



## Synthesis and applications of triblock and multiblock copolymers using telechelic oligopropylene

Daisuke Sasaki<sup>a,\*</sup>, Yoshihiro Suzuki<sup>a</sup>, Toshiki Hagiwara<sup>b</sup>, Shoichiro Yano<sup>b</sup>, Takashi Sawaguchi<sup>b,\*\*</sup>

<sup>a</sup> Research and Development Division, San-ei Kogyo Corporation, 3-347 Togasaki, Misato-shi, Saitama 341-0044, Japan

<sup>b</sup> Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, 1-8-14 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

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### ABSTRACT

Isotactic polypropylene (iPP)–polystyrene (PS) and iPP–poly(methyl methacrylate) (PMMA) multiblock copolymers were synthesized by atom transfer radical coupling (ATRC) of PS–iPP–PS and PMMA–iPP–PMMA triblock copolymers obtained by atom transfer radical polymerization (ATRP) of styrene (St) and methyl methacrylate (MMA), respectively, using  $\alpha,\omega$ -dibromoisobutyrate oligopropylene (iPP–Br) as a bifunctional macroinitiator. The iPP–Br was prepared by hydroxylation and subsequent esterification of telechelic oligopropylene having terminal vinylidene double bonds at both ends obtained by controlled thermal degradation of iPP. ATRP of St and (meth) acrylic monomers using iPP–Br formed the corresponding triblock copolymers. It was confirmed that the PMMA–iPP–PMMA triblock copolymer was effective as the compatibilizer for the iPP/PMMA blend. An iPP–PS multiblock copolymer ( $M_n$ : 25 000 g/mol and  $M_w/M_n$ : 4.1) was prepared by ATRC of PS–iPP–PS triblock copolymer ( $M_n$ : 8900 g/mol and  $M_w/M_n$ : 1.3). ATRC with St of PMMA–iPP–PMMA triblock copolymer ( $M_n$ : 13 000 g/mol and  $M_w/M_n$ : 1.4) provided an iPP–PMMA multiblock copolymer containing St chains ( $M_n$ : 39 000 g/mol and  $M_w/M_n$ : 2.8).

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## 1. Introduction

Over 80 million tons of polyolefins are produced currently in the world, and they comprise a large fraction of the plastics in use. Their widespread use has been made possible by important advances in production and processing technology. Nevertheless, polyolefins lack compatibility with other materials such as polar polymers and metals, and the improvement of their compatibility is essentially a problem involving their functionalization. Attempts have been made to resolve this problem by copolymerizing olefins with polar monomers, and by surface modification. Recently, functionalized polyolefins with controlled structure have been actively investigated using metallocene and post-metallocene catalysts [1–6]. Moreover, living radical polymerization techniques continue to be developed rapidly because they allow various vinyl monomers to be used and the polymerization temperature is above room temperature. Of these, atom transfer radical polymerization (ATRP), in which a transition metal complex catalyst and a halogenated initiator compound are used, has received the most research attention. Macroinitiators are polymers that possess initiation sites

for the attachment of terminal or graft chains, and are often used for the synthesis of block or graft copolymers. As for industrially important polyolefins, copolymerization with various vinyl monomers by ATRP has been studied for functionalization and modification. Polyolefin macroinitiators have been obtained by copolymerization with functional monomers or by functionalization of chain ends by living polymerization [7–9]. Matsugi et al. [8] synthesized  $\alpha$ -bromoisobutyrate polyethylene by esterification of 2-bromo-2-methylpropionic bromide (BMPB) with  $\alpha$ -hydroxylate polyethylene obtained using a metallocene catalyst, and used it for ATRP of MMA. The morphology of the resulting block copolymer depended on its block composition, and it was an effective compatibilizer for polyethylene and PMMA. Polyolefins surface-modified by ultraviolet or gamma rays, and degraded PP have also been used for ATRP [10–13]. Yamamoto et al. [11] synthesized a PMMA grafted to polyethylene (PE) and iPP by ATRP initiated from peroxides on PE and iPP which generated by  $\gamma$ -ray irradiation in air. Kaneko et al. [13] synthesized iPP-*b*-PMMA and iPP-*b*-poly(*N*-isopropylacrylamide) using an iPP macroinitiator (with functionality 0.24–1.1) obtained by thermal degradation of iPP. The above-mentioned reports introduced initiation sites at terminal or graft positions on chains. However, reports of initiation sites introduced at both ends of a polymer chain are few. Additionally, ATRP has not been reported using iPP as a bifunctional initiator with initiation sites at both ends.

\* Corresponding author. Tel.: +81 48 955 1632; fax: +81 48 952 5543.

\*\* Corresponding author. Tel.: +81 33 259 0819; fax: +81 33 293 7572.

E-mail addresses: [sasaki@misato-net.com](mailto:sasaki@misato-net.com) (D. Sasaki), [sawaguti@chem-cst.nihon-u.ac.jp](mailto:sawaguti@chem-cst.nihon-u.ac.jp) (T. Sawaguchi).

These polymers obtained by ATRP have terminal halogen atoms, and applications exploiting their reactivity have been reported [14–17]. In particular, atom transfer radical coupling (ATRC), that is, the coupling reaction between halide polymers, is facile since the reaction proceeds rapidly under mild conditions. For instance, telechelic polymers were prepared by ATRC of a heterotelechelic polymer obtained by ATRP using initiators possessing functional groups in addition to initiation sites [18–22]. There have also been interesting reports of multiblock copolymers synthesized by ATRC of telechelic polymers having halogens at both ends, obtained by ATRP using bifunctional initiators [23,24]. This method is a very important reaction for the synthesis of various telechelic polymers and multiblock copolymers.

We have reported the selective synthesis of  $\alpha,\omega$ -diisopropenyl-oligopropylene (iPP–TVD) by the controlled thermal degradation of iPP [25–28], and the subsequent use of its functional groups to generate multiblock copolymers [29,30]. The terminal vinylidene double bond of iPP–TVD was converted to other functional groups by conventional organic synthesis techniques. However, the multiblock copolymers synthesized by step-growth polymerization had a low degree of polymerization due to the necessity of ensuring equal mole ratios and reactivity of functionalized oligopropylene. This problem may be solved by chain-growth copolymerization of functionalized oligopropylene.

In this study, iPP–TVD prepared by controlled thermal degradation of iPP was converted to  $\alpha,\omega$ -hydroxyoligopropylene (iPP–OH) by hydroxylation, which was followed by esterification to introduce bromine groups, yielding iPP–Br. iPP–Br was used as a macroinitiator for ATRP of St and (meth) acrylic monomers. Synthesis of multiblock copolymers was studied by carrying out ATRC to form triblock copolymers containing iPP as the middle block.

## 2. Experimental section

### 2.1. Materials

Commercially available PP (Japan Polypropylene Corporation, NOVATEC EA9,  $M_n$ : 160 000 g/mol) was used for iPP. PMMA ( $M_n$ : 80 000 g/mol) was purchased from Aldrich. Borane–THF complex in THF (1 M), toluene, St and copper were purchased from Kanto Chemical. BMPB was purchased from Tokyo Chemical Industry. MMA, ethyl acrylate (EA), *n*-butyl acrylate (*n*BA), *t*-butyl acrylate (*t*BA), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) and CuBr were purchased from Wako Pure Chemical Industries. All other reagents were purchased from commercial sources. MMA, St, EA, *n*BA and *t*BA were distilled under vacuum prior to use.

### 2.2. Preparation of iPP–OH and iPP–Br

iPP–TVDs were prepared by controlled thermal degradation of commercially available iPP [25]. Molecular characteristics of iPP–TVDs are shown in Table 1. The average number of terminal vinylidene double bonds per molecule ( $f_{TVD}$ ): 1.8 was statistically estimated as telechelics:monocheleics:paraffin = 80:19:1 mol% [25]. iPP–OHs were prepared by hydroboration and subsequent oxidation [29].

**Table 1**  
Molecular characteristics of iPP–TVDs

	$M_n$ (g/mol)	$M_w/M_n$	$f_{TVD}$	$T_m$ (°C)	Tacticity		
					<i>mm</i>	<i>mr</i>	<i>rr</i>
iPP–TVD	1000	1.01	1.80	85	85	11	4
iPP–H–TVD	14 000	1.74	1.71	159	95	3	2

Low molecular weight iPP–Br ( $M_n$ : 1000 g/mol) was prepared by esterification of iPP–OH with BMPB, and was used for kinetic experiment. iPP–OH (10 g, 10 mmol) and triethylamine (4.05 mL, 40 mmol) were dissolved in chloroform (50 mL). A solution of BMPB (4.7 mL, 40 mmol) in chloroform (10 mL) was added dropwise, and this reaction mixture was stirred at room temperature for 24 h. The mixture was then poured into methanol, and the iPP–Br was filtered and dried under reduced pressure.

High molecular weight iPP–H–Br ( $M_n$ : 14 000 g/mol) was prepared as follows, and was used only as compatibilizer for polymer blend. iPP–H–OH (21 g, 1.5 mmol) and triethylamine (2.1 mL, 15 mmol) were dissolved in toluene (100 mL) at 80 °C. A solution of BMPB (1.77 mL, 15 mmol) in toluene was added dropwise, and this reaction mixture was stirred at 80 °C for 24 h. The mixture was then poured into methanol, and the iPP–H–Br was filtered and dried under reduced pressure.

### 2.3. ATRP from iPP–Br macroinitiator

In a typical procedure, iPP–Br (0.0635 g, 0.05 mmol) and CuBr (0.0143 g, 0.10 mmol) were added to a Schlenk tube equipped with a stir bar. After the tube was sealed with a rubber septum, it was degassed and backfilled with nitrogen three times and then left under nitrogen. MMA (1.06 mL, 10 mmol), *o*-xylene (5 mL), PMDETA (20.9  $\mu$ L, 0.1 mmol) and anisole (0.1 mL, as GC standard) were then added, and the mixture was stirred at 100 °C. Samples were periodically taken via a syringe to follow the polymerization kinetics by GC and GPC. After a certain time, the polymerization mixture was poured into methanol, and the PMMA–iPP–PMMA triblock copolymer was filtered and dried under reduced pressure.

### 2.4. Preparation of PMMA–iPP–PMMA for polymer blend

iPP–H–Br (0.7 g, 0.05 mmol) and CuBr (0.0143 g, 0.1 mmol) were added to a Schlenk tube equipped with a stir bar. After the tube was sealed with a rubber septum, it was degassed and backfilled with nitrogen three times and then left under nitrogen. MMA (2.13 mL, 20 mmol), *o*-xylene (5 mL), and PMDETA (20.9  $\mu$ L, 0.1 mmol) were then added, and the mixture was stirred at 120 °C for 5 h. After the reaction, the polymerization mixture was poured into methanol, and the PMMA–iPP–PMMA triblock copolymer was filtered and dried under reduced pressure. Monomer conversion was 41%, and molar composition of PMMA–iPP–PMMA triblock copolymer determined by  $^1\text{H}$  NMR spectrum was iPP:PMMA = 1:0.9, and weight composition is iPP:PMMA = 1:2.5.

### 2.5. Preparation of PS–iPP–PS for ATRC

iPP–Br (1.275 g, 1 mmol) and CuBr (0.286 g, 2 mmol) were added to a reaction flask equipped with a stir bar and three-way stopcock. After the flask was degassed and backfilled with nitrogen three times and then left under nitrogen, it was sealed with rubber septum. St (23 mL, 200 mmol), *o*-xylene (60 mL), and PMDETA (418  $\mu$ L, 2 mmol) were then added, and the mixture was stirred at 80 °C for 3 h. After the reaction, the polymerization mixture was poured into methanol, and the PS–iPP–PS triblock copolymer was filtered and dried under reduced pressure. Monomer conversion was 35%,  $M_n$  and  $M_w/M_n$  were 8900 g/mol and 1.3.

### 2.6. Preparation of PMMA–iPP–PMMA for ATRC

iPP–Br (2.54 g, 2 mmol) and CuBr (0.5738 g, 4 mmol) were added to a reaction flask equipped with a stir bar and three-way stopcock. After the flask was degassed and backfilled with nitrogen three times and then left under nitrogen, it was sealed with rubber septum. MMA (42.6 mL, 400 mmol), *o*-xylene (150 mL), and

PMDETA (836  $\mu\text{L}$ , 2 mmol) were then added, and the mixture was stirred at 80 °C for 3 h. After the reaction, the polymerization mixture was poured into methanol, and the PS-*i*PP-PS triblock copolymer was filtered and dried under reduced pressure. Monomer conversion was 55%,  $M_n$  and  $M_w/M_n$  were 13 000 g/mol and 1.4.

### 2.7. ATRC of PS-*i*PP-PS triblock copolymer

In a typical procedure, PS-*i*PP-PS triblock copolymer ( $M_n$ : 8700 g/mol,  $M_w/M_n$ : 1.3, 0.87 g, 0.10 mmol), CuBr (0.0144 g, 0.10 mmol) and Cu (0.1272 g, 2.0 mmol) were added to a Schlenk tube equipped with a stir bar. After the tube was sealed with a rubber septum, it was degassed and backfilled with nitrogen three times and then left under nitrogen. Subsequently, *o*-xylene (1 mL) and PMDETA (460  $\mu\text{L}$ , 2.2 mmol) were added, and the mixture was stirred at 80 °C. Samples were taken via syringe periodically to follow the molecular weight characteristics of the polymerization by GPC. After a certain time, the coupling mixture was poured into methanol, and the *i*PP-PS multiblock copolymer was filtered and dried under reduced pressure.

### 2.8. ATRC of PMMA-*i*PP-PMMA triblock copolymer with styrene

In a typical procedure, PMMA-*i*PP-PMMA triblock copolymer ( $M_n$ : 13 000 g/mol,  $M_w/M_n$ : 1.4, 1.3 g, 0.10 mmol), CuBr (0.0287 g, 0.20 mmol) and Cu (0.2546 g, 4.0 mmol) were added to a Schlenk tube equipped with stir bar. After the tube was sealed with a rubber septum, it was degassed and backfilled with nitrogen three times and then left under nitrogen. Next, *o*-xylene (1 mL), St (1.15 mL) and PMDETA (882  $\mu\text{L}$ , 4.2 mmol) were added, and the mixture was stirred at 80 °C. The polymerization was monitored by GPC as mentioned above. After a certain time, the coupling mixture was poured into methanol, and the *i*PP-PS multiblock copolymer was filtered and dried under reduced pressure.

### 2.9. NMR

A JEOL JNM-GX400 spectrometer was used for  $^1\text{H}$  NMR (399.65 MHz) measurements. The samples were dissolved in  $\text{CDCl}_3$  with tetramethylsilane and spectra were measured at 23 °C.

### 2.10. GPC

The number average molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) were determined by GPC (TOSOH HLC-8220GPC) with a TOSOH TSKgel GMH<sub>XL</sub>-G3000H<sub>XL</sub>-G2000H<sub>XL</sub> column system. The molecular weight was calibrated using polystyrene standards. Tetrahydrofuran was used as an eluent, and the measurement was performed at 40 °C.

### 2.11. GC

Monomer conversion was determined on a Hewlett Packard G1530A gas chromatograph equipped with a flame ionization detector using a capillary column (HP-1, 5 m  $\times$  0.53 mm  $\times$  2.65  $\mu\text{m}$  film thickness, Hewlett Packard Development Company, L.P.). Anisole, which was added initially to the mixture, was used as an internal standard for this measurement.

### 2.12. DSC

The melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ) were determined by differential scanning calorimetry (Seiko Instruments, Inc. DSC6100). Measurements were performed under  $\text{N}_2$  and in the second heating cycle, with a sample weight of ca. 5 mg at a heating rate of 10 °C  $\text{min}^{-1}$ .

### 2.13. Polymer blending and SEM micrograph

Triblock copolymer as compatibilizer for polymer blend was prepared by ATRP of MMA using high molecular weight oligopropylene ( $M_n = 14\,000$ ,  $M_w/M_n = 1.7$ ) as macroinitiator. The molar composition of triblock copolymer determined by  $^1\text{H}$  NMR spectrum was *i*PP:PMMA = 1:0.9. *i*PP ( $M_n$ : 160 000 g/mol, 2.5 g) and PMMA ( $M_n$ : 80 000 g/mol, 2.5 g) with and without PMMA-*i*PP-PMMA triblock copolymer (0.5 g) were dissolved in hot xylene (200 mL). The solution was poured into methanol (2000 mL), and precipitated blend powder was collected by filtration. The blend pellets were prepared by melt mixing blend powder by laboratory mixing extruder (Atlas Corp.) at 200 °C. The blend sheets were obtained by hot pressed blend pellet at 200 °C. The blend sheets were fractured in liquid nitrogen and the fractured surfaces were etched with chloroform in order to remove all soluble PMMA. After drying overnight under vacuum, the samples were sputter coated with a thin layer of Pt-Pd to improve the electrical conductivity. Morphological investigations were performed with a scanning electron microscope (SEM) (Hitachi S-2000N) at an acceleration voltage of 15 kV.

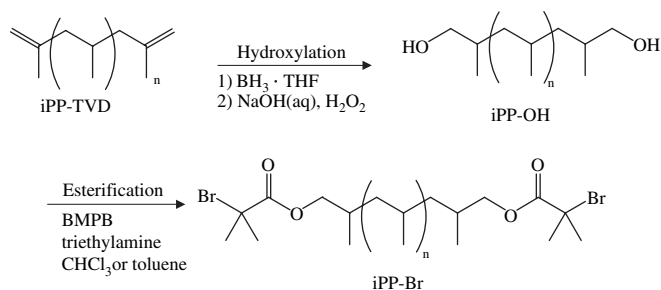
## 3. Results and discussion

### 3.1. Synthesis of bifunctional *i*PP macroinitiator

The synthetic route to the bifunctional *i*PP macroinitiator is shown in Scheme 1. Fig. 1 shows  $^1\text{H}$  NMR spectra of *i*PP-TVD, *i*PP-OH, and *i*PP-Br. The peaks at 0.85, 1.22, and 1.57 ppm in all spectra corresponded to methyl, methylene, and methine protons on the *i*PP main chain. Terminal olefin protons (a) of *i*PP-TVD were detected at 4.65 and 4.72 ppm. The signals at 2.07 and 1.70 ppm were from methylene (b) and methyl (c) protons, respectively, of the terminal olefins. For *i*PP-OH, the multiple peaks at 3.5 ppm were assigned to methylene (d) protons at the termini. For *i*PP-Br, the multiple peaks at 4.0 ppm and the singlet peak at 1.94 ppm corresponded to terminal methylene (f) and methyl (g) protons, respectively. These structural analyses showed that hydroxylation and subsequent esterification of terminal vinylidene double bonds proceeded almost quantitatively. The utility of *i*PP-Br as a macroinitiator for ATRP of vinyl monomers was therefore confirmed.

### 3.2. Atom transfer radical polymerization using *i*PP-Br as macroinitiator

ATRP from *i*PP-Br as macroinitiator was performed by a general method using *o*-xylene, PMDETA, CuBr, and selected vinyl monomers (Scheme 2). Fig. 2 shows plots of monomer conversion and  $\ln[M_0]/[M]$  versus time at different temperatures. The polymerization rate increased with increasing temperature, reaching a high degree of conversion in a short time. Monomer conversion showed an almost linear relationship versus time at early stage, indicating



Scheme 1. Synthesis of bifunctional *i*PP macroinitiator.

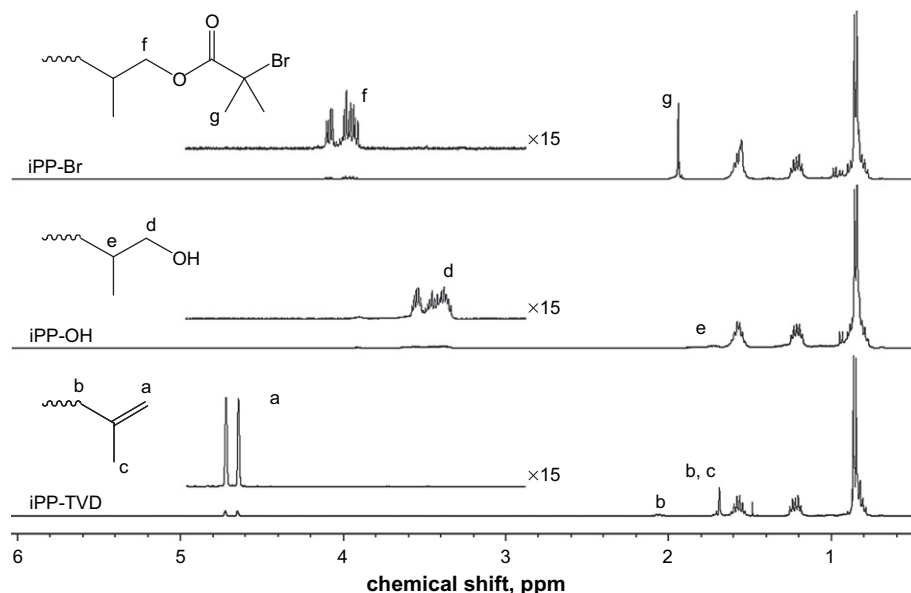


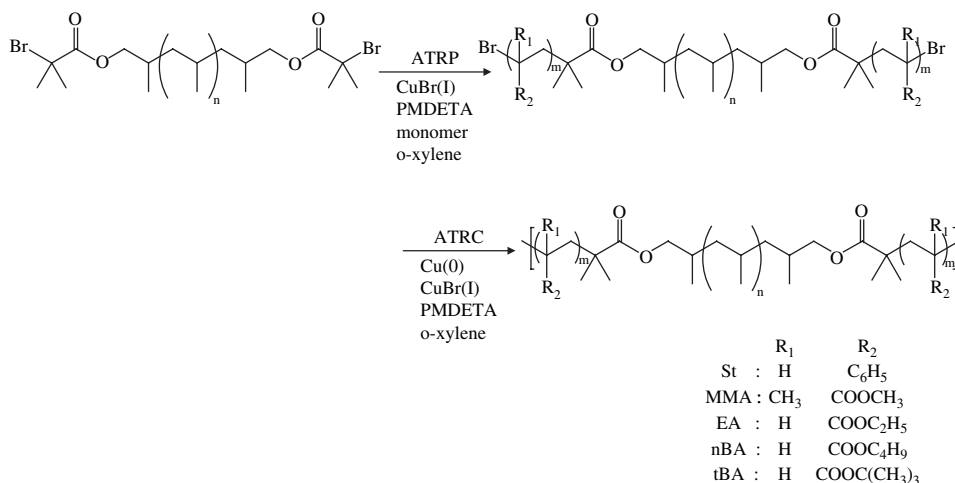
Fig. 1.  $^1\text{H}$  NMR spectra of iPP-TVD, iPP-OH and iPP-Br.

constant radical concentration. However, monomer conversion decreased drastically at later stage. This might be an influence of the termination and/or chain transfer reaction. Fig. 3 shows monomer conversion versus  $M_n$  and  $M_w/M_n$ . The straight line in the figure is the theoretical molecular weight ( $M_{n,\text{th}}$ ) estimated from the feed.  $M_n$  increased linearly with monomer conversion, but  $M_w/M_n$  was constant regardless of the monomer conversion. This tendency is a typical feature of living polymerizations. However, in the plots, the values of  $M_n$  were higher than  $M_{n,\text{th}}$  due to the functionality ( $f_{\text{TVD}} = 1.8$ ) of iPP-TVD and correction with standard polystyrene. GPC curves of the products at each value of monomer conversion are shown in Fig. 4. The main peak shifted to higher molecular weight with increasing monomer conversion. The peak detected at 0% conversion corresponded to the macroinitiator. Macroinitiator was efficiently consumed at low monomer conversion (20.9%). However, macroinitiator wasn't completely consumed, and it has decreased with increase of monomer conversion. Therefore, polydispersity might have broadened. In addition, a small amount of macroinitiator remained even at later stage of the polymerization (77.5%). This was probably a small

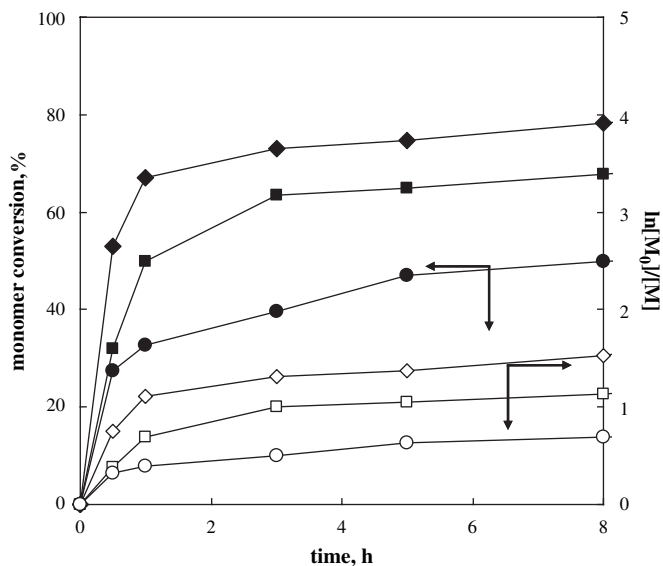
amount of paraffin included in iPP-TVD, since preparation of iPP-Br was confirmed by  $^1\text{H}$  NMR spectra.

iPP-PMMA triblock copolymer for compatibilizer was prepared by ATRP using oligopropylene ( $M_n = 14000$ ,  $M_w/M_n = 1.7$ ) as macroinitiator, and examined as compatibilizer for improving the interfacial interactions between blended polymers. Fig. 5 shows the effect of iPP-PMMA triblock copolymer as compatibilizer on the resultant phase domains. The non-compatibilized iPP/PMMA blend (Fig. 5a) shows large dispersed holes which are the PMMA phase being etched out by chloroform solvent. The PMMA phase domains become significantly smaller at blend containing 10 wt% of iPP-PMMA triblock copolymer (Fig. 5b). These morphologies clearly demonstrate the improvement of miscibility of iPP/PMMA blends due to the presence of iPP-PMMA triblock copolymer.

Table 2 summarizes the molecular weight characteristics of triblock copolymers obtained by ATRP from the iPP-Br macroinitiator ( $M_n = 1000$ ) with certain vinyl monomers. In all cases, the macroinitiator was nearly used up, and the resulting triblock copolymer was of the expected  $M_n$ . ATRP of St resulted in a triblock copolymer possessing low  $M_n$  and narrow  $M_w/M_n$ .  $M_n$  and  $M_w/M_n$



Scheme 2. ATRP of vinyl monomers from iPP-Br macroinitiator and ATRC.

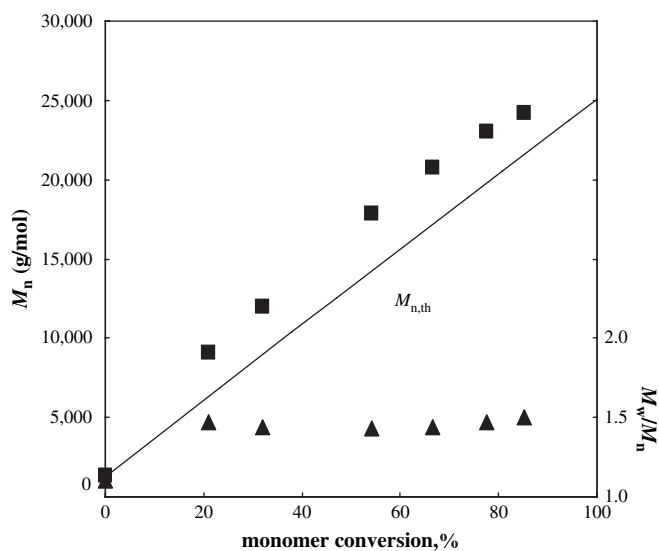


**Fig. 2.** Kinetic plots for ATRP of MMA from iPP-Br macroinitiator at 80 °C (○ and ●), 100 °C (□ and ■), and 120 °C (◆ and ◇). Polymerization conditions: [iPP-Br]<sub>0</sub> = 0.05 mmol; [CuBr]<sub>0</sub> = 0.10 mmol; [PMDETA]<sub>0</sub> = 0.20 mmol; [MMA]<sub>0</sub> = 10.0 mmol; *o*-xylene = 5 mL.

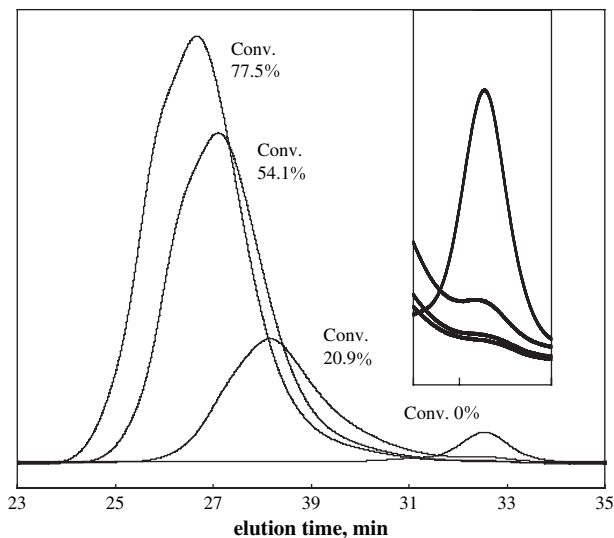
for acrylic monomers, especially *n*BMA, were higher and broader than for St, because the propagation rates of these monomers were higher than for St. It was necessary to tune the monomer concentration, ligand species, polymerization temperature and so on to obtain good control of  $M_n$  and  $M_w/M_n$  when polymerizing monomers with high propagation rates. Precise control of ATRP for these vinyl monomers is now under investigation.

### 3.3. ATRC of telechelic triblock copolymer obtained by ATRP from iPP macroinitiator

Polymers possessing halogen end groups obtained by ATRP are frequently used in copolymerization, and these halogens are also commonly converted to other functional groups. In particular, ATRC that promotes coupling by raising the radical concentration in the



**Fig. 3.** Dependence of  $M_n$  (■) and  $M_w/M_n$  (▲) on monomer conversion during ATRP of MMA. Polymerization conditions: [iPP-Br]<sub>0</sub> = 0.05 mmol; [CuBr]<sub>0</sub> = 0.10 mmol; [PMDETA]<sub>0</sub> = 0.20 mmol; [MMA]<sub>0</sub> = 10.0 mmol; *o*-xylene = 5 mL; temp. = 100 °C.



**Fig. 4.** Evolution of GPC chromatograms with monomer conversion. Polymerization conditions: [iPP-Br]<sub>0</sub> = 0.05 mmol; [CuBr]<sub>0</sub> = 0.10 mmol; [PMDETA]<sub>0</sub> = 0.20 mmol; [MMA]<sub>0</sub> = 10.0 mmol; *o*-xylene = 5 mL; temp. = 100 °C.

reaction by use of a Cu complex is often used for the synthesis of multiblock copolymers by starting with a polymer that has halogens at both ends. We report here ATRC using a Cu/PMDETA system for PS-iPP-PS and a Cu/PMDETA/St system [19] for PMMA-iPP-PMMA (Scheme 2).

Fig. 6 shows the change in GPC curves with time of an ATRC reaction involving PS-iPP-PS ( $M_n$ : 8900 g/mol and  $M_w/M_n$ : 1.3). The PS-iPP-PS peak decreased with reaction time, and that of the coupling products increased. Some dimer formation occurred in the first 0.5 h, and  $M_n$  and  $M_w/M_n$  hardly changed. After 1.0 h, the PS-iPP-PS peak had decreased significantly, and peaks appeared corresponding to molecules larger than the dimer. The PS-iPP-PS peak had almost disappeared at 3.5 h. In addition,  $M_w/M_n$  increased to 4.1,  $M_n$  increased to 25 000 g/mol, and the maximum molecular weight was over  $10^6$  g/mol. The chemical structure of PS-iPP-PS obtained by ATRP and the corresponding ATRC product were determined by  $^1\text{H}$  NMR spectra. The skeletal protons of iPP and PS were detected in both spectra. The broad peak at 3.2–3.66 ppm was assigned to methylene protons next to the ester groups. Although terminal methine protons were detected at 4.3–4.6 ppm before ATRC, this peak disappeared upon removal of bromine atoms after ATRC. These molecular weight characteristics and structural analyses confirmed the rapid progression of ATRC and the formation of an iPP-PS multiblock copolymer.

The extent of the ATRC reaction ( $q$ ) [23] was estimated by

$$q = 1 - M_{n0}/M_n \quad (1)$$

where  $M_{n0}$  and  $M_n$  are number average molecular weights of initial starting material and product, respectively. The value of  $q$  indicated the progress of the coupling reaction, with  $q = 1$  implying that the coupling reaction proceeded quantitatively. Fig. 7 shows plot of coupling time versus  $q$ . ATRC was performed at Cu/PS-iPP-PS molar ratios of 10, 20, 40, and 100. When this molar ratio was 10,  $q$  was 0.5, rather low. In contrast,  $q$  reached its maximum value of 0.64 when this ratio was over 20, and when the ratio exceeded 40, the coupling reaction was finished in 0.5 h.

These facts indicated that the coupling reaction could be carried out in a short time by selecting the appropriate conditions. The polydispersity of the multiblock copolymer grew progressively broader as the coupling reaction proceeded. This was clear from the

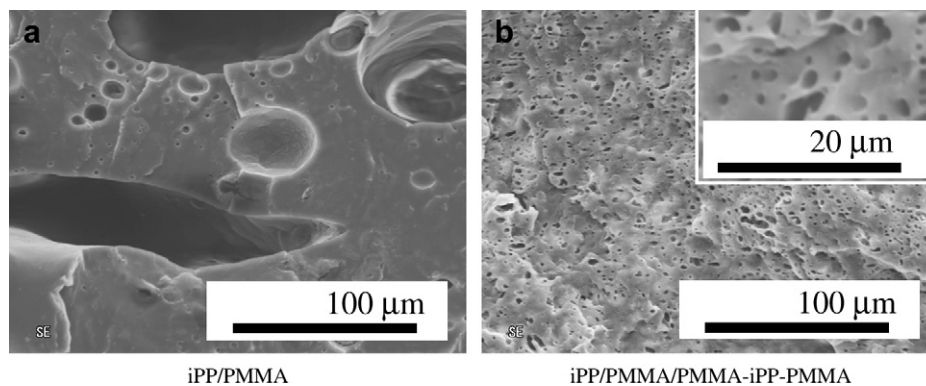


Fig. 5. SEM micrographs of the blends: (a) iPP/PMMA = 50/50 wt%; (b) iPP/PMMA/PMMA-iPP-PMMA = 45/45/10 wt%.

Table 2

Molecular weight characteristics of iPP triblock copolymers obtained by ATRP from an iPP-Br macroinitiator using various vinyl monomers

Monomer	$M_n$ (g/mol)	$M_w/M_n$
St	8600	1.2
MMA	11 000	1.6
EA	10 000	1.6
nBA	10 000	2.3
tBA	12 000	1.6

Polymerization condition: [iPP-Br]<sub>0</sub> ( $M_n$ : 1000 g/mol) = 0.05 mmol, [CuBr]<sub>0</sub> = 0.10 mmol, [PMDETA]<sub>0</sub> = 0.10 mmol, [M]<sub>0</sub> = 10.0 mmol, *o*-xylene = 3 mL, time = 3 h, temp. = 120 °C.

plot of  $q$  versus  $M_w/M_n$  (Fig. 8). Although the value of  $M_w/M_n$  was 1.3 before the coupling reaction, it increased linearly to 2.0 when  $q < 0.4$ . For  $q > 0.4$ ,  $M_w/M_n$  rapidly increased to 4.1 at  $q = 0.65$ . If there were no reactions other than the coupling reaction, the theoretical polydispersity could be estimated [23] by the straight line in Fig. 8:

$$M_w/M_{n,th} = M_w/M_{n0} + q[2 - M_w/M_{n0}] \quad (2)$$

where  $M_w/M_{n0}$  is the polydispersity before coupling. The remaining PS-iPP-PS and the observed value greatly exceeded  $M_w/M_{n,th}$ , possibly due to side reactions (e.g., disproportionation) as reported by Fukuda et al. [23]. This will be improved by selecting ligand [23].

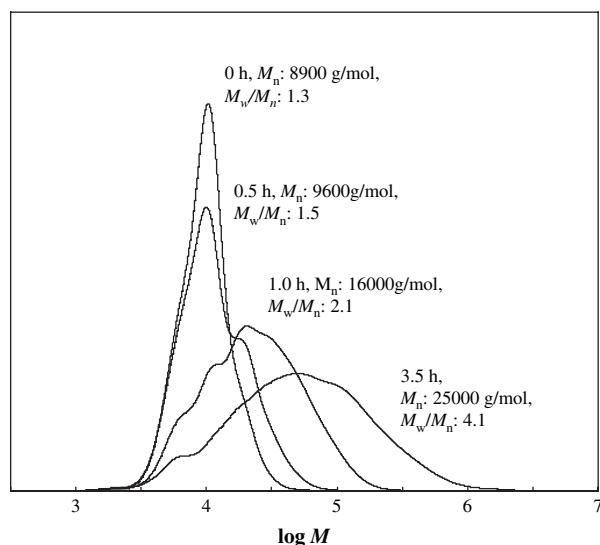


Fig. 6. Evolution of GPC chromatograms with molecular weight characteristics of ATRC products. Coupling conditions: [PS-iPP-PS]<sub>0</sub> = 0.1 mmol; [Cu]<sub>0</sub> = 2.0 mmol; [CuBr]<sub>0</sub> = 0.2 mmol; [PMDETA]<sub>0</sub> = 2.2 mmol; *o*-xylene = 1 mL; temp. = 80 °C.

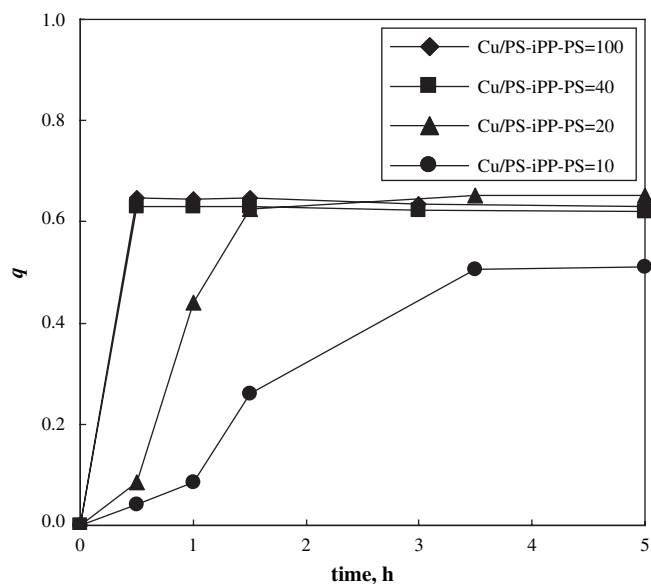


Fig. 7. Plot of time versus extent of reaction ( $q$ ) for ATRC with different molar ratios of Cu for PS-iPP-PS at 80 °C.

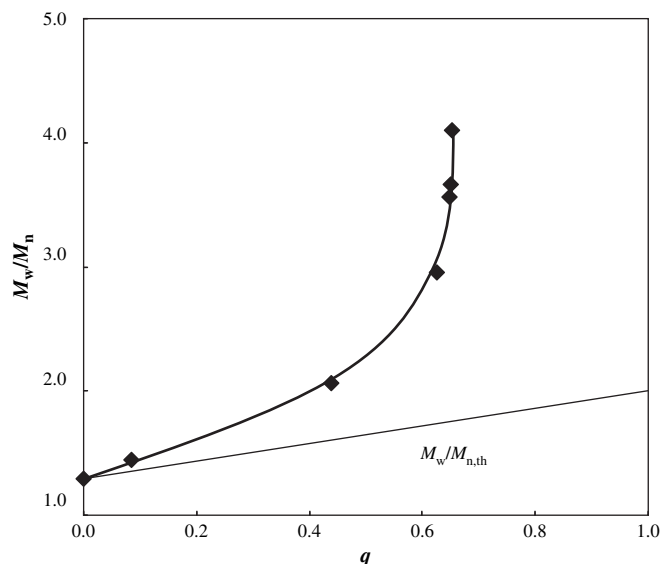
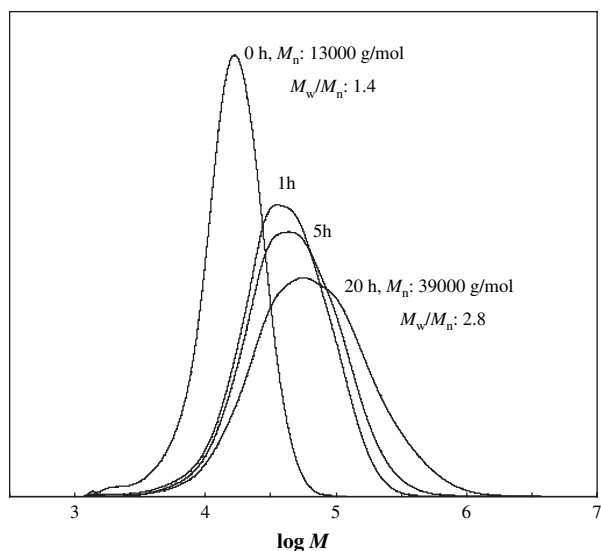


Fig. 8. Plot of  $M_w/M_n$  versus extent of reaction ( $q$ ) for bifunctional systems.



**Fig. 9.** Evolution of GPC chromatograms with molecular weight characteristics of products of ATRC with styrene. Coupling conditions:  $[PMMA\text{-}iPP\text{-}PMMA]_0 = 0.1$  mmol;  $[Cu]_0 = 4.0$  mmol;  $[CuBr]_0 = 0.2$  mmol;  $[PMDETA]_0 = 4.2$  mmol;  $[St]_0 = 10$  mmol; *o*-xylene = 1 mL; temp. = 80 °C.

The thermal properties of the *iPP*–*PS* multiblock copolymers were evaluated by DSC. For *iPP*–Br, the endothermic peak at 85 °C corresponded to  $T_m$  of isotactic propylene sequences. For *PS*–*iPP*–*PS*, however, this endothermic peak disappeared, and a  $T_g$  was observed at 50 °C. In the DSC curve of *iPP*–*PS* multiblock copolymer,  $T_g$  increased significantly to 60 °C. It was presumed that the oligopropylene  $T_m$  disappeared and the *PS*  $T_g$  was detected in triblock and multiblock copolymers, because the crystallization of oligopropylene was inhibited by the *PS* chains. In addition, the multiblock copolymer had a higher  $T_g$  than did the triblock copolymer, since the *PS* chain was extended by coupling.

ATRC is dependent on the type of termination in the radical polymerization, and recombination and disproportionation are advantageous for *St* and *MMA*, respectively. In fact, the coupling reaction of *PMMA*–*iPP*–*PMMA* did not proceed under the same conditions as for *PS*–*iPP*–*PS*. The GPC curves shown in Fig. 9 were obtained when ATRC of *PMMA*–*iPP*–*PMMA* was performed with *St* [19]. While  $M_n$  and  $M_w/M_n$  before ATRC were 13 000 g/mol and 1.4, respectively, they increased to  $M_n$ : 39 000 g/mol and  $M_w/M_n = 2.8$  after 20 h. This was thought to be due to the increase in molecular weight by coupling between terminal *St* radicals resulted from the reaction of *St* with terminal *MMA* radicals formed by abstraction of bromine atoms. Radical polymerization with *St* was more favorable than the coupling reaction because of the relatively high initial concentration of *St*. After the *St* concentration was sufficiently reduced, it appeared that coupling did proceed, whereas the polymerization of *St* was nearly halted. If nothing other than polymerization of *St* had occurred,  $M_w/M_n$  would have been narrow, but  $M_w/M_n$  exceeded 2 because of the coupling reaction. The synthesis of a multiblock copolymer by ATRC of *St* with *PMMA*–

*iPP*–*PMMA* triblock copolymer demonstrated the feasibility of extending this method to other (meth) acrylic polymers.

#### 4. Conclusions

A hydroxylation and esterification sequence effected the conversion of terminal vinylidene double bonds to bromoisobutyryloxy groups to yield a telechelic oligopropylene macroinitiator. ATRP using  $\alpha,\omega$ -dibromoisobutyrate oligopropylene formed the corresponding triblock copolymers from *St* and (meth) acrylic monomers. *PMMA*–*iPP*–*PMMA* triblock copolymer was effective as compatibilizer for *iPP*/*PMMA* blend. An *iPP*–*PS* multiblock copolymer was prepared by ATRC of *PS*–*iPP*–*PS* triblock copolymer obtained by ATRP, and an *iPP*–*PMMA*–*PS* multiblock copolymer was prepared by ATRC of a small amount of *St* with *PMMA*–*iPP*–*PMMA* obtained by ATRP. These multiblock copolymers are likely to possess uniquely useful physical properties, and may find application as compatibilizers. The preparation of *iPP*–*PS* and *iPP*–*PMMA*–*PS* multiblock copolymers is an important step in the development of new polymer materials.

#### References

- [1] Ittel SD, Johnson LK. *Chem Rev* 2000;100:1169–203.
- [2] Boffa LS, Novak BM. *Chem Rev* 2000;100:1479–94.
- [3] Imanishi Y, Naga N. *Prog Polym Sci* 2001;26:1147–98.
- [4] Chung TC. *Prog Polym Sci* 2002;27:39–85.
- [5] Gibson VC, Spitzmesser SK. *Chem Rev* 2003;103:283–315.
- [6] Lopez RG, Franck D, Boisson C. *Prog Polym Sci* 2007;32:419–54.
- [7] Kaneyoshi H, Inoue Y, Matyjaszewski K. *Macromolecules* 2005;38:5425–35.
- [8] Matsugi T, Kojoh S, Kawahara N, Matsuo S, Kaneko H, Kashiwa N. *J Polym Sci Part A Polym Chem* 2003;41:3965–73.
- [9] Inoue Y, Matsugi T, Kashiwa N, Matyjaszewski K. *Macromolecules* 2004;27:3651–8.
- [10] Desai SM, Solanky SS, Mandale AB, Rathore K, Singh RP. *Polymer* 2003;44:7645–9.
- [11] Yamamoto K, Tanaka H, Sakaguchi M, Shimada S. *Polymer* 2003;44:7661–9.
- [12] Yang Q, Tian J, Hu M, Xu Z. *Langmuir* 2007;23:6684–90.
- [13] Kaneko H, Matsugi T, Kawahara N, Matsuo S, Kojoh S, Kashiwa N. *Kinet Catal* 2006;47:227–33.
- [14] Matyjaszewski K, Nakagawa Y, Gaynor SG. *Macromol Rapid Commun* 1997;18:1057–66.
- [15] Coessens V, Matyjaszewski K. *J Macromol Sci Pure Appl Chem* 1999;36:811–26.
- [16] Coessens V, Nakagawa Y, Matyjaszewski K. *Polym Bull* 1998;40:135–42.
- [17] Coessens V, Matyjaszewski K. *Macromol Rapid Commun* 1999;20:127–34.
- [18] Yurteri S, Cianga I, Yagci Y. *Macromol Chem Phys* 2003;204:1771–83.
- [19] Sarbu T, Lin K, Spanswick J, Gil RR, Siegwart DJ, Matyjaszewski K. *Macromolecules* 2004;37:9694–700.
- [20] Otazaghine B, David G, Boutevin B, Robin JJ, Matyjaszewski K. *Macromol Chem Phys* 2004;205:154–64.
- [21] Otazaghine B, Boutevin B. *Macromol Chem Phys* 2004;205:2002–11.
- [22] Qin Y, Cui C, Jäkle F. *Macromolecules* 2007;40:1413–20.
- [23] Yoshikawa C, Goto A, Fukuda T. *e-Polymers* 2002. No. 013.
- [24] Nagelsdieck R, Keul H, Höcker H. *e-Polymers* 2005. No. 049.
- [25] Sawaguchi T, Ikemura T, Seno M. *Macromolecules* 1995;28:7973–8.
- [26] Sawaguchi T, Seno M. *Polym J* 1996;28:817–20.
- [27] Sasaki D, Okada Y, Suzuki Y, Hagiwara T, Yano S, Sawaguchi T. *Polym Degrad Stab* 2007;92:271–9.
- [28] Sasaki D, Suzuki Y, Hagiwara T, Yano S, Sawaguchi T. *J Anal Appl Pyrolysis* 2007;80:312–8.
- [29] Hagiwara T, Saitoh H, Tobe A, Sasaki D, Yano S, Sawaguchi T. *Macromolecules* 2005;38:10373–8.
- [30] Hagiwara T, Matsumaru S, Okada Y, Sasaki D, Yano S, Sawaguchi T. *J Polym Sci Part A Polym Chem* 2006;44:3406–9.