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Synthesis and hydrophilic property of polypropylene-*graft*-poly(polyethylene glycol-methacrylate) (PP-*g*-P(PEGMA))

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Abstract Polypropylene-*graft*-poly(polyethylene glycol-methacrylate) (PP-*g*-P(PEGMA)), which is a hydrophobic-hydrophilic graft copolymer, was synthesized by a combination of an atom transfer radical polymerization (ATRP) of PEGMA with brominated polypropylene (PP-Br), which was synthesized from PP-OH prepared by metallocene-catalyzed copolymerization. Its structure was confirmed by ^{1}H NMR and GPC analyses. Transmission electron microscope (TEM) micrographs of PP-*g*-P(PEGMA) revealed the nanometer level microphase-separation morphology between the PP segment and the P(PEGMA) segment. The obtained PP-*g*-P(PEGMA) showed water-absorbing property as well as thermostability.

Keywords Metallocene · Polypropylene · ATRP · Polymer hybrid · Amphiphilic property

Introduction

Polyolefins are one of the most widespread commodity plastics due to their outstanding combination of cost performance and excellent physical properties [1]. However, the lack of polar and/or reactive groups on their backbone has restricted some end-use fulfillment, end-uses such as compatibilizers, modifiers, adhesives, and so on.

Thus far, a lot of scientists have studied the creation of functional polyolefins to overcome their disadvantages, by introducing functional groups into the polyolefins [2]. Incorporation of functional groups such as hydroxyl, carboxyl, or amino groups to the polyolefin main-chain has been one idea to broaden the polyolefin applications. Theoretically, there would be two possible approaches to the synthesis

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of functional polyolefins, namely: (a) direct copolymerization of olefins with functional monomers and (b) post polymerization reaction with polyolefins. The direct copolymerization of olefins with functional monomers possessing polar groups is regarded as a very attractive method to synthesize well-defined structural polymers because in many cases they were synthesized by using metallocene catalyst systems [3–11]. However, this method is limited by the ability of functional groups to coordinate with the catalyst/cocatalyst components, thus, causing catalyst deactivation. Furthermore, the amounts of incorporated functional monomers are few and far between. Post polymerization reactions with polyolefins are common methods, for example, treated polyolefins with radical initiators and functional chemicals such as maleic anhydride, halogen, (meth)acrylate monomers, etc. [12–14]. However, these functionalization reactions are usually accompanied with many undesirable side reactions such as crosslinking and degradation. Therefore, these common methods are far from ideal.

Recent advances in polyolefin chemistry have led to the creation of polyolefin hybrid linking between different polymer segments, namely crystal polyolefins, amorphous polyolefens, and other polar polymers to create polyolefin materials with novel functionalities possessing polarity, etc. [15, 16]. It is possible to design a new class of polymer materials based on polyolefins with unique topology and compositions [17–24]. Although synthesized polymer hybrids have characteristics resulting in new functions as new materials as a result of their synergic effect, hydrophilic materials based on polyolefins are not known. Therefore, there seems to be room for investigating hydrophilic properties of polymer hybrid materials.

In this article, we would like to report on the synthesis of polypropylene-*graft*-poly(polyethylene glycol-methacrylate) (PP-*g*-P(PEGMA)), as a hydrophobic-hydrophilic graft copolymer, prepared by an atom transfer radical polymerization (ATRP) with a brominated polypropylene (PP-Br), which was synthesized using a metallocene-catalyzed polymerization technique. Also, we would like to report on their hydrophilic properties.

Experimental

General procedures and materials

All manipulations of air- and water-sensitive materials were performed under dry N_2 atmosphere in a N_2-filled glove box. Copper bromide (CuBr(I)), 10-undecen-1-ol, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and 2-bromoisobutyric bromide (BiBB) were purchased from Wako Pure Chemical Industries and used without further purification. Poly(ethylene glycol) methacrylates (PEGMA, M_n = 350 and 1,100) were purchased from Aldrich Co and used without further purification. Dimethylsilylenebis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride ($Me_2Si(MePhInd)_2ZrCl_2$) was prepared according to a previous paper [25]. Propylene was obtained from Mitsui Chemicals. Methylaluminoxane (MAO) was purchased from Albemarle as 1.2 M toluene solution with the remaining trimethylalminum and evaporated in vacuo before use. Triisobutylaluminum

(TIBAL) was purchased from Tosoh Finechem Co. Toluene and *n*-hexane used as a solvent were dried over Al_2O_3 and degassed by bubbling with N_2 gas.

Preparation of PP macroinitiator (PP-Br)

Toluene (800 ml) was introduced to a N_2-purged 1-l glass reactor equipped with a mechanical stir bar, a temperature probe, and a condenser and stirred vigorously. The reactor was kept at 40 °C with an oil bath and then TIBAL (3.3 mmol) and 10-undecen-1-ol (3.0 mmol) were added. After 10 min, $Me_2Si(MePhInd)_2ZrCl_2$ (0.002 mmol) and 1.31 M toluene solution of MAO (1.0 mmol) were introduced into the reactor and immediately the feeding of propylene gas was started. After adding isobutyl alcohol, the polymerization mixture was poured into acidic methanol. The polymer was collected by filtration, washed with methanol, and dried in vacuo at 80 °C for 10 h. Obtained PP-OH (15 g), BiBB (1.09 ml), and *n*-hexane (150 ml) were introduced into a N_2-purged 500-ml glass reactor equipped with a mechanical stir bar and then stirred vigorously at 60 °C for 3 h. The reaction mixture was cooled to 25 °C and poured into 1 l of acetone. The resulting polymer was collected by filtration, washed with water and acetone, and dried in vacuo at 80 °C for 10 h to give 19.0 g of PP-Br. By repeating this procedure, a sufficient amount of PP-Br for this study was obtained.

Radical polymerization with PP macroinitiator

A typical ATRP process is as follows: PP-Br (25 g), PEGMA (100 ml), and xylene (200 ml) were placed in a 500-ml glass reactor equipped with a mechanical stir bar and then N_2 gas was fed into the reactor at 70 °C. A solution of CuBr(I)/PMDETA in toluene (1.0 mmol as a copper atom) was added to the reactor and the mixture was maintained at 70 °C for 2 h under stirring. The polymerization was stopped by cooling the mixture in an ice bath and then quenched by the addition of methanol. The resulting mixture was filtered, $\leq$ and the obtained polymer was washed by methanol and then dried in vacuo at 80 °C for 10 h.

Analysis

^1H NMR spectra were recorded on JEOL GSX-400 spectrometers using *o*-dichlorobenzene-d_4 as a solvent at 120 °C. For the measurements of contact angle, the specimens were prepared by compression molding at 200 °C for 5 min in a laboratory press.

The contact angles were measured by the DropMaster500 with FAMAS software system (Kyowa Interface Science Co., Ltd.) using distilled water at 23 °C at 50% relative humidity. The static contact angles were measured by the sessile drop method with a water drop being placed on the surface of the specimens. The reported contact angles were the average of five measurements taken at different positions on each sample. The contact angle variability is within 5°.

The gel permeation chromatograms calibrated with PS were recorded by using a CFC T-150A (Mitsubishi Kagaku Corp.) equipped with three columns (Shodex AT-806MS) and an IR spectrometer Miran 1ACVF at 140 °C in *o*-dichlorobenzene.

The peaks of melting temperatures of the polymer samples were measured with a Shimazu DSC-60 differential scanning calorimeter (DSC). The samples were heated to 200 °C at 50 °C min^{-1}, maintained at 200 °C for 10 min, and cooled to 30 °C at 10 °C min^{-1} for recrystallization followed by reheating to 200 at 10 °C min^{-1}. In order to estimate the thermal history, the thermogram of each sample was recorded during the second heating run. The instrument was calibrated with the melting points of indium and lead.

Transmission electron microscopy (TEM) observations were carried out with a Hitachi H-7000 transmission electron microscope at an acceleration voltage of 75 kV. Ultrathin (*ca.* 100 nm) sections of the polymer samples, which had been pressed into a sheet, were cut on a Reica Ultracut microtome equipped with a diamond knife at a low temperature and were then stained with RuO_4.

Swelling experiments with water were carried out at ambient temperature with specimens cut from the sheet. The dried and weighed specimens were placed in water. They were periodically removed from the water. An excess liquid was removed by blotting with tissue paper, and weighed. Swelling curves were obtained by plotting the ratio of the absorbed water to the dried specimens (wt%) versus time.

Results and discussion

Preparation of PP-Br and PP-*g*-P(PEGMA)

The synthetic route of the PP macroinitiator is shown in Fig. 1.

In the first step, PP-OH possessing hydroxyl groups at the side-chain ends were successfully obtained through the copolymerization of propylene with aluminum-

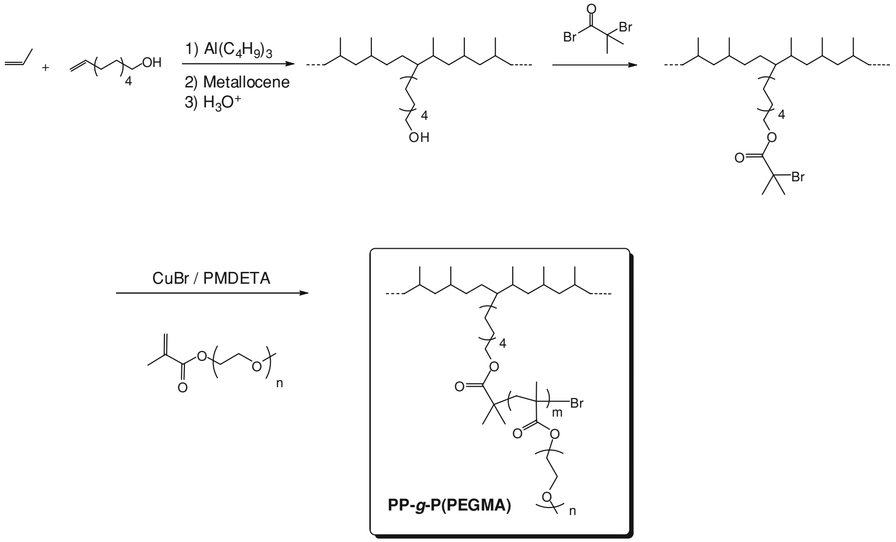


Fig. 1 Synthetic pathway of PP-*g*-P(PEGMA)

capped 10-undecen-1-ol using a metallocene catalyst system. In the second step, the hydroxyl groups in PP-OH were reacted with BiBB to produce a 2-bromoisobutyrate group containing PP (PP-Br) which could initiate the controlled radical polymerization.

Figure 2 shows the ^{1}H NMR spectra of PP-OH and PP-Br. For PP-OH (Fig. 2a), the triplet signals of δ 3.7 ppm are assigned to methylene protons (–CH_2–OH) by reference to a previous paper [26]. For PP-Br (Fig. 2b), other triplet signals of δ 4.1 ppm corresponded to the methylene protons (–CH_2–OCO–) and the single signal of δ 1.8 ppm corresponded to the methyl protons (–OCOC(CH_3)$_2$Br). In contrast, there is a weak signal observable at δ 3.7 ppm corresponding to the methylene protons (–CH_2–OH). This result would indicate 95 mol% of the hydroxyl groups in PP-OH were converted to the 2-bromoisobutyrate groups. From the relative intensities of the signals between the PP backbone and the 2-bromoisobutyrate groups, the content of the 2-bromoisobutyrate groups was calculated to be 0.14 mol% according to ^{1}H NMR measurements. From the number-average molecular weight of the obtained PP-Br ($M_w = 66{,}400$), the average number of the 2-bromoisobutyrate groups as the initiation site can be estimated to be 2.2 units per chain. The thus-obtained PP-Br was used as a macroinitiator for the controlled radical polymerization.

It is well known that transition metal catalyzed radical polymerization results in the controlled radical polymerization of various vinyl monomers, represented by (meth)acrylates, to produce precisely controlled polymers. In particular, it is a very effective method for the synthesis of graft copolymers when using macroinitiators. We applied this method, namely the ATRP method, to create the PP-*g*-P(PEGMA) with the obtained PP-Br as a PP macroinitiator using a CuBr(I)/PMDETA catalyst system.

Since PP-Br was not dissolved at 70 °C in polymerization, the ATRP proceeded as a slurry state. In order to remove the homopolymer, P(PEGMA), contained in the

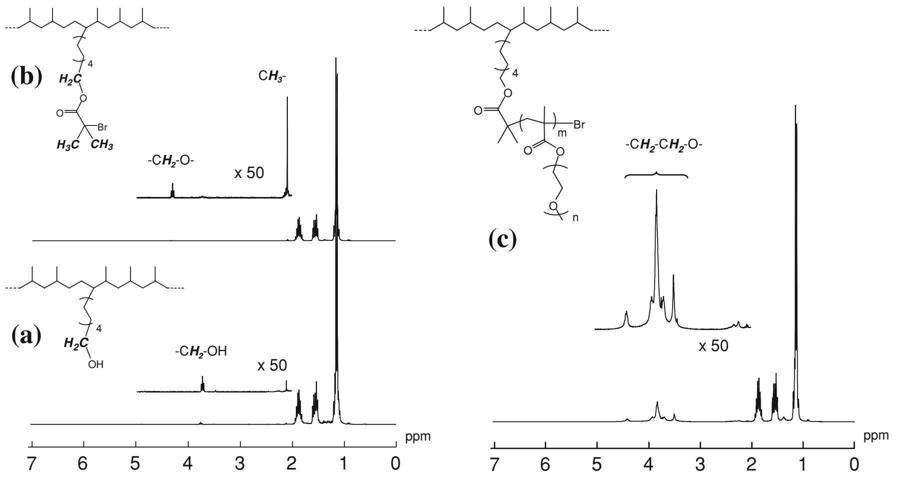


Fig. 2 ^{1}H NMR spectra of PP-OH **a**, PP-Br **b** and PP-*g*-P(PEGMA) (**c**, Run 1)

obtained graft copolymer, the polymers were purified by Soxhlet extraction with boiling methanol. The results of ATRP are summarized in Table 1. The purified graft copolymers were analyzed by ^{1}H NMR at 120 °C in *o*-dichlorobenzene-d$_4$ as a solvent. The ^{1}H NMR spectra of some purified graft copolymer (Run 1 in Table 1) is shown in Fig. 2c. From the ratio of the integrated intensities between both signals assigned to propylene and polar monomer units, the content of the polar segments in the graft copolymers could be calculated as shown in Table 1.

Molecular weight of each purified PP-*g*-P(PEGMA) was measured by GPC. The GPC traces of purified PP-*g*-P(PEGMA) (Run-2 and Run-4, PP-Br as a control) are shown in Fig. 3. In all the cases, the GPC curves showed monomodal molecular weight distributions, and a high molecular weight tailing was not observed, suggesting no radical coupling reaction under those polymerization conditions. The peak maximum of the GPC curves of PP-*g*-P(PEGMA) gradually shifted to the higher molecular weight regions compared with PP-Br, which indicates the successful chain extension of P(PEGMA) from the PP-Br macroinitiator.

Figure 4 shows TEM micrographs of the resulting polymers, stained by RuO$_4$ as the minor component P(PEGMA) in a PP matrix. The TEM images of these resulting polymers revealed the microphase-separation morphology at the nanometer level between PP and P(PEGMA) segments compared with the image of the PP/P(PEGMA) blend, and distinctive morphologies were observed at different P(PEGMA) contents.

These results would indicate that PP-*g*-P(PEGMA) was successfully synthesized.

Properties of PP-*g*-P(PEGMA)

Thermal and hydrophilic properties of resulting graft copolymers are summarized in Table 2. The melting temperature (T_m) and heat of fusion (ΔH_{whole}) were apparently changed after graft copolymerization. In the DSC data, T_m of PP-Br was 156.3 °C [fusion enthalpy (ΔH) = 103 J/g]. Melting points of PP-*g*-P(PEGMA) graft copolymers were observed around 160 °C for each P(PEGMA) content at a range from 17.8

Table 1 Results of ATRP[a] of PEGMA with PP-Br

Run number	PEGMA		Xylene (ml)	Polymerization time (h)	Yield (g)	P(PEGMA) contents[b] (wt%)
	M_n	mmol				
1	350	300	300	0.5	29.93	17.8
2	350	300	300	1.0	37.14	30.9
3	350	300	300	2.0	50.12	49.5
4	350	450	250	2.0	59.93	57.4
5	1100	100	300	2.0	27.92	10.6
6	1100	100	300	1.0	30.55	17.8
7	1100	200	200	2.0	46.22	46.0

[a] Polymerization conditions; PP-Br (25 g), PEGMA and xylene in a 500-ml glass reactor, 70 °C. Catalysts CuBr(I)/PMDETA = 1.0 mmol/2.0 mmol

[b] Estimated by ^{1}H NMR

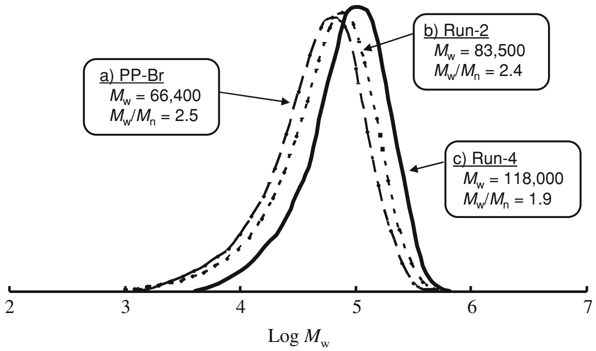
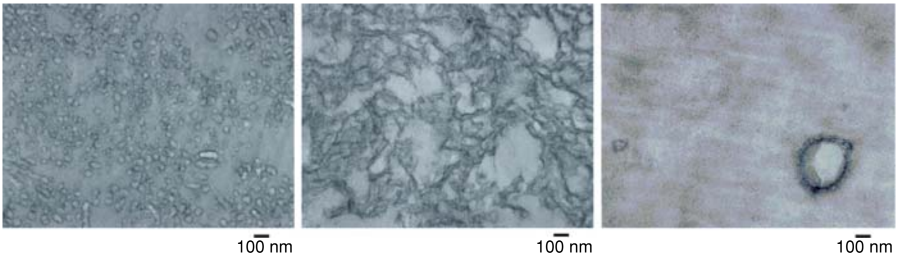


Fig. 3 GPC curves of **a** PP-Br and PP-*g*-P(PEGMA) [**b** Run-2, **c** Run-4]



Run 2 Run 4 PP/P(PEGMA) blend

Fig. 4 TEM images of PP-*g*-P(PEGMA)

Table 2 Properties of PP-*g*-P(PEGMA)

Run number	P(PEGMA) contents[a] (wt%)	T_m^b (°C)	ΔH_{whole}^b (J/g)	ΔH_{pp}^c (J/g)	Contact angle[d] (°)
1	17.8	159.9	82.9	100.9	83
2	30.9	160.7	65.3	94.5	77
3	49.5	160.1	48.4	95.8	59
4	57.4	160.8	38.2	89.7	52
5	10.6	159.2	87.4	97.8	86
6	17.8	160.5	80.2	97.6	79
7	46.0	160.4	48.1	89.1	45
(PP-Br)	–	156.3	103.0	103.0	101

[a] Estimated by ^{1}H NMR

[b] Determined by DSC

[c] Estimated from the values of ΔH_{whole} and PP contents in block copolymers

[d] Measured with water

to 58.3 wt%. Though ΔH_{whole} values of the resulting graft copolymers decreased with increasing contents of PEGMA, the ΔH_{pp} values, which indicated net heat of fusion for the PP segments, were constant (around 100 J/g). These results could suggest that the crystallinity of the PP segment was kept for each P(PEGMA) content.

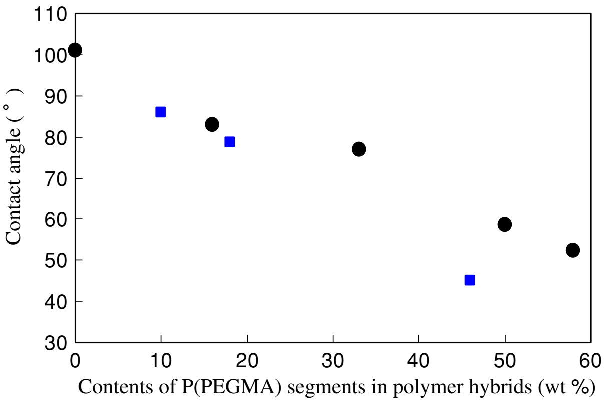


Fig. 5 Relationship between contents of P(PEGMA) segments in PP-*g*-P(PEGMA) and contact angle, *filled circle* PEGMA ($M_n = 350$), *filled square* PEGMA ($M_n = 1,100$)

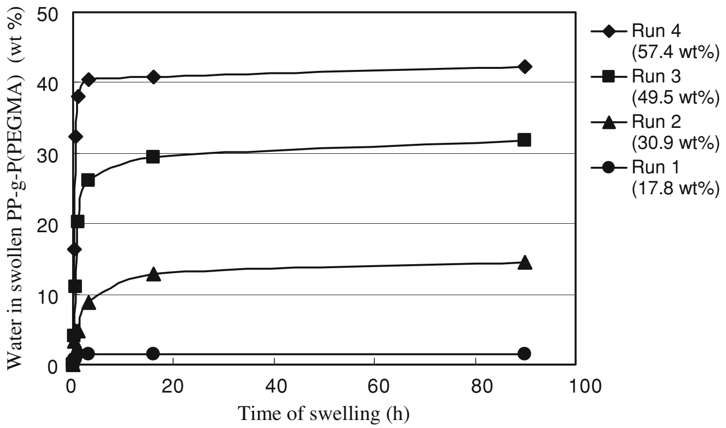


Fig. 6 Swelling curves of PP-*g*-P(PEGMA) in water

The obtained PP-*g*-P(PEGMA) showed a good hydrophilicity. In Fig. 5, the contact angles with water on the PP-*g*-P(PEGMA) specimens decreased with increasing contents of PEGMA. The value of the contact angle of the specimen was 52° when the content of the P(PEGMA) segment (whose M_n of PEGMA was 350) was 57.4 wt% in the graft copolymer. In the case of PEGMA ($M_n = 1,100$), the value of the contact angle was 45° when the content of the P(PEGMA) segment in the graft copolymer was 46.0 wt%.

Figure 6 shows characteristic swelling curves of the synthesized graft copolymers, PP-*g*-P(PEGMA) (PEGMA; $M_n = 350$), in water. In the case of the Run 1 sample, the percentage of water in the swollen graft copolymer was very small, 1.8 wt%. In contrast, the one in Run 4 reached equilibrium swelling in about 3 h with the weight fraction of water being over 40 wt%. These results show that the amounts of water in the swollen graft copolymer are related to the amount of P(PEGMA) segments in the graft copolymer. From this result, it is thought that the PP-*g*-P(PEGMA) possessed good potential as a water absorption material.

Conclusion

We have successfully synthesized PP-*g*-P(PEGMA) by ATRP of PEGMA with PP-Br, which was synthesized from PP-OH prepared by metallocene-catalyzed copolymerization. These structures were confirmed by ^{1}H NMR analysis. TEM micrographs of the PP-*g*-P(PEGMA) indicate the nanometer level microphase-separation morphology between the PP segment and the P(PEGMA) segment, thus evidence exists for the production of PP-*g*-P(PEGMA). The obtained PP-*g*-P(PEGMA) showed good performance in hydrophilicity as well as good thermostability. Therefore, PP-*g*-P(PEGMA) is expected to be good for hydrophilic-hydrophobic graft copolymers.

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