Polymer Bulletin 46, 277–283 (2001)

Polymer Bulletin

Phosphonamidates as thermally latent initiators in the polymerization of epoxides

Moonsuk Kim[1], Fumio Sanda[1], Takeshi Endo[2] ✉

[1] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan
[2] Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan
e-mail: tendo@poly.yz.yamagata-u.ac.jp, Tel.: +81-238-26-3090, Fax: +81-238-26-3092

Received: 26 February 2001/Revised version: 12 April 2001/Accepted: 13 April 2001

Summary

Phosphonamidates, *O,O*-di-*tert*-butyl 1-piperidinyl phosphonamidate (**BP-1**) and *O-tert*-butyl di-*1*-piperidinyl phosphonamidate (**BP-2**), were synthesized by the reaction of phosphorus oxychloride and piperidine in the presence of triethylamine, followed by the reaction with *tert*-butyl alcohol in the presence of sodium hydride. The polymerization of GPE was carried out at 110-190 °C for 12 h with **BP-1** and **BP-2** as thermally latent initiators (3 mol %). The polymerization with *O-tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate (**BP**) previously reported was also examined for comparison. No polymerization of GPE took place below 110 °C, whereas it proceeded rapidly above the temperature. The activity order was **BP-2** > **BP** > **BP-1**. Epikote 828 was cured with **BP** (5 mol %) at 190 °C to afford the solvent-insoluble gelled epoxy resin quantitatively. A mixture of GPE and phosphonamidate **BP** (3 mol %) did not react at 50 °C for 4 months.

Introduction

Thermosetting materials are commonly cured by mixing two components, reactive resin and catalysts (initiators) just before use. This method is accompanied by several problems such as inefficient processability and material loss. It is desirable to develop one component system consisting of premixed reactive resin and initiators. "Latent initiators" show no activity under normal conditions but form active species to initiate polymerization by certain external stimulation like heating and photoirradiation. Latent initiators make one component system possible, because they can control initiation and curing steps [1]. Various onium salts such as sulfonium [2], pyridinium [3], phosphonium salts [4], diaryliodonium and triarylsulfonium salts [5] have been developed as latent thermal- and photo-initiators. Through the studies for several decades, some onium-salt-type latent initiators are now commercially available and utilized in industrial fields such as paints, inks, adhesives, epoxy molding compounds, and photoresists [6].

However, onium-salt-type latent initiators possesses several problems: low solubility in monomers and solvents, remaining of inorganic compounds in polymers, and high cost. To overcome these problems, it is desirable to design a novel latent initiator without a salt structure. We have developed non-salt-type latent initiators such as *N*-substituted phthalimides [7], aminimides [8], carboxylates [9], sulfonates [10], and phosphonium ylides [11]. We have recently selected organophosphorus compounds as a new candidate of non-salt-type latent initiator because of the easy molecular design and synthesis, wide application, and low cost [12]. We have recently reported that phosphonates serve as thermally latent cationic initiators in the polymerization of glycidyl phenyl ether (GPE) [13]. More recently, we have communicated that a phosphonamidate, *O*-*tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate (**BP**), can serve as an excellent thermally latent anionic initiator for the polymerization of GPE, where the active species is piperidine formed *via* the reaction of **BP** with GPE by heating as shown in Scheme 1 [14]. This paper examines the possibility of novel phosphonamidates (**BP-1** and **BP-2**) and phosphonamide (**DPA**) as thermally latent anionic initiators for GPE, and as hardeners for epoxy resin.

Scheme1

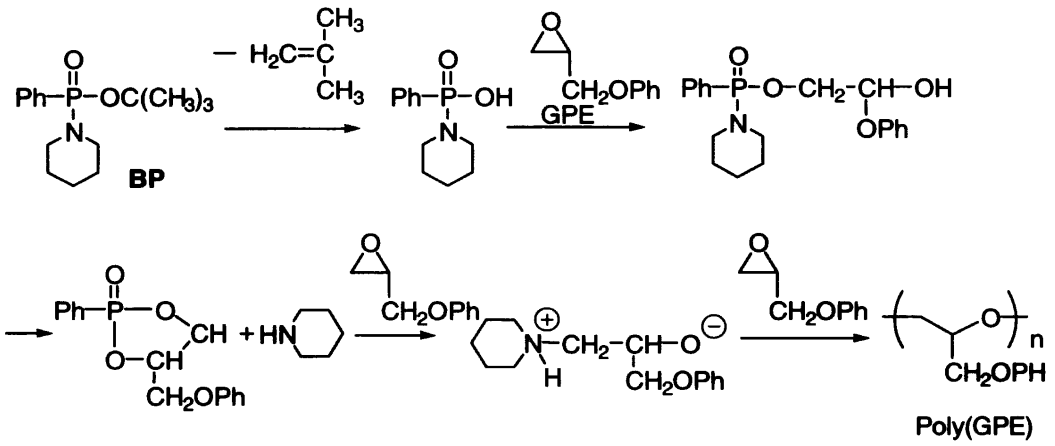
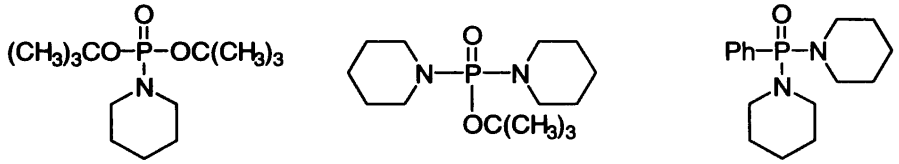


Chart 1



Experimental

Materials

Commercially available extra pure phosphorus oxychloride, piperidine, and *tert*-butyl alcohol were used as received without further purification. Tetrahydrofuran (THF) was dried over Na-benzophenone and distilled under a nitrogen atmosphere before use. GPE was dried and distilled over calcium hydride. Bisphenol-A-type epoxide oligomer (Epikote 828) was obtained from Yuka Shell Epoxy Co. and used as received. *O*-*tert*-Butyl *P*-phenyl 1-piperidinyl phosphonamidate (**BP**) was synthesized according to the reported procedure [12].

Measurements

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a JEOL EX-400 spectrometer using tetramethylsilane or 85% H_3PO_4 as an internal or external standard in $CDCl_3$. IR spectra were measured with a JASCO JIR-5300 spectrophotometer. Melting points (mp) were measured on a Yanaco Micro Melting Point Apparatus. Number- and weight-average molecular weights (M_n and M_w) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8120 system, equipped with two consecutive polystyrene gel columns (TSK gels G4000HXL and G2500HXL), using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive index and ultraviolet detectors. Elemental analyses were carried out with a Yanaco Type MT-5 CHN, and a SX-Elements micro analyzer YS-10. TGA was done with a Seiko Instruments TG / DTA 220 at a heating rate of 10 °C/min under a nitrogen atmosphere.

*Synthesis of O,O-Di-tert-butyl 1-Piperidinyl Phosphonamidate (**BP-1**)*

To a solution of piperidine (0.84 g, 9.9 mmol) and triethylamine (1.97 g, 19.5 mmol) in THF (30 mL) was added a solution of phosphorus oxychloride (1.67 g, 10.9 mmol) in THF (20 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature overnight. The precipitate formed in the reaction mixture was filtered off and washed with THF. After removal of THF, crude 1-piperidinyl phosphonic dichloride was obtained as light yellow oil.

To a solution of sodium hydride (0.88 g (60 % in oil), 22 mmol) in THF (20 mL) was added a solution of *tert*-butyl alcohol (1.94 g, 25.8 mmol) in THF (30 mL). After evolution of hydrogen gas stopped, a solution of crude 1-piperidinyl phosphonic dichloride in THF (30 mL) was added to the solution at 0 °C. The resulting solution was stirred at room temperature for 1 h and refluxed for 5 h. After removal of THF by evaporation, the residue was dissolved in chloroform and the resulted solution was washed with water several times and a dilute sodium bicarbonate aqueous solution. The organic phase was dried over anhydrous magnesium sulfate and concentrated by evaporation of chloroform to give light yellow oil, which was crystallized from *n*-hexane to give white powder (57%). Mp: 49-50 °C. IR (KBr, cm^{-1}): 3297, 2932, 2854, 1454, 1369, 1261, 1161, 1076, 1041, 978, 729, 576. ^{1}H NMR ($CDCl_3$): δ 3.00-3.02 (m, 4H, -N(CH_2-)$_2$), 1.45-1.52 (m, 24H, -2(CH_3)$_3$, -(CH_2)$_2$$CH_2$). ^{13}C NMR ($CDCl_3$): δ 80.1, 45.4, 30.1, 30.0, 25.8, 25.7, 24.7. ^{31}P NMR ($CDCl_3$): δ -0.08. Anal. Calcd for $C_{13}H_{28}NPO_3$: C, 56.30; H, 10.18; N, 5.05. Found: C, 56.43; H, 10.42; N, 4.88.

*Synthesis of O-tert-Butyl Di-1-piperidinyl Phosphonamidate (**BP-2**)*

Compound **BP-2** was synthesized in the similar manner with **BP-1** from phosphorus oxychloride (2.54 g, 16.6 mmol) and piperidine (2.71 g, 31.8 mmol), followed by the reaction with *tert*-butyl alcohol (1.3 g, 17.3 mmol) in the presence of sodium hydride. It was purified by silica gel column chromatography eluted with solution of *n*-hexane and ether. Yield: 2.91 g (10.1 mmol, 61%, light yellow oil). IR (NaCl, cm^{-1}): 2974, 2932, 2851, 1452, 1367, 1226, 1161, 1072, 987, 952, 729, 578. ^{1}H NMR ($CDCl_3$): δ 3.02 (m, 8H, -2N(CH_2-)$_2$), 1.46-1.51 (m, 21H, -(CH_3)$_3$, -2((CH_2)$_2$$CH_2$)). ^{13}C NMR ($CDCl_3$): δ 79.3, 45.2, 30.1, 26.1, 24.7. ^{31}P NMR ($CDCl_3$): δ 10.9. Anal. Calcd for $C_{14}H_{29}N_2PO_2$: C, 58.31; H, 10.14; N, 9.71. Found: C, 58.39; H, 10.11; N, 9.55.

*Synthesis of P-Phenyl Di-1-piperidinyl Phosphonic diamide (**DPA**)*

DPA was synthesized from phenyl phosphonic dichloride (3.09 g, 15.8 mmol) and piperidine (3.02 g, 35.5 mmol) in the similar manner as **BP-1**. Yield: 3.13 g (10.7 mmol, 68%, white powder). Mp: 59.5-61.5 °C. IR (KBr, cm^{-1}): 3051, 2932, 2850, 1438, 1379, 1278, 1204, 1157, 1116, 1067, 1027, 950, 855, 728,700, 573. ^{1}H NMR ($CDCl_3$): δ 7.79-7.41 (m, 5H, $-C_6H_5$), 3.08-3.00 (m, 8H, $2(-N(CH_2-)_2)$), 1.57-1.47 (m, 12H, $2(-(CH_2)_2CH_2)$). ^{13}C NMR ($CDCl_3$): δ 131.2, 131.8, 130.9, 128.2, 45.0, 26.1, 24.7. ^{31}P NMR ($CDCl_3$): δ 25.77. Anal. Calcd for $C_{16}H_{25}N_2OP$: C, 65.73; H, 8.62; N, 9.58. Found: C, 65.33; H, 8.53; N, 9.51.

Polymerization

Typical procedure: initiator **BP-1** (41.6 mg, 0.15 mmol) was fed into a glass tube. The tube was closed with a three-way stopcock and a cycle of vacuum-nitrogen was repeated three times to remove oxygen. GPE (751 mg, 5 mmol) was fed into the glass tube with a syringe under nitrogen. The tube was sealed under vacuum using the freeze-thaw technique, and heated at a set temperature in an oil bath. After a set time, the tube was cooled into a dry ice-acetone bath and the reaction mixture was diluted with chloroform (1 mL). The mixture was then poured into *n*-hexane (70 mL) to precipitate a polymer. The polymer was separated from the supernatant by decantation and dried *in vacuo*. The monomer conversion was determined by ^{1}H NMR spectroscopy before precipitation with *n*-hexane, and the molecular weight of the polymer was determined by GPC. The obtained polymer was identified to be polyGPE by ^{1}H NMR, ^{13}C NMR, and IR spectra.

Results and discussion

Initiator Synthesis

The novel phosphonamidates ((**BP-1** and **BP-2**) were synthesized by the reaction of phosphorus oxychloride and piperidine in the presence of triethylamine, followed by the reaction with *tert*-butyl alcohol in the presence of sodium hydride. The structures were confirmed by ^{1}H, ^{13}C, ^{31}P NMR, IR spectroscopy, and elemental analysis. One and two piperidine moieties could be selectively incorporated according to the ratios to phosphorus oxychloride.

Polymerization of GPE with Phosphonamidates

Our previous paper has reported that *O-tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate (**BP**) can serve as a thermally latent anionic initiator for the polymerization of GPE, where the initiating species is piperidine released by cyclization after the reaction with GPE (Scheme 1) [14]. The polymerization of GPE was carried out with *P*-phenyl di-1-piperidinyl phosphonamide, **DPA** (3 mol %) without ester group at 190 °C for 12 h to confirm the role of the ester group. **BP** could convert 92% of GPE, but **DPA** could not at all under this condition. The ^{31}P NMR spectroscopic signal of **DPA** in the reaction mixture did not change before and after the polymerization, indicating no decomposition of **DPA**. It was confirmed that the ester group was necessary to release piperidine as an initiating species. We examined the polymerization of GPE with 3 mol % of **BP-1** and **BP-2** having one and two piperidine moieties, respectively, as thermally latent initiators at 110-190 °C for 12 h. Figure 1 shows the temperature-conversion relationships in the polymerization along with **BP**. No polymerization of GPE took place below 110 °C, whereas it proceeded rapidly above the temperature. It was confirmed that the phosphonamidates served as thermally latent initiators for the polymerization of GPE. The polymer yields increased

according to the conversion. The obtained polymers had number-average molecular weights ranging from 600 to 1000. The activity order of the phosphonamidates was **BP-2** > **BP** > **BP-1**. Further, time-conversion was monitored in the polymerization of GPE with 3 mol % of **BP-1** and **BP-2** at 150 °C to elucidate the initiator activity, as shown in Figure 2. **BP-2** showed activity slightly higher than **BP-1**.

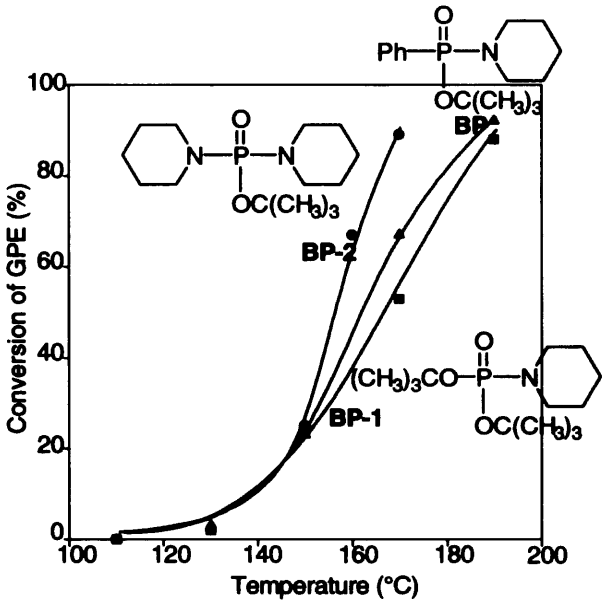


Figure 1. Temperature-conversion curves in the polymerization of GPE with phosphonamidates BP-1, BP-2, and BP (3 mol %) for 12 h.

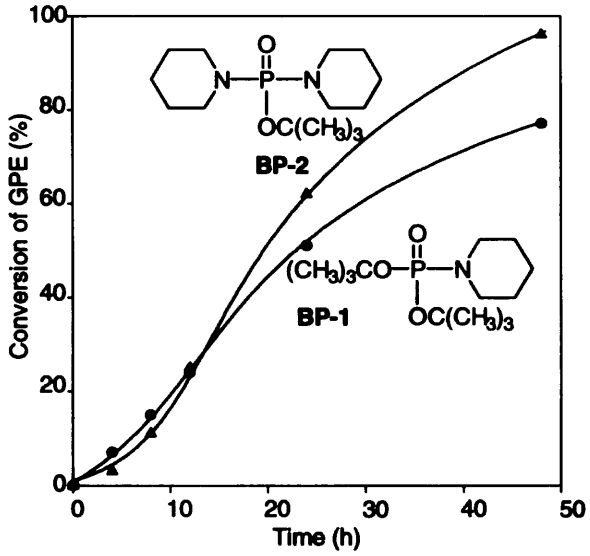


Figure 2. Time-conversion curves in the polymerization of GPE with phosphonamidates BP-1 and BP-2 (3 mol %) at 150 °C.

Curing of Epoxy Resin

As the results described above, we confirmed that the phosphonamidates could act as efficient thermally latent anionic initiators in the polymerization of GPE. We further examined curing of epoxy resin (Epikote 828) with **BP** (5 mol %) at

190 °C for 12 h. A solvent-insoluble gelled epoxy resin was obtained quantitatively. Figure 3 shows the IR spectra of the resin before and after curing. The absorption assignable to C-O stretching of epoxide at 916 cm^{-1} almostly disappeared after curing, indicating that **BP** served as an efficient hardener of the epoxy resin. Figure 4 shows the TGA thermograms of the epoxy resin before and after curing with phosphonamidate **BP** (5 mol %). The epoxy resin cured with **BP** showed thermal stability higher than that before curing.

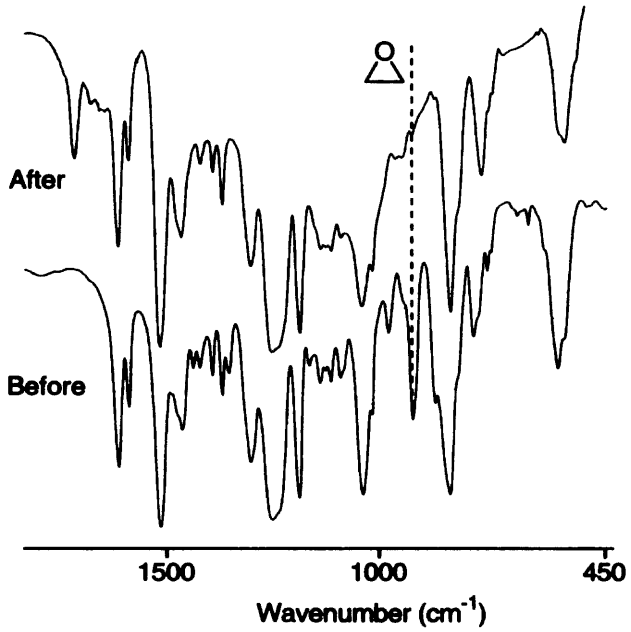


Figure 3. IR spectra of Epikote 828 before and after curing with BP (5 mol %) at 190 °C for 12 h.

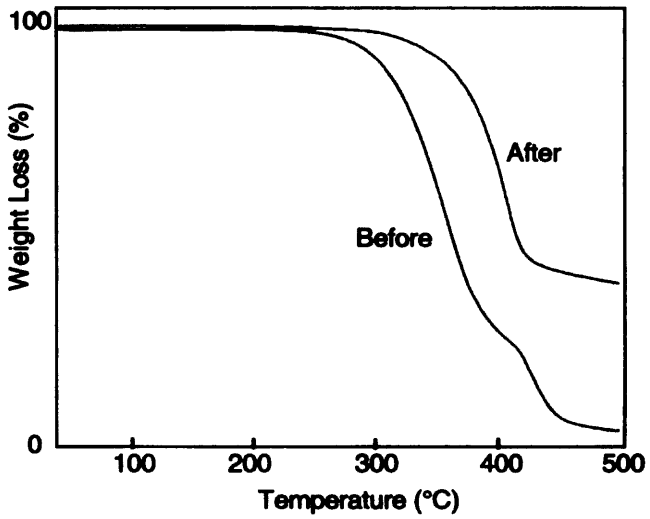


Figure 4. TGA curves of Epikote 828 before and after curing with BP (5 mol %) at 190 °C for 12 h.

Storage Stability

Storage stability is one of the most important properties for one component thermosetting resin. A mixture of GPE and phosphonamidate **BP** (3 mol %) was allowed to stand for 6 months at room temperature and for 4 months at 50 °C to

examine the storage stability. No change took place in ^{1}H and ^{31}P NMR spectroscopic patterns of this mixture under these conditions. No polymerization of GPE was also confirmed by GPC.

In summary, we could demonstrate that the phosphonamidates can serve as thermally latent anionic initiators in the polymerization of GPE and hardener in curing of epoxy resin, along with long storage stability.

References

1. Pappas SP, Hill LW (1981) J Coat Technol 53(675): 43
2. (a) Endo T, Uno HJ (1985) Polym Sci Polym Lett Ed 23: 359 (b) Endo T, Arita H, (1985) Makromol Chem Rapid Commun 6: 137 (c) Morio K, Murase H, Tsuchiya H, Endo T, (1986) J Appl Polym Sci 23: 5727 (d) Takata T, Endo T (1988) Macromolecules 21: 900 (e) Endo T, Kikkaw A, Uno H, Sato H, Hiza M, Takata T (1989) J Polym Sci Polym Lett Ed 27: 73 (f) Hamazu F, Akashi S, Koizumi T, Endo T (1991) J Polym Sci Polym Chem Ed 29: 1675 (g) Kikkawa A, Takata T, Endo T (1991) J Polym Sci Polym Chem Ed 29: 1089 (h) Hamazu F, Akashi S, Koizumi T, Endo T (1992) Makromol Chem Rapid Commun 13: 203 (i) Shimomura O, Sato T, Tomita I, Endo T (1998) Macromolecules 31: 2013 (j) Shimomura O, Sato T, Tomita I, Endo T (1999) J Polym Sci Part A Polym Chem 37: 217 (k) Shimomura O, Sato T, Tomita I, Endo T (2000) J Polym Sci Part A Polym Chem 38: 18
3. (a) Uno H, Takata T, Endo T (1988) J Polym Sci Polym Lett Ed 26: 453 (b) Uno H, Endo T (1988) Chem Lett 935 (c) Lee SB, Takata T, Endo T (1990) Chem Lett 2019 (d) Lee SB, Takata T, Endo T (1991) Macromolecules 24: 2689 (e) Lee SB, Takata T, Endo T (1991) Synthesis 368
4. (a) Takuma K, Takata T, Endo T (1993) Macromolecules 26: 862 (b) Takuma K, Takata T, Endo T (1993) Makromol Chem Rapid Commun 14: 203 (c) Takuma K, Takata T, Endo T (1993) J Photopolym Sci Technol 6: 67 (d) Toneri T, Sanda F, Endo T (1998) J Polym Sci Part A Polym Chem 36: 1957 (e) Toneri T, Watanabe K, Sanda F, Endo T (1998) Macromolecules 32: 1293
5. (a) Crivello JV, Lam HW (1979) J Polym Sci Polym Chem Ed 17: 977 (b) Crivello JV (1981) Developments in Polymer Photochemistry Chapter 1. Allen NS (ed) Applied Science Publishers, Essex England
6. Endo T, Sanda F (1996) Macromol Symp 107: 237
7. Takata T, Menceloglu YZ, Endo T (1992) J Polym Sci Part A Polym Chem 30: 501
8. Lee SD, Sanda F, Endo T (1997) J Polym Sci Part A Polym Chem 35: 689
9. Moriguchi T, Endo T, Takata T, Nakane Y (1995) Macromolecules 28: 4334
10. (a) Lee SD, Takata T, Endo T (1996) Macromolecules 29: 3317 (b) Lee SD, Takata T, Endo T (1999) J Polym Sci Part A Polym Chem 37: 293
11. Kobayashi M, Sanda F, Endo T (1999) Macromolecules 32: 4751
12. Pudovik AN (1989) Chemistry of Organophosphorus Compound. Mir Publishers, Moscow
13. (a) Kim MS, Sanda F, Endo T (1999) Macromolecules 32: 8291 (a) Kim MS, Sanda F, Endo T (2000) Chem Lett 100 (c) Kim MS, Sanda F, Endo T (2000) Macromolecules 33: 2359
14. Kim MS, Sanda F, Endo T (2000) Macromolecules 33: 3499