St copolymerization to yield PMMA-*b*-PS block copolymers.



**Figure 6** Differential scanning calorimetry (DSC) curve of a PMMA-*b*-PSt sample.



## REFERENCES

1. Otsu, T.; Yoshida, M. *Makromol Chem Rapid Commun* 1982, 3, 127.
2. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987.
3. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
4. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
5. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.P.T.; 6. Mayadunne, R. T. A.; Meijs, G.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S.H. *Macromolecules* 1998, 31, 5559.
6. Otsu, T.; Matsumoto, A. *Adv Polym Sci* 1998, 136, 75.
7. Otsu, T.; Matsunaga, T.; Doi, T.; Matsumoto, A. *Eur Polym J* 1995, 31, 67.
8. Yang, X. M.; Qiu, K. Y. *J Appl Polym Sci* 1996, 61, 513.
9. Yang, X. M.; Qiu, K. Y. *J Macromol Sci Pure Appl Chem* 1997, 34, 315.
10. Qin, S. H.; Qiu, K. Y. *Acta Polym Sin* 1999, 4, 509.
11. Qin, S. H.; Qiu, K. Y. *J Appl Polym Sci* 2000, 75, 1350.
12. Qin, S. H.; Qiu, K. Y. *Acta Polym Sin*, 2000, 3, 375.
13. Otsu, T.; Tazaki, T. *Polym Bull* 1986, 16, 277.
14. Qin, S. H.; Qiu, K. Y.; Swift, G.; Westmoreland, D. G.; Wu, S. G. *J Polym Sci Part A: Polym Chem* 1999, 37, 4610.
15. Bledzki, A.; Braun, D. *Makromol Chem* 1983, 184, 745.
16. Bledzki, A.; Balard, H.; Brawn, D. *Makromol Chem* 1981, 182, 1057.
17. Tazaki, T.; Otsu, T. *Polym Bull* 1987, 17, 127.
18. Otsu, T.; Matsumoto, A.; Tazaki, T. *Polym Bull* 1987, 17, 323.
19. DeLeon, M. E.; Gnanou, Y.; Guerrero, R. *Polym Prepr* 1997, 38, 667.