

Polypropylene-*block*-Poly(methyl methacrylate) and -*block*-Poly(*N*-isopropylacrylamide) Block Copolymers Prepared by Controlled Radical Polymerization with Polypropylene Macroinitiator¹

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Abstract—Polypropylene-*block*-poly(methyl methacrylate) (PP-*b*-PMMA) and Polypropylene-*block*-poly(*N*-isopropylacrylamide) (PP-*b*-PNIPAAm) block copolymers were successfully synthesized by radical polymerizations of MMA or NIPAAm with polypropylene (PP) macroinitiators. Polypropylene macroinitiators were prepared by a series of end functionalization of pyrolysis PP via hydroalumination, oxidation and esterification reactions. The PP macroinitiators thus obtained could initiate radical polymerizations of MMA or NIPAAm by using transition metal catalyst systems, and ¹H NMR analysis and gel permeation chromatography measurement confirmed the formation of PP-*b*-PMMA and PP-*b*-PNIPAAm block copolymers. In addition, the length of the incorporated PMMA or PNIPAAm segments in these block copolymers was controllable by the feed ratio between the monomer and the PP macroinitiator, and their molecular weights were estimated to be 35 700 and 68 700 (PMMA) and 1760 and 13 300 (PNIPAAm), respectively. Transmission electron microscopy of the polymers obtained by NIPAAm polymerization revealed specific morphological features that reflected the difference of PNIPAAm segment length.

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INTRODUCTION

Recent advances in polyolefin (PO) chemistry have led to the creation of hybrid polymers linking between POs and the other POs or polar polymer segments by combination between functionalized POs and several polymerization processes such as radical, anionic, cationic, coordination polymerizations. Especially, combinations of POs with polar polymers by chemical linkage have been attracting much attention as hybrid polymers between immiscible segments such as crystalline/amorphous or polar/nonpolar segments. They are expected to bring about some improved and unique properties in the PO industry, broadening the applications of POs to highly profitable fields. As one of these new hybrid polymers, A–B type diblock copolymers, possessing a chemical linkage between PO and polar polymer segments, have potential to improve low interfacial interactions between PO and polar materials. So far, only a few synthetic approaches for them have been reported, such as a sequential living polymerization and a postpolymerization process. In former approach, several kinds of block copolymers were obtained by sequential living polymerization of α -olefin and polar monomers [1–3]. However, the types of monomers and the polymerization conditions are gen-

erally restricted because this method depends on a coordination polymerization with a transition metal catalyst. Then, to diversify structures and compositions of segments in block copolymers, a postpolymerization process by using PO macroinitiators, which are obtained by transforming a variety of functionalized POs to radical or anionic polymerization initiators, was developed as an alternative approach. To obtain the functionalized POs, chain transfer reaction and olefin copolymerization with functional monomers and terminally unsaturated PO have been reported as useful tools. For example, Chung et al. reported the syntheses of block copolymers by using borane- and *p*-methylstyrene(*p*MS)-terminated PO, which were obtained by chain transfer reaction or copolymerization, in combination with radical or anionic polymerization of methyl methacrylate (MMA) or styrene [4]. In our previous papers, we reported on functionalized polyethylenes (PEs) with reactive groups such as hydroxyl or amino groups under precise control of the positions of the functional groups [5, 6]. In particular, this methodology could selectively prepare the terminally functionalized PE.

The recent development of a controlled radical polymerization has extended the possibility of synthesizing a variety of styrenic and/or (meth)acrylic block copolymers [7–9]. The combination of this technique with the functionalized POs was realized to prepare the well-

¹ The text was submitted by the authors in English.

Table 1. Preparation of PP macroinitiators

Sample	PP- <i>t</i> -Vd			PP- <i>t</i> -Br				
	M_n^a	M_w/M_n^a	Content of Vd ^b , mol %	M_n^a	M_w/M_n^a	content of Br ^b , mol %	functionality ^c (unit-Br/chain)	conversion of Vd to Br ^d , %
PP- <i>t</i> -Br1	5980	1.79	1.1	5270	1.47	0.80	0.98	73
PP- <i>t</i> -Br2	13000	2.09	0.38	13900	2.05	0.14	0.46	37
PP- <i>t</i> -Br3	17400	2.11	0.24	17800	2.08	0.11	0.46	46

^a Determined by GPC calibrated with PP.^b Determined by ¹H NMR.^c Calculated between the content of Br and M_n .^d Calculated from the content of Vd and Br.**Table 2.** Results of MMA polymerization by using PP macroinitiator

Run	PP Macroinitiator		[PP- <i>t</i> -Br]/[CuBr]/[PMDETA]/[MMA] molar ratio	$T_{\text{polymn.}}^{\circ}\text{C}$	$t_{\text{polymn.}}$, h	Yield, g	MMA Conversion ^a , %	
		g	mM					
1	PP- <i>t</i> -Br1	0.47	15	1/1.2/2.4/250	90	2.5	1.01	61
2	PP- <i>t</i> -Br3	35.9	8.0	1/3/6/1000	120	7.0	88.5	57
3	PP- <i>t</i> -Br3	71.8	6.6	1/1.5/3/500	120	2.0	132.8	66

^a Determined by GC analysis.

defined PO/polar polymer block copolymers. Typically, our terminally functionalized PE could be converted to a PE macroinitiator for controlled radical polymerization to give polyethylene-*block*-poly(methyl methacrylate) (PE-*b*-PMMA) block copolymer [10].

In this article, we synthesized PP macroinitiators by functionalization of the terminal vinylidene group in pyrolysis PP to produce structurally well-defined polypropylene-*block*-poly(methyl methacrylate) (PP-*b*-PMMA) and polypropylene-*block*-poly(*N*-isopropylacrylamide) (PP-*b*-PNIPAAm) block copolymers by controlled radical polymerization. In addition, their microphase structures were investigated by transmission electron microscopy (TEM) analysis.

EXPERIMENTAL

General procedures and materials. All manipulations of air- and water-sensitive materials were performed under a dry nitrogen atmosphere in a conventional nitrogen-filled glove box. CuBr(I), *N,N,N',N",N'*-pentamethyldiethylenetriamine (PMDETA), RuCl₂(PPh₃)₃, Al(O-*i*-Pr)₃, triethylamine, and 2-Bromoisobutyryl bromide (BiBB) were purchased from Wako Pure Chemical Industries and used without further purification. MMA (Wako Pure Chemical Industries) was dried over CaH₂ and distilled *in vacuo*. NIPAAm (Wako Pure Chemical Industries) was recrystallized in hexane. Decane and *o*-xylene used as a solvent were dried over Al₂O₃ and degassed by bubbling with N₂ gas. Diisobutylaluminum hydride (DIBAL-H) was purchased from Tosoh-Finechem Co. Ltd. All other

chemicals were obtained commercially and used as received.

Preparation of PP macroinitiator (PP-*t*-Br). A typical process is as follows: Decane (800 ml) and pyrolysis PP containing a terminal vinylidene group (PP-*t*-Vd, 1.2 unit-Vd/chain; 93.6 g) were placed in a 1-l glass reactor equipped with a mechanical stir bar and then PP-*t*-Vd was dissolved at 110°C for 2 h. Then, DIBAL-H (14.3 ml) was added and the mixture was maintained at 110°C for 4 h under stirring. Dried air was then continuously fed (100 l/h) into the system at 110°C. After 6 h, the reaction mixture was added to 2 l of acidic methanol. The polymer was collected by filtration, washed with methanol, and dried *in vacuo* at 120°C for 10 h to give 104 g of hydroxylated PP (PP-*t*-OH, 0.63 unit-OH/chain). The PP-*t*-OH (50 g) and toluene (300 ml) thus obtained were placed in a 500-ml glass reactor equipped with a mechanical stir bar. Triethylamine (3.0 ml) and BiBB (2.5 ml) were added to the reactor and then the mixture was stirred at 80°C for 3 h. The reaction mixture was poured into 2 l of acidic methanol. The resulting polymer was collected by filtration, washed with methanol, and dried *in vacuo* at 40°C for 10 h to give 42 g of PP containing a terminal ester group (PP-*t*-Br, 0.46 unit-Br/chain). By selecting the pyrolysis PPs, three kinds of PP-*t*-Br with different molecular weights (PP-*t*-Br1, PP-*t*-Br2, and PP-*t*-Br3) were obtained as shown later in Table 1 and then used as a PP macroinitiator.

MMA polymerization with PP macroinitiator. A typical polymerization process is as follows: after PP-*t*-Br1 (0.47 g, 0.088 mmol as 2-bromoisobutyrate)

Table 3. Results of NIPAAm polymerization by using PP macroinitiator^a

Run	PP Macroinitiator ^b		[PP- <i>t</i> -Br]/[NIPAAm], molar ratio	Yield, g	Content of NIPAAm, wt % ^c
	g	mM			
4	10.42	23	1/87	11.27	6
5	6.94	23	1/347	9.72	31

^a Polymerization conditions: $[\text{RuCl}_2(\text{PPh}_3)_3]/[\text{Al}(i\text{-OPr})_3] = 10/40$ (mM), in *o*-xylene, $120^\circ\text{C} \times 9$ h.

^b PP-*t*-Br₂ was used.

^c Determined by ¹H NMR.

was placed in a 30-ml Schlenk tube equipped with a stirring bar, *o*-xylene (1.4 ml), MMA (2.36 ml), and a solution of CuBr(I)/PMDETA in *o*-xylene (0.106 mmol as a copper atom) were added and the mixture was heated at 90°C for 2.5 h. After cooling, the reaction mixture was poured into 400 ml of methanol and the white solid was collected by filtration, washed with methanol, and dried at 80°C *in vacuo*. As shown later in Table 2, three kinds of polymers were obtained.

NIPAAm polymerization with PP macroinitiator. A typical polymerization process is as follows: after PP-*t*-Br₂ (6.94 g, 0.20 mmol as 2-bromoisobutyrate) was placed in a 100-ml Schlenk tube equipped with a stirring bar, *o*-xylene (10 ml), NIPAAm (9.05 g), Al(*O*-*i*-Pr)₃ (81.7 mg), and RuCl₂(PPh₃)₃ (95.9 mg) were added to the tube and the mixture was heated at 120°C for 9 h. After cooling, the reaction mixture was poured into 600 ml of acetone and the white solid was collected by filtration, washed with acetone, and dried at 120°C *in vacuo*. As shown later in Table 3, two kinds of polymers were obtained.

Analytical procedures. ¹H NMR spectra were recorded on JEOL GSX-400 (400 MHz) spectrometers using *o*-dichlorobenzene-*d*₄ as a solvent. The gel permeation chromatograms (GPC) at 140°C in 1,2-dichlorobenzene were recorded by using a Waters Alliance GPC2000 equipped with four TSKgel columns (two sets of TSKgelGMH6-HT and two sets of TSKgelGMH6-HTL) calibrated with PP.

TEM analysis. Ultrathin (~ 100 nm) sections of the polymer, which had been pressed into a sheet, were cut on a Reica Ultracut microtome equipped with a diamond knife at a low temperature and then were stained with RuO₄. TEM observations were made with a Hitachi H-7000 transmission electron microscope at an acceleration voltage of 75 kV.

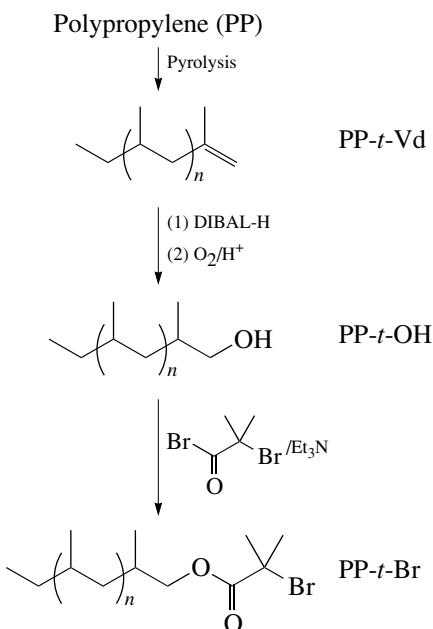
RESULTS AND DISCUSSION

Preparation of PP Macroinitiators

The synthesis of PP macroinitiator consisted of three steps (scheme). In the first step, PP-*t*-Vd, which possessed the vinylidene group at its chain end, was obtained by pyrolysis of PP. In the second step, the vinylidene end group was converted to the hydroxyl group by hydroalumination and oxidation to give PP-*t*-

OH, according to the previous literature [11]. In the third step, the hydroxyl chain end was reacted with BiBB to produce PP-*t*-Br, which could initiate the controlled radical polymerization mediated by a transition metal catalyst. By selecting the pyrolysis conditions of PP, three kinds of PP-*t*-Br with different molecular weights, PP-*t*-Br₁, PP-*t*-Br₂, and PP-*t*-Br₃, were obtained.

Figure 1 shows the ¹H NMR spectra of PP-*t*-Br₃ and its precursors, PP-*t*-Vd and PP-*t*-OH. For PP-*t*-Vd (Fig. 1a), two signals of δ 4.6–4.7 ppm are assigned to vinylidene (=CH₂). For PP-*t*-OH (Fig. 1b), the multiple signals of δ 3.25–3.45 ppm are assigned to methylene protons ($-\text{CH}_2\text{OH}$). For PP-*t*-Br₃ (Fig. 1c), the multiple signals of δ 3.8–4.1 ppm correspond to methylene protons ($-\text{CH}_2\text{O}-$) and the single signal of δ 1.9 ppm corresponds to methyl protons ($-\text{OCOC}(\text{CH}_3)_2\text{Br}$). In addition, a small amount of methylene protons assigned to the hydroxyl group were observed. From the relative intensities of these signals, the conversion of the hydroxyl group to ester group was estimated to be about 87%. Table 1 summarizes the preparation results



Scheme. Synthetic scheme of PP macroinitiator.

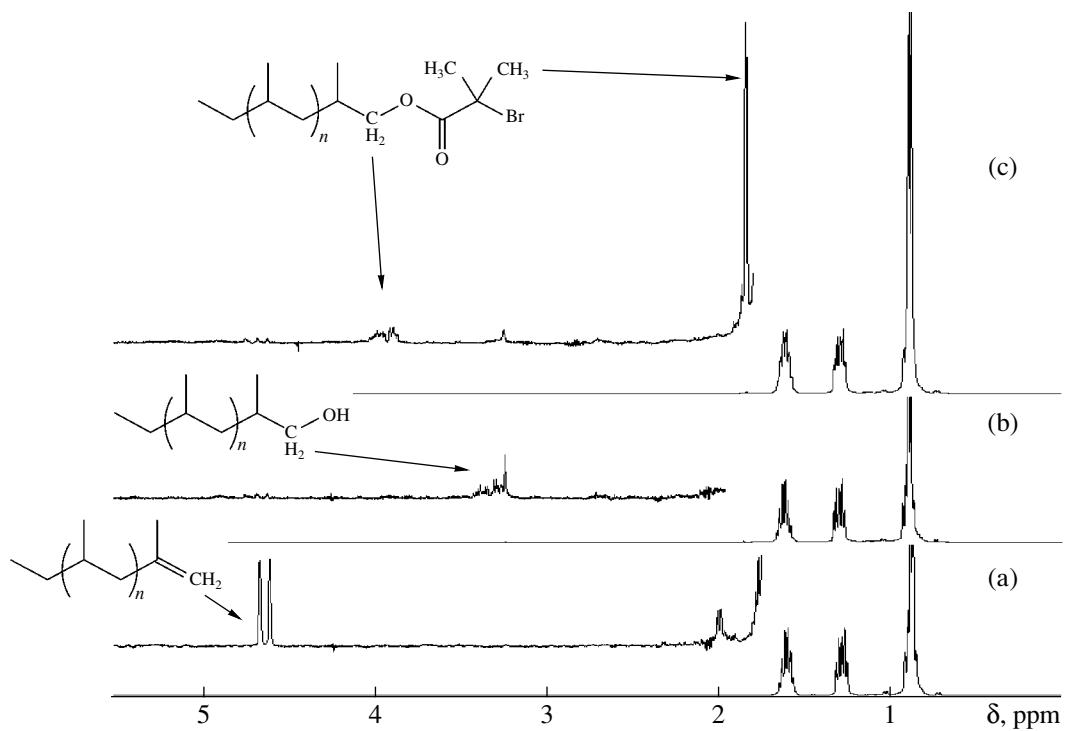


Fig. 1. ^1H NMR spectra of PP-*t*-Vd (a), PP-*t*-OH (b), and PP-*t*-Br3 (c) (400 MHz in *o*-dichlorobenzene- d_4 at 120°C).

of PP macroinitiators with different molecular weights. For PP-*t*-Br1 with the lowest molecular weight, the functionality of the terminal ester group was 0.98 and the overall conversion of the vinylidene group to ester group was 73% from the number-averaged molecular weight (M_n) and the contents of the vinylidene and ester groups. On the other hand, in the case of PP-*t*-Br2 and PP-*t*-Br3 with higher molecular weight, both functionality and overall conversion were much lower than those in the case of PP-*t*-Br1. These results would be due to the difficulty of the oxidation and esterification because of their higher molecular weights. The PPs thus obtained with the terminal ester group were used

as a macroinitiator for the transition metal mediated radical polymerization.

Radical Polymerization of MMA Initiated by PP Macroinitiator

It is well known that transition metal mediated radical polymerization realized the controlled radical polymerization of various vinyl monomers, represented by (meth)acrylates and styrenes, to give precisely controlled polymers [7, 8]. Especially, in the case of using functionalized PO as a macroinitiator, this polymerization system is more advantageous than anionic polymerization because of its higher polymerization temperature. The polymerization of MMA was carried out in an *o*-xylene solution by using CuBr/PMDETA as a catalyst system. Two types of PP-*t*-Br with different molecular weights were used as macroinitiators, and polymerization with the lower molecular weight macroinitiator (PP-*t*-Br1) was carried out at 90°C, while that with the higher molecular weight macroinitiator (PP-*t*-Br3) was carried out at 120°C because of its poor solubility. The viscosity of the polymerization system increased with increasing time and it indicated the progress of MMA polymerization to give a PP-*b*-PMMA block copolymer with higher molecular weight compared with the macroinitiator. Table 2 summarizes the results by altering polymerization conditions in various ways. In all cases, the polymer yields were larger than the amount of macroinitiator and MMA conversions observed by GC analysis were in a range of 57–

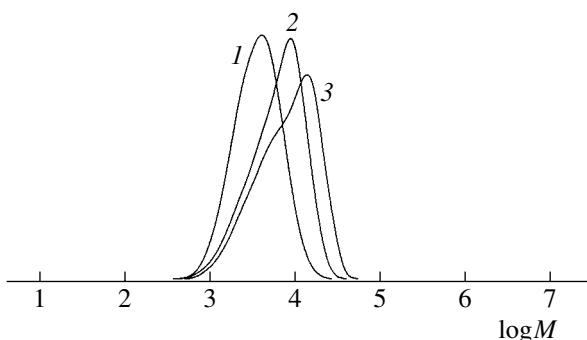


Fig. 2. GPC traces of PP-*t*-Br1 ($M_n = 5270$, $M_w/M_n = 1.47$) (1), PP-*b*-PMMA ($M_n = 8850$, $M_w/M_n = 1.66$, polymerization time 0.5 h) (2), and PP-*b*-PMMA ($M_n = 12440$, $M_w/M_n = 1.94$, polymerization time 2.5 h) (3) at Run 1.

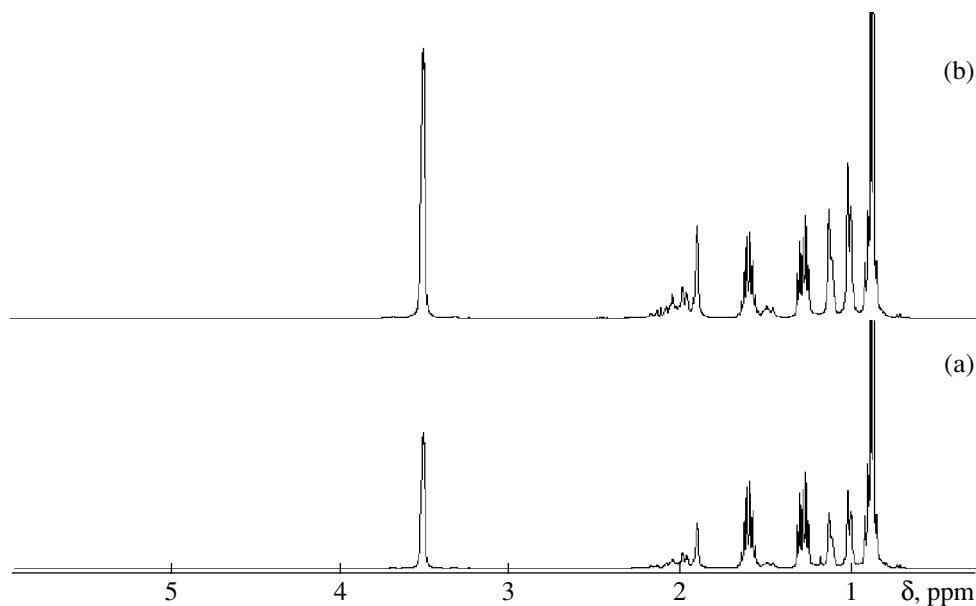


Fig. 3. ^1H NMR spectra of the polymers obtained by MMA polymerization with PP macroinitiator (PP-*t*-Br3) at (a) Run 2 and (b) Run 3 (400 MHz in *o*-dichlorobenzene- d_4 at 120°C).

66%. In addition, the Soxhlet extraction of the obtained polymers with boiling THF confirmed that the obtained polymers contained only a small amount of homo-PMMA. These results indicate the formation of PP-*b*-PMMA block copolymer.

Figure 2 shows the GPC traces of the obtained polymer (Run 1) and its lap samples. GPC measurements revealed that the molecular weight of the obtained polymer increased with increasing reaction time. It indicated the proceeding of the controlled radical polymerization of MMA to give a linear block copolymer. On the other hand, the molecular weight distribution of the obtained polymer was broadened with increasing reaction time and it seems that part of the starting material remained during the progress of the polymerization. Its possible explanation is that the macroinitiator used was prepared from the pyrolysis PP, which is a mixture of the polymer with the vinylidene group at both ends of its chain, at one end of its chain, and without the vinylidene group as reported previously [12], and PP without the vinylidene group cannot be converted to the macroinitiator. Therefore, the unreacted PP was observed as a shoulder in the GPC trace.

Structural Analysis of the Polymer Obtained by Radical Polymerization of MMA

The obtained polymers were analyzed at 120°C by ^1H NMR with *o*-dichlorobenzene- d_4 as a solvent. Figure 3 shows the ^1H NMR spectra of the polymers obtained by radical polymerization of MMA with PP macroinitiator, PP-*t*-Br3 (Table 2, Runs 2 and 3). From the relative intensities between δ 3.6 ppm assigned to the methyl ester protons of the PMMA and δ 0.9–

1.8 ppm assigned to the propylene unit and PMMA backbone, MMA contents in these polymers were calculated to be 48 and 64 wt %, respectively. As shown in Table 1, the functionality and M_n of PP macroinitiator (PP-*t*-Br3) were 0.46 unit-Br/chain and 17800. Assuming that the efficiency of the initiation site in this macroinitiator was almost 100%, it is considered that these obtained polymers consisted of 54% PP without PMMA segment and 46% PP-*b*-PMMA block copolymer. Therefore, M_n of the attached PMMA segment in each PP-*b*-PMMA block copolymer can be estimated to be 35700 and 68700, respectively.

Radical Polymerization of NIPAAm Initiated by PP Macroinitiator

The polymerization of NIPAAm initiated by PP macroinitiator (PP-*t*-Br2) was carried out at 120°C in *o*-xylene with two commonly used catalyst systems, CuBr/PMDETA and RuCl₂(PPh₃)₃/Al(O-*i*-Pr)₃. In the case of the copper catalyst system, polymerization of NIPAAm did not proceed. On the other hand, in the case of the ruthenium catalyst system, the polymerization of NIPAAm was initiated by PP macroinitiator and the content of NIPAAm in the obtained polymer could be controlled by the feed ratio between the NIPAAm monomer and the macroinitiator as shown in Table 3. One of the reasons for no polymerization in the case of the copper catalyst system is that NIPAAm interacted with the copper bromide directly and deactivated this catalyst system because of its highly active N–H bond. The contents of NIPAAm in the obtained polymers were determined by ^1H NMR. The ^1H NMR spectrum of the obtained polymer (Run 5) is shown in Fig. 4. In

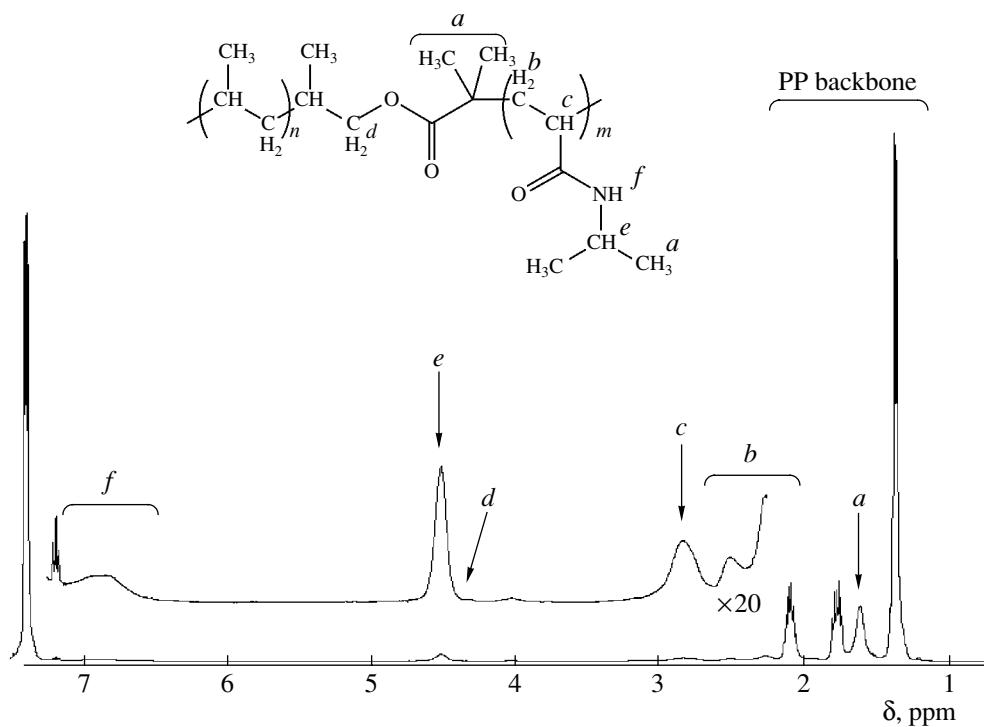


Fig. 4. ^1H NMR spectrum of the polymer obtained by NIPAAm polymerization with PP macroinitiator (PP-*t*-Br2) at Run 5 (400 MHz in *o*-dichlorobenzene- d_4 at 120°C).

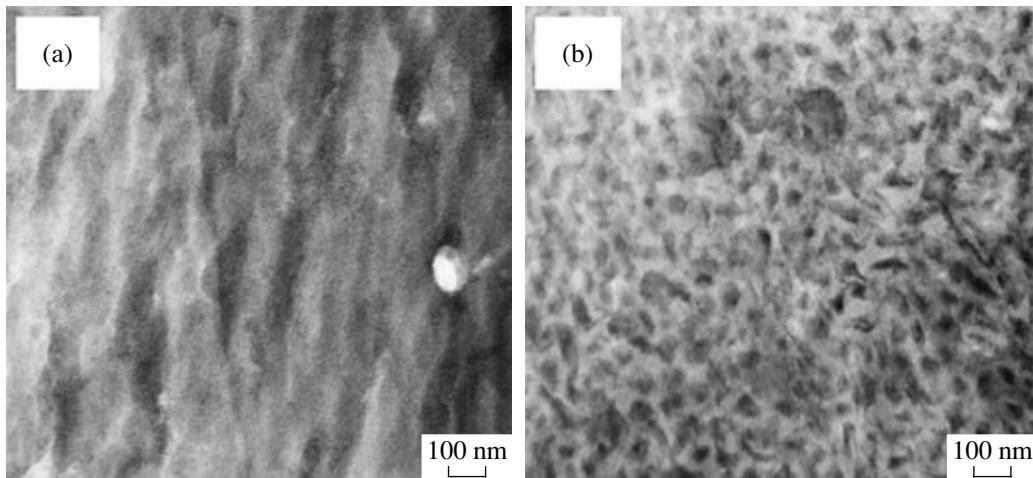


Fig. 5. TEM micrographs of the polymers obtained by NIPAAm polymerization with PP macroinitiator (PP-*t*-Br2) at (a) Run 4 (NIPAAm content 6 wt %) and (b) Run 5 (NIPAAm content 31 wt %).

in this spectrum, some specific signals were observed at δ 1.15 ppm (*a*, methyl protons of initiation site and isopropyl group of NIPAAm), δ 1.5–2.1 ppm (*b*, methylene protons of PNIPAAm backbone), δ 2.2–2.6 ppm (*c*, methyne proton of PNIPAAm backbone), δ 4.05 ppm (*e*, methyne proton of isopropyl group of NIPAAm), and δ 6.0–6.6 ppm (*f*, amine proton of NIPAAm). From the relative intensities between these signals, the contents of NIPAAm in the obtained polymers (Runs 4, 5) were estimated to be 6 and 31 wt %, respectively. From the functionality (0.46 unit-Br/chain) and M_n (13900)

of PP macroinitiator, the obtained polymers included 46% PP-*b*-PNIPAAm block copolymer and PNIPAAm segments attached to PP segments were estimated to have 1760 and 13300 of M_n , respectively.

Morphology of the Polymers Obtained by Radical Polymerization of NIPAAm

Figure 5 shows TEM micrographs of two polymers with 6 and 31 wt % NIPAAm contents. The TEM images of these polymers reveal the microphase-sepa-

ration morphology at the nanometer level between the PP segment and PNIPAAm segment and the distinctive phases were observed at different PNIPAAm contents. In the case of the lower PNIPAAm content (6 wt %, Fig. 5a), the PNIPAAm segment stained easily by RuO₄ dispersed at less than 10 nm in the PP matrix because of the short PNIPAAm segment ($M_n = 1760$) compared with the PP segment ($M_n = 13900$). In contrast, in the case of higher PNIPAAm content (31 wt %, Fig. 5b), enough long PNIPAAm segment ($M_n = 13300$) easily aggregated and spherical PNIPAAm-rich domains of about 50 nm in diameter were observed in the PP matrix. These results demonstrate that the microphase morphology is controllable by changing the length of the chemically linked PNIPAAm segment in PP-*b*-PNIPAAm block copolymer.

CONCLUSIONS

PP macroinitiators were prepared by a series of end functionalization of pyrolysis PP with the vinylidene end group via hydroalumination, oxidation, and esterification. By using these PP macroinitiators, transition metal mediated radical polymerizations of MMA or PNIPAAm were carried out to give PP-*b*-PMMA and PP-*b*-PNIPAAm block copolymers. These structures and compositions could be confirmed by ¹H NMR analysis. From TEM observation of the polymers obtained by PNIPAAm polymerization, the microphase-separation morphology at the nanometer level between PP and PNIPAAm segments was observed and its morphology

was remarkably altered by the length of the attached PNIPAAm segment.

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