Polymacromonomers with Polyolefin Branches Synthesized by Free-Radical Homopolymerization of Polyolefin Macromonomer with a Methacryloyl End Group

Hideyuki Kaneko, Shin-ichi Kojoh, Nobuo Kawahara, Shingo Matsuo,
*Tomoaki Matsugi, Norio Kashiwa**

R&D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan

Summary: Polymacromonomers with polyolefin branches were successfully synthesized by free-radical homopolymerization of polyolefin macromonomer with a methacryloyl end group. Propylene-ethylene random copolymer (PER) with a vinylidene end group was prepared by polymerization using a metallocene catalyst. Then, the unsaturated end group was converted to a hydroxy end group via hydroalumination and oxidation. The PER with the hydroxy end group was easily reacted with methacryloyl chloride to produce methacryloyl-terminated PER (PER macromonomer; PERM). The free-radical polymerization of thus-obtained PERM was done using 2,2'-azobis(isobutyronitorile) (AIBN) as a free-radical initiator. From NMR analyses, the obtained polymers were identified as poly(PERM). Based on gel permeation chromatography (GPC), the estimated degree of polymerization (D_p) of these polymers were about 30. Thus, new class of polymacromonomers with polyolefin branches was synthesized.

Keywords: functionalization of polymers; graft copolymers; macromonomers; polyolefins; radical polymerization

Introduction

Macromonomers, which consist of a macromolecular segment and a polymerizable chain end segment, are useful as a starting material for producing new polymer architectures. Homopolymerization and copolymerization of macromonomer yield various polymers that have unique topologies and properties. For example, polymacromonomers, which are produced by homopolymerization of macromonomer, can have unique molecular morphologies ranging from star-shaped spheres to rodlike cylinders by controlling the degree of polymerization (D_p) of the backbone and the length of the branch chains.[1] However, previous studies on macromonomers have been limited to polymers obtained by radical,

DOI: 10.1002/masy.200450930

cationic, and anionic polymerizations, such as polymethacrylate, polystyrene, and poly(ethylene oxide).

Synthesis and copolymerization of macromonomer possessing a polyolefin segment obtained by coordination polymerization have also been reported. For example, Mülhaupt *et al.* reported the synthesis of methacryloyl-terminated polypropylene via vinylidene-terminated polypropylene obtained by metallocene-catalyzed polymerization and the free-radical copolymerization of this polyolefin macromonomer with methyl methacrylate.[2] Matyjaszewski *et al.* reported the synthesis of methacryloyl-terminated polyethylene obtained by Pd-mediated living polymerization and the copolymerization of this polyethylene macromonomer with *n*-butyl acrylate by atom transfer radical polymerization.[3] However, there have been no reports on homopolymerization of polyolefin macromonomer to give a graft copolymer consisting of polar polymer backbone and polyolefin branches.

In this study, we focused on the macromonomers based on lower molecular weight PER as a polyolefin segment. These PER macromonomers (PERMs) were expected to have the advantage of facile homopolymerization because those have low viscosity and are easily soluble by many hydrocarbon solvents. By using such new class of polyolefin macromonomers obtained by the functionalization of vinylidene-terminated PER, we successfully synthesized polymacromonomers possessing polyolefin branches by the free-radical homopolymerization. Furthermore, the nature of the obtained polymacromonomer that consisted of a polymethacrylate backbone and PER branch chains was investigated. This is a first report of a polyolefin-based polymacromonomer with unique polymer architecture.

Experimental Section

Materials. Dicyclopentadienylzirconium dichloride (Cp_2ZrCl_2), Bis(1,3-dimethylcyclopentadienyl)zirconium dichloride ($(1,3\text{-}Me_2Cp)_2ZrCl_2$), methacryloyl chloride, triethylamine, and AIBN were commercially obtained and used without further purification. Ethylene was purchased from Sumitomo Seika Co., Ltd., and propylene was obtained from Mitsui Chemicals, Inc. Methylalminoxane (MAO) was purchased from Albemarle as a 1.2M toluene solution, and the trimethylaluminum, which is considered an impurity was evaporated in vacuo prior to use. Diisobutylaluminum hydride (DIBAL-H) was purchased from Tosoh-Finechem Co. Ltd. All other chemicals were obtained commercially and used as received.

Preparation of PER. PER with vinylidene end group has been prepared by copolymerization of propylene with ethylene using Cp_2ZrCl_2/MAO (Al/Zr=1000) catalyst system at 50°C for 5 h.

Hydroxylation of PER. PER (50 g, 0.071 mol as vinylidene end group) and toluene (250 ml) were placed in 500-ml glass reactor and stirred. Then DIBAL-H (50 ml, 0.28 mol) was added, and the system was then heated at 110 °C for 6 h. Dried air at 110 °C was then continuously fed (100 l/h) into the system. After 3 h, the reaction mixture was washed with *aq.*HCl and distilled water. After evaporation of solvent, hydroxylated PER was obtained as a yellow viscous liquid.

Synthesis of Methacryloyl-terminated PER (PERM). After hydroxylated PER (20 g, 12.7 mmol as hydroxy group) and toluene (30 ml) was placed in a 100-ml Schlenk tube, triethylamine (2.7 ml) and methacryloyl chloride (2.5 ml) were added to the tube, and then the mixture was stirred at room temperature for 3.5 h. The reaction mixture was washed with *aq.*HCl and distilled water. After the solvent was evaporated, the product was purified by liquid chromatography.

Homopolymerization of PERM. After PERM (3.0 g, 2.98 mmol as methacryloyl group) was placed in a 100-ml Schlenk tube, toluene (20 ml) and AIBN (75 mg) were added to the tube, and the mixture was heated at 70 °C for 30 h. The reaction mixture was washed with *aq.*HCl and distilled water. After the solvent was evaporated, a viscous liquid was obtained.

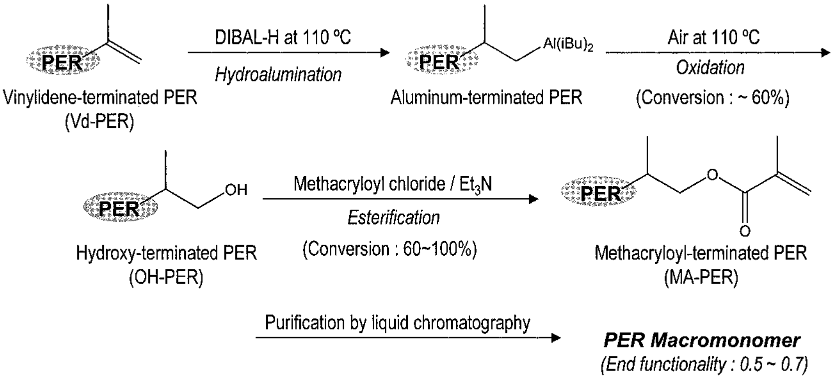
Polymer Fractionation. First, the polymer obtained by homopolymerization of PERM was dissolved in *n*-hexane and poured into a glass column packed with silica gel. Then, the first fraction was eluted by *n*-hexane and the second fraction by *n*-hexane/CH_2Cl_2 (2:1) mixed solvent. After evaporation of the solvent, each fraction was analyzed by GPC, ^1H NMR, and ^{13}C NMR.

Analytical Procedures. ^1H NMR and ^{13}C NMR spectra were recorded by JEOL GSX-270 or GSX-400 spectrometers with tetramethylsilane as the internal standard using chloroform-*d* or 1,2-dichlorobenzene-d_4 as a solvent. The gel permeation chromatograms (GPC) of the polymers were recorded by using a Waters Alliance GPC2000 equipped with four TSKgel columns (two sets of TSKgelGMH$_6$-HT and two sets of TSKgelGMH$_6$-HTL) at 140 °C and 1,2-dichlorobenzene as the solvent. The molecular weights of the polymers were determined by polystyrene standard.

Results and Discussion

Synthesis of PERM.

The synthetic route of PERM developed in this study is shown in Scheme 1. Vinylidene-terminated PERs were obtained by propylene copolymerization with ethylene by using typical metallocene catalysts. Unsaturated chain ends of the polymer were converted into hydroxy end groups by hydroalumination or hydroboration and subsequent oxidation, as previously reported.[4] Hydroalumination of vinylidene end groups by DIBAL-H was then carried out at 110 °C in toluene, as recommended in the literature.[4] Then, dried air was fed into the resulting mixture at 110 °C to convert the alkylaluminum end groups to hydroxy end groups. The obtained hydroxy end groups easily reacted with methacryloyl chloride in the presence of a Lewis base at room temperature to produce methacryloyl end groups. The PER with a methacryloyl end group was useful as PERM owing to the polymerizable methacryloyl end group. By selecting the polymerization conditions and catalyst, we prepared two types of functionalized PERs with different molecular weights (PER1 and PER2).



Scheme 1. Synthetic route of PERM

Figures 1(i), (ii), and (iii) show the ^{1}H NMR spectra of PER1 with a vinylidene end group (Vd-PER1), with a hydroxy end group (OH-PER1), and with a methacryloyl end group (MA-PER1), respectively. In Figure 1(i), the signals assigned to the vinylidene group protons (*c*; 4.6-4.8 ppm), were detected in addition to the signals of PER main chain protons at 0.7 to 1.8 ppm. These additional signals are generated from the chain transfer reaction induced by monomers when the propagating chain end was a propylene unit.[5] The content of vinylidene, ethylene, and propylene units was 4.0, 38, and 58 mol%, respectively, calculated from the relative intensities of the protons of each unit in the ^{1}H NMR spectrum. In Figure 1(ii), the new signals assigned to the hydroxymethylene group protons (*e*; 3.3-3.6 ppm) were detected in addition to the signals of unreacted vinylidene protons. The calculated content of the hydroxymethylene and vinylidene groups in OH-PER1 was 2.4 mol% and 0.09 mol%, respectively, indicating that about 60% of the vinylidene end groups in Vd-PER1 were hydroxylated and that the other vinylidene end groups were converted to the saturated end groups.

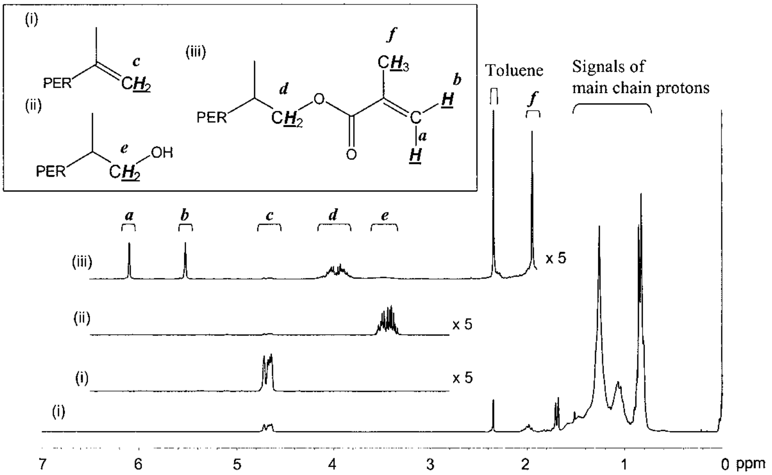


Figure 1. ^{1}H NMR spectra of (i)Vd-PER1, (ii)OH-PER1 and (iii) MA-PER1 (270 MHz, in $CDCl_3$)

This hydroxylation efficiency of 60% would be reasonable, because we previously reported that the hydroxylation efficiency of alkylaluminum-terminated PP was 52%.[6] In Figure 1(iii), the new signals assigned to the methacryloyl end group protons (*a*, *b*, *d* and *f*; 6.1, 5.5, 3.8-4.2 and 1.95 ppm, respectively) were detected. From the relative intensities of the protons of each group, the calculated content of the methacryloyl, hydroxymethylene, and vinylidene groups was 2.4, 0.37, and 0.08 mol%, respectively, indicating that almost all hydroxy end groups in OH-PER1 were converted to methacryloyl end groups.

To remove the undesirable PER that has a saturated vinylidene or hydroxy end group, the obtained MA-PER1 was purified by liquid chromatography. The content of the methacryloyl, ethylene, and propylene units of the purified MA-PER1 was 3.9, 35, and 61 mol%, respectively, calculated from ^{1}H NMR analysis, and the number average molecular weight (M_n) was 670 estimated from the GPC measurement.

Therefore, the estimated end functionality (f_{MA}) of the obtained MA-PER1 was 0.68. The absence of vinylidene and hydroxymethylene end groups in the ^{1}H NMR spectrum indicates that residual chain ends were saturated end groups. Using the same purification method as for MA- PER1, MA-PER2 with higher M_n than MA-PER1 was obtained.

Table 1. Functionalization Results for PER Chain Ends

		Vd-PER [a]	OH-PER	MA-PER	
				before purification	after purification
PER1	M_n [b]	520	520	690	670
	Content of				
	vinylidene end group (mol%)[c]	4.0	0.09	0.08	n.d. [d]
	hydroxy end group (mol%)[c]	-	2.4	0.37	n.d. [d]
	methacryloyl end group (mol%)[c]	-	-	2.4	3.9
	(End functionality; f_{MA})				(0.68)
PER2	M_n [b]	1,550	1,650	1,960	1,330
	Content of				
	vinylidene end group (mol%)[c]	1.4	0.04	n.d. [d]	n.d. [d]
	hydroxy end group (mol%)[c]	-	0.85	0.01	0.10
	methacryloyl end group (mol%)[c]	-	-	0.52	1.6
	(End functionality; f_{MA})				(0.53)

[a] Polymerization conditions: (PER1) 0.01 mmol of Cp_2ZrCl_2, 10 mmol of MAO, ethylene/propylene flowrate of 10/90 (l/h), in 800 ml of toluene, 50 °C, 5 h, (PER2) 0.02 mmol of $(1,3\text{-}Me_2Cp)_2ZrCl_2$, 20 mmol of MAO, ethylene/propylene flowrate of 20/80 (l/h), in 800 ml of toluene, 50 °C, 2 h.

[b] Determined by GPC.

[c] Calculated from ^{1}H NMR.

[d] Not detected.

Table 1 summarizes these functionalization results. For the synthesis of MA-PER2, both the conversion of the vinylidene end groups to hydroxy end groups and that of the hydroxy end groups to methacryloyl end groups were about 60%. Such low conversion of the hydroxy end groups to methacryloyl end groups in PER2 is probably due to the higher viscosity of PER2 than that of PER1. After purification, the estimated f_{MA} of the obtained MA-PER2 was 0.53 from ^1H NMR analysis and GPC measurement. The obtained MA-PER1 (f_{MA} = 0.68) and MA-PER2 (f_{MA} = 0.53) were then used as PERMs for free-radical polymerization without further purification.

Homopolymerization of PERM.

Homopolymerization of the PER1 macromonomer (PERM1) and PER2 macromonomer (PERM2) was carried out at 70°C and 60°C, respectively, in toluene in the presence of AIBN as a radical initiator. Each resulting product was pale yellow viscous oil. Figure 2 shows the GPC traces for PERMs and the corresponding homopolymerized products. Each GPC trace of the homopolymerized product showed a new peak at a higher M_n region (over 10^4 mol/g) in addition to a peak of PERM at a lower M_n region (under 10^4 mol/g). These peaks indicate the formation of polymacromonomer. The estimated M_n of poly(PERM1) and poly(PERM2) was 18,760 and 45,920, respectively, from the higher M_n part of GPC traces. From a calculation based on M_n values for the two PERMs (670 for PERM1, and 1,330 for PERM2), the estimated D_p of these poly(PERM1) and poly(PERM2) was about 28 and 35, respectively.

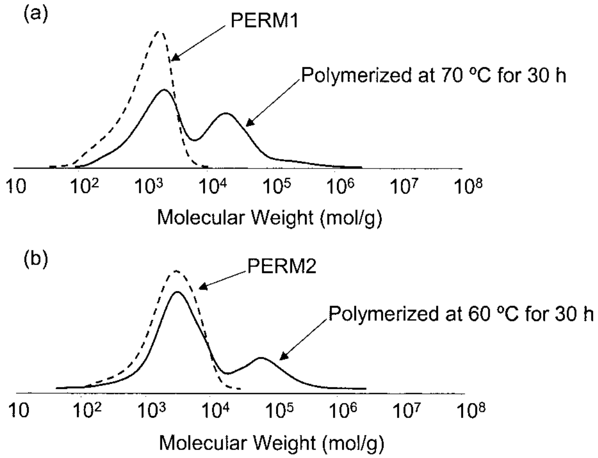


Figure 2. GPC traces for homopolymerization of (a)PERM1 and (b)PERM2

Although these two D_p values cannot be directly compared due to differences in polymerization conditions, these two macromonomers indicate nearly equal efficiency of polymerization, despite the different M_n.

Fractionation and Characterization of Poly(PERM1).

To isolate the higher M_n region, the mixture was fractionated by liquid chromatography using a silica gel column into two fractions, *n*-hexane and *n*-hexane / dichloromethane (2:1) eluates. The GPC traces of these two fractions were shown in Figure 3. From a calculation based on M_n value (670) for the PERM1, the first fraction was estimated to be the poly(PERM1) (D_p = 30) and the second fraction the unpolymerized PERM1 containing the oligomer of PERM1 (D_p= 2~3). Based on the ^{1}H NMR spectrum, the second fraction contained unreacted methacryloyl end groups.

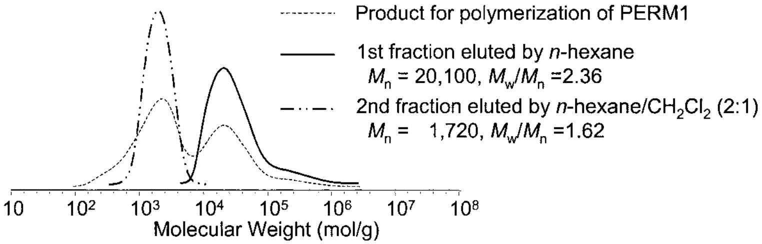


Figure 3. GPC traces of the product for polymerization of PERM1 and fractions obtained by liquid chromatography

Figures 4 and 5 show the ^{1}H and ^{13}C NMR spectra of the isolated poly(PERM1), respectively. In the ^{1}H NMR spectrum, the signals of methacryloyl group protons of PERM1 (1.95, 5.5, and 6.1 ppm) disappeared and the signals of methylene protons adjoining ester group shifted from 3.8-4.2 ppm to 3.4-4.1 ppm (*a*) in comparison with the ^{1}H NMR spectrum of PERM1 in Figure 1(iii) (MA-PER1). In addition, the signals of methylene protons in polymethacrylate backbone appeared at 1.7-2.0 ppm (*b*). In the ^{13}C NMR spectrum, in addition to the signals of PER chain carbons, signals appeared at 15-20, 45, 52-55, 70, and 176-178 ppm. Based on the ^{13}C NMR measured in DEPT mode, these signals are respectively assigned to methyl carbon (*e*), quaternary carbon (*d*) and methylene carbon (*c*) in the polymethacrylate main chain, methylene carbon (*b*) adjoining ester group, and carbonyl carbon (*a*), respectively.

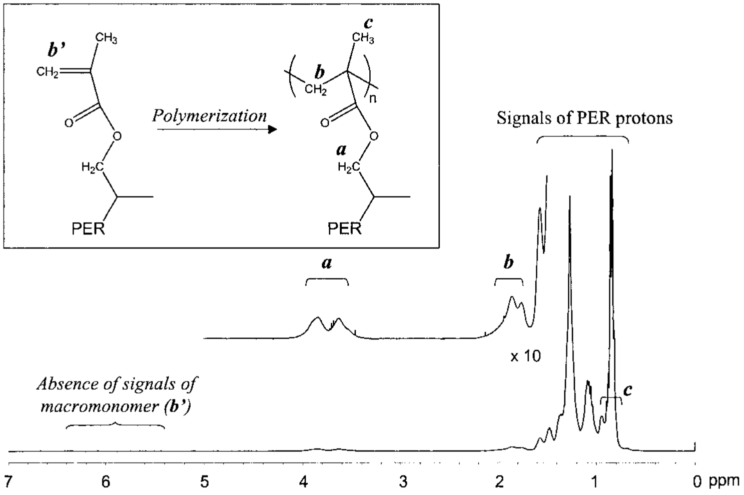


Figure 4. ^1H NMR spectrum of poly(PERM1)
(400 MHz, in 1,2-dichlorobenzene-d_4 at 118 °C)

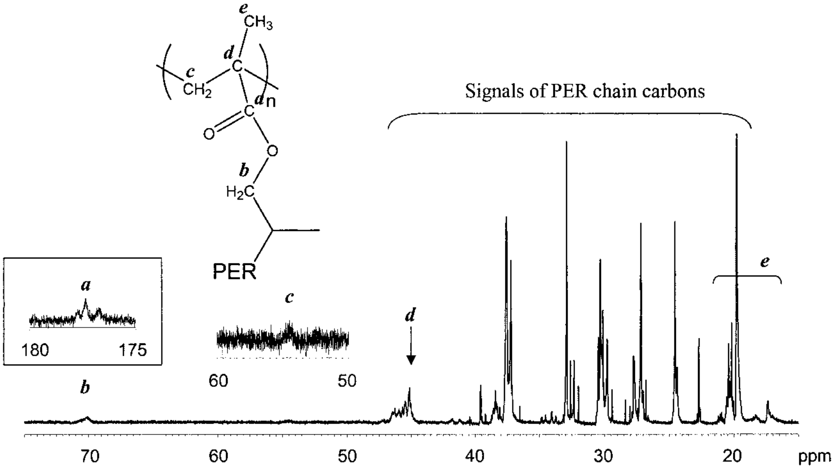


Figure 5. ^{13}C NMR spectrum of poly(PERM1)
(100 MHz, in 1,2-dichlorobenzene-d_4 at 118 °C)

Thus, NMR analyses revealed the formation of poly(PERM1).

Based on the D_p obtained by GPC measurement, this poly(PERM1) consists of a polymethacrylate backbone (M_n = 2,550) and 30 PER branch chains (M_n = 585). This is the first report of such unique polymer architecture, which is expected to be the hybrid materials consisting of polyolefins and polar polymers. Despite having the polymethacrylate backbone, this poly(PERM1) is a viscous liquid polymer and soluble even in non-polar hydrocarbon solvents such as *n*-hexane, due to the high branch density and the high content of PER segment (87 wt%).

In addition, the result of liquid chromatography indicates that the polarity of this poly(PERM1) was lower than that of unpolymerized macromonomers in *n*-hexane, despite having the same composition (the molar ratio of methacryloyl segment to PER segment was considered to be equal). One interpretation of this lower polarity for poly(PERM1) than that for PERM1 is as follows. This poly(PERM1) consists of two different segments, polar polymethacrylate and non-polar PER. Therefore, in non-polar solvent such as *n*-hexane, this poly(PERM1) would form a core-shell type structure, in which the polar core of the polymethacrylate backbone is inside the non-polar shell formed by PER side branches. Consequently, the apparent polarity of the poly(PERM1) in *n*-hexane is decreased.

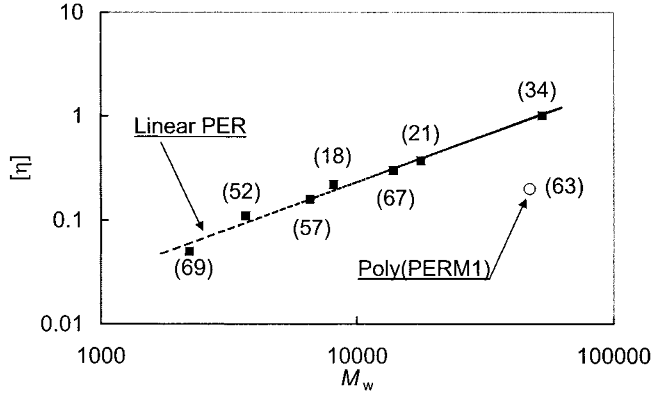


Figure 6. Double-logarithmic polts of [η] vs M_w for linear PERs and poly(PERM1).
(Values in parentheses are the propylene content (mol%) in PER.)

The relationship between M_w and the intrinsic viscosity ([η]; measured in decalin at 135°C) of PERs obtained by using metallocene catalysts is shown in Figure 6. In the case of linear PER, a linear relationship was observed independent of monomer composition. On the other hand, the obtained poly(PERM1) located obviously below this line. This result shows that poly(PERM1) has a lower viscosity than the linear PER with the same molecular weight owing to its unique polymer topology and composition.

Conclusions

Polymacromonomers with polyolefin branches were successfully synthesized by homopolymerization of methacryloyl-terminated PER macromonomer, which were synthesized by the conversion of the vinylidene-terminated PER obtained by metallocene-catalyzed polymerization. The obtained polymacromonomer could be isolated by liquid chromatography with a silica gel column. Based on ^{1}H and ^{13}C NMR analyses and GPC measurement, the obtained polymer consisted of a polymethacrylate backbone and 30 PER branch chains. This novel polymacromonomer exhibited the nature of PER rather than the nature of polymethacrylate because of its unique polymer architecture such as the high concentration of polyolefin branches. It is expected that various unique polymers having both polar polymer segment and polyolefin segment could be synthesized by applying this synthetic route.

[1] Y. Tsukahara, K. Mizuno, A. Segawa, Y. Yamashita, *Macromolecules* **1989**, *22*, 1546. K. Terao, T. Hokajo, Y. Nakamura, T. Norisuye, *Macromolecules* **1999**, *32*, 3690. M. Wintermantel, M. Gerie, K. Fisher, M. Schmidt, I. Wataoka, H. Urakawa, K. Kajiwara, Y. Tsukahara, *Macromolecules* **1996**, *29*, 978. M. Gerle, K. Fisher, S. Roos, A. H. E. Müller, M. Schmidt, S. S. Sheiko, S. Prokhorova, M. Möller, *Macromolecules* **1999**, *32*, 2629. S. S. Sheiko, M. Gerle, K. Fisher, M. Schmidt, M. Möller, *Langmuir* **1997**, *13*, 5368.
[2] T. Duschek, R. Mulhaupt, *Polym. Prepr.* **1992**, *33*, 170.
[3] S. C. Hong, S. Jia, M. Teodorescu, T. Kowalewski, K. Matyjaszewski, A. C. Gottfried, M. Brookhart, *J. Polym. Sci., Part A* **2002**, *40*, 2736.
[4] K. K. Kang, T. Shiono, T. Ikeda, *Macromolecules* **1997**, *30*, 1231. T. C. Chung, H. L. Lu, W. Janvikul, *Polymer* **1997**, *38*, 1495.
[5] T. Tsutsui, A. Mizuno, N. Kashiwa, *Polymer* **1989**, *30*, 428.
[6] S. Kojoh, T. Tsutsui, M. Kioka, N. Kashiwa, *Polym. J.* **1999**, *31*, 332.