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SYNTHESIS OF POLYPROPYLENE-POLY(METH)ACRYLATE BLOCK COPOLYMERS USING METALLOCENE CATALYZED PROCESSES AND SUBSEQUENT ATOM TRANSFER RADICAL POLYMERIZATION

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SYNTHESIS OF POLYPROPYLENE-POLY(METH)ACRYLATE BLOCK COPOLYMERS USING METALLOCENE CATALYZED PROCESSES AND SUBSEQUENT ATOM TRANSFER RADICAL POLYMERIZATION

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ABSTRACT

The synthesis of block copolymers containing low molar mass polypropylene and poly(meth)acrylates is reported. Vinyl-terminated polypropylene ($M_{n\,SEC} = 3{,}100$; $M_w/M_n = 1.45$) was used to prepare a macroinitiator for atom transfer radical polymerization (ATRP) via hydrosilation with 1-(2-bromoisobutyryloxy)propyl-tetramethyldisiloxane. Polar segments were then incorporated to polypropylene by chain extension using either methyl methacrylate, or *n*-butyl acrylate. While blocking efficiency was limited in this system, well-defined PP-*b*-PMMA ($M_n = 22{,}220$; $M_w/M_n = 1.14$) was obtained by extraction of unreacted polypropylene with diethyl ether.

Key Words: Polypropylene copolymers; Polyolefin containing polar segments; Atom transfer radical polymerization (ATRP)

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INTRODUCTION

Polyolefins are important commodity polymers with the largest volume of production due to their low cost and good mechanical properties. However, limitations in the range of functionality of many polyolefins often hinder their application in a variety of systems. Thus, the preparation of polyolefin copolymers possessing polar segments is an area of great interest as a route to obtain novel materials with improved properties.[1,2] A wide range of systems have been explored in the design of catalysts that target direct copolymerization of ethylene/α-olefins with polar monomers (e.g., methacrylates) by suppression of monomer interactions with the transition metal complex.[3–5] While the development of new ligands has been a major focus of this research, other approaches, such as transformation of olefin polymerization to alternative polymerization processes have been explored. In particular, the application of controlled/living radical polymerization (CRP) has been conducted in the preparation of polyolefin based block and graft copolymers containing polar segments.

Advantages of the CRP chemistry arise from both facile functionalization of polymers to incorporate initiating functional groups, as well as a high tolerance to a wide range of polymerizable monomers.[6,7] These concepts have been utilized in the preparation of various block and graft copolymers using either functional macroinitiators, or macromonomers.[8,9] Polyolefin containing copolymers have been synthesized using similar synthetic routes. Examples of these materials include the use difunctional and multifunctional polyisobutene as macroinitiators for the chain extension of styrene (Sty), methyl acrylate (MA) and methyl methacrylate (MMA) using atom transfer radical polymerization (ATRP).[10–13] The synthesis of polar graft copolymers was also conducted using ATRP by functionalization of a commercially available poly(ethylene-co-glycidyl methacrylate) copolymers with ATRP initiating groups (e.g., α-halo esters) followed by chain extension with (meth)acrylate monomers.[14] Functional random copolymers of poly-(ethylene-*random*-styrene) and poly(ethylene-*random*-butylene) were also used as macroinitiators for ATRP to incorporate grafts of poly-(meth)acrylates.[15,16]

Among the commercially important polyolefins, polypropylene (PP) has not been used extensively in CRP systems. Recent strategies to introduce CRP initiating sites into PP based materials include copolymerization of propylene with alkoxyamine containing alkenes,[17,18] or chain transfer reactions of PP chains with alkylboranes.[19,20] Subsequent use of these functionalized PP macroinitiators enabled the synthesis of both block and graft copolymers from either nitroxide, or borane mediated polymerizations. While these CRP systems offer the advantage of facile incorporation of initiating moieties into the PP backbone, the range of polymerizable monomers and control of molar mass is compromised relative to other processes.

Recent work by our group, reported the incorporation of activated alkyl halide end-groups to either vinyl or silane terminated poly(dimethylsiloxane) (pDMS) via hydrosilation techniques.[13,21,22] From this approach, the ability to convert vinyl, or silane terminated polymers into a macroinitiators for ATRP was demonstrated, enabling chain extension of nonpolar macromolecules with polar (meth)acrylate monomers.

Herein, we report the synthesis of polypropylene-*block*-poly(methyl methacrylate) (PP-*b*-PMMA) and polypropylene-*block*-poly(*n*-butyl acrylate) (PP-*b*-PBA) using a tandem approach of a metallocene mediated polymerization of propylene followed by ATRP. The preparation of a functional vinyl-terminated PP was conducted using a zirconocene/methyl aluminoxane catalyst systems that favored β-methyl over β-hydride elimination as the major mode of termination.[3,23] This vinyl-terminated PP was then able to be functionalized and used as a macroinitiator for ATRP to prepare block copolymers containing polar segments.

EXPERIMENTAL

Materials

Karstedt's catalyst (platinum (0) divinyldisiloxane complex in xylenes), 1,1,3,3-tetramethyldisiloxane were purchased from Gelest and used as received. Copper (I) bromide and 4,4′-(di-5-nonyl)-2,2′-bipyridine were purified and prepared as detailed in previous reports.[24] *n*-Butyl acrylate and methyl methacrylate (Acros) were stirred over calcium hydride and distilled before use. Allyl 2-bromoisobutyrate (Aldrich) and 2-methyl-1,4-napthoquinone (Aldrich) were used as received.

Characterization

^{1}H NMR was conducted using a 300 MHz Bruker spectrometer using the Tecmeg software package for data analysis. ^{1}H NMR experiments were all done in deuterated chloroform ($CDCl_3$). Size exclusion chromatorgraphy was performed in HPLC grade tetrahydrofuran delivered using a Waters 515 isocratic pump, through PSS styragel columns with pore sizes 10^5 Å, 10^3 Å and 10^2 Å. A Waters 2410 differential refractometer was also employed to detect elution of polymer products.

Synthesis of Vinyl-Terminated Polypropylene

The polymerization of propylene was performed in a 200 mL Buechi glass reactor at constant temperature and propylene pressure, using a [1,2-Bis-(η5-9-fluorenyl)-1-(R)-phenylethane]zirconocene dichloride catalyst.

The autoclave was charged with 100 mL of dry toluene and 42.6 mL of MAO (1.5 M in toluene; ratio Al:Zr = 2000:1), heated to 70°C and charged with 5 bar propylene pressure.

Injecting 35 μmol catalyst started the reaction. The propylene flow and the temperature was controlled and monitored online. The polymerization was stopped after 30 min by quenching with MeOH and the PP was precipitated by pouring the toluene solution into excess acidified MeOH. The product was filtered of, washed exhaustively with MeOH and dried over night at 40°C. The yield was 9.94 g which translates into a catalyst activity of 200 kg PP/(Zr [C_3] h).

Synthesis of 1-(2-Bromoisobutyryloxy)propyltetramethyldisiloxane

An oven dried 100 mL three-neck round bottom flask was cooled under nitrogen and charged with both 1,1,3,3-tetramethyldisiloxane (42.7 mL; 241.5 mmol) and allyl 2-bromoisobutyrate (5 g; 24.15 mmol). The flask was then put into an ice bath and a mixture of Karstedt's catalyst (0.096 mol/L; 5.03 mL; 0.483 mmol) and 2-methyl-1,4-naphtoquinone (0.266 g; 0.966 mmol) in xylene was then added dropwise, leading to a gold homogeneous solution. The mixture was stirred under nitrogen at 30°C for 2 h, then at 50°C for 40 h. The excess of tetramethyldisiloxane and the residual allyl 2-bromoisobutyrate were removed under reduced pressure (5 mmHg) and high vacuum (10^{-7} mmHg). Aliquots were removed after 1 and 2 h of reaction 30°C and after 2, 16, and 40 h at 50°C.

Synthesis of 2-Bromoisobutyrate Functional Polypropylene Macroinitiator

A 50 mL three-neck round bottom flask was backfilled with nitrogen and charged with vinyl-terminated polypropylene (1.5 g; 0.5 mmol). The polymer was dissolved into 3 mL of xylene and 1-(2-bromoisobutyryloxy)-propyltetramethyldisiloxane (7.71 g; 2.5 mmol). A mixture of Karstedt's catalyst (0.096 mol/L; 104.16 μL; 0.01 mmol) and 2-methyl-1,4-naphthoquinone (3.45 mg; 0.02 mmol) in xylene solution was then added dropwise, leading to an orange homogeneous solution. An initial sample was removed, and the mixture was stirred under nitrogen at 20°C for 1 h, then at 50°C for 2 h. Aliquots were removed after 30 and 60 min of reaction at room temperature and after 2 h at 50°C. The polymer was precipitated into 50 mL, redissolved into 10 mL of anhydrous ether and filtered through a 0.2-μm filtration membrane. Ether was evaporated under reduced pressure and a sample was removed for analysis. The polymer was dissolved again in 10 mL of anhydrous ether and precipitated into 100 mL of methanol. The solvents were then evaporated under low (10^{-2} mmHg) to high vacuum (10^{-7} mmHg) for 2 and 4 h, respectively.

Synthesis of Polypropylene-*block*-Poly(Methyl Methacrylate)

The polypropylene-based macroinitiator (0.671 g; 1.16% of Br; 97.4 µmol) in 2.1 mL of xylene, 1.042 mL (9.74 mmol) of MMA and 45.5 µL of diphenyl ether (internal standard, 5% wt/monomer) were placed into a sealed Schlenk flask and were deoxygenated by a bubbling of nitrogen for 30 min. The mixture was frozen into a liquid nitrogen bath and the Schlenk flask was degassed and backfilled with nitrogen. Then, copper(I) chloride (9.64 mg; 97.4 µmol) and dNBipy (39.82 mg: 97.4 µmol) were added to the frozen mixture and the flask was degassed and backfilled with nitrogen 3 times. The liquid nitrogen bath was removed and the mixture was stirred, as it became a dark red liquid. An initial sample was removed and the mixture was stirred at 90°C for 30 h. Aliquots removed during the polymerization after 30 min 1, 2, 4, 6, 8, 20, and 30 h of reaction. The dark viscous mixture obtained was dissolved into 5 mL of THF and precipitated into 100 mL of a MeOH for 12 h at –15°C. The mixture was then filtered, leaving a white powder that was dried under high vacuum (10^{-7} mmHg) for 4 h.

Synthesis of Polypropylene-*block*-Poly(*n*-Butyl Acrylate)

The polypropylene-based macroinitiator (530 mg; 1.05% of Br; 69.6 µmol) in 2 mL of xylene and 1 mL (6.96 mmol) of BA were placed into a sealed Schlenk flask and were deoxygenated by a bubbling of nitrogen for 30 min. The mixture was frozen into a liquid nitrogen bath and the Schlenk flask was degassed and backfilled with nitrogen. Then, copper(I) bromide (9.98 mg; 69.6 µmol), dNBipy (28.5 mg: 69.6 µmol) and *p*-dimethoxybenzene as an internal standard (44.6 mg; 5% wt. monomer) were added to the frozen mixture and the flask was degassed and backfilled with nitrogen 3 times. The liquid nitrogen bath was removed and the mixture was stirred, as it became a dark red liquid. An initial sample was removed and the mixture was stirred at 90°C for 48 h. Aliquots removed during the polymerization after 1, 2, 4, 6, 8, 24 and 48 h of reaction. The dark viscous mixture obtained was dissolved into 5 mL of THF and precipitated into 100 mL of a MeOH/H_2O (80/20) for 12 h at –15°C. The polymer obtained was dissolved in 10 mL of ether and precipitated again into 100 mL of a MeOH/H_2O (80/20) for 12 h at –15°C.

RESULTS/DISCUSSION

Synthesis of 2-Bromoisobutyrate Terminated PP

The starting material, vinyl-terminated PP, was prepared by coordination polymerization using a zirconocene catalyst with methyl aluminoxane (MAO) as a cocatalyst. Key features of PP synthesized from this catalytic system was the low molar mass and presence of terminal vinyl groups at one chain end of the polymer. Additionally, the atactic stereochemistry of the backbone (isotacticity = 32%), enabled facile dissolution of PP in a variety of organic solvents. Molecular weight, assessed by ^{13}C NMR and ^{1}H NMR (Fig. 1) from the integration ratio of carbon signals from the chain to carbon signals from the double bond was determined to be $M_{nNMR} = 3{,}000$ g/mol. SEC measurements relative to linear polystyrene standards also indicated comparable molar masses relative to NMR ($M_n = 3{,}100$; $M_w/M_n = 1.45$), indicating a high degree of functionality.

The attachment of 2-bromoisobutyrate groups as initiators for ATRP to PP was conducted via hydrosilation reactions. Two general synthetic strategies were attempted. In the first route, vinyl terminated PP was reacted with chlorodimethylsilane (CDS) via platinum catalyzed hydrosilation, followed by reduction of the silyl chloride end-group via lithium aluminum hydride ($LiAlH_4$). The silane terminated PP (PP-SiH) was then reacted with allyl 2-bromoisobutyrate (ABiB) via hydrosilation to incorporate ATRP initiating groups (Sch. 1a). In the second route, a difunctional coupling agent, 1-(2-bromoisobutyryloxy)propyltetramethyldisiloxane (BTDS, Sch. 1b), bearing both silane (Si-H) and 2-bromoisobutyrate groups was first prepared by hydrosilation using a large excess of volatile 1,1,3,3-tetramethyldisiloxane (TMDS). The macroinitiator for ATRP was then prepared by a second hydrosilation reaction of vinyl terminated PP with the BTDS (Sch. 1b).

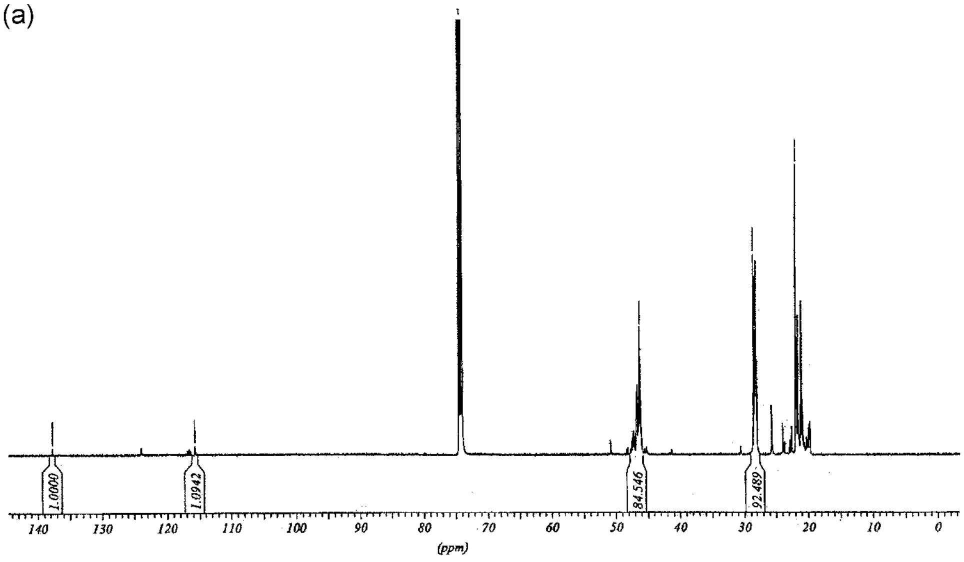


Figure 1. a) ^{13}C NMR of vinyl-terminated PP prepared via zirconocene catalyzed processes; b) ^{1}H NMR of vinyl-terminated PP prepared via zirconocene catalyzed processes.

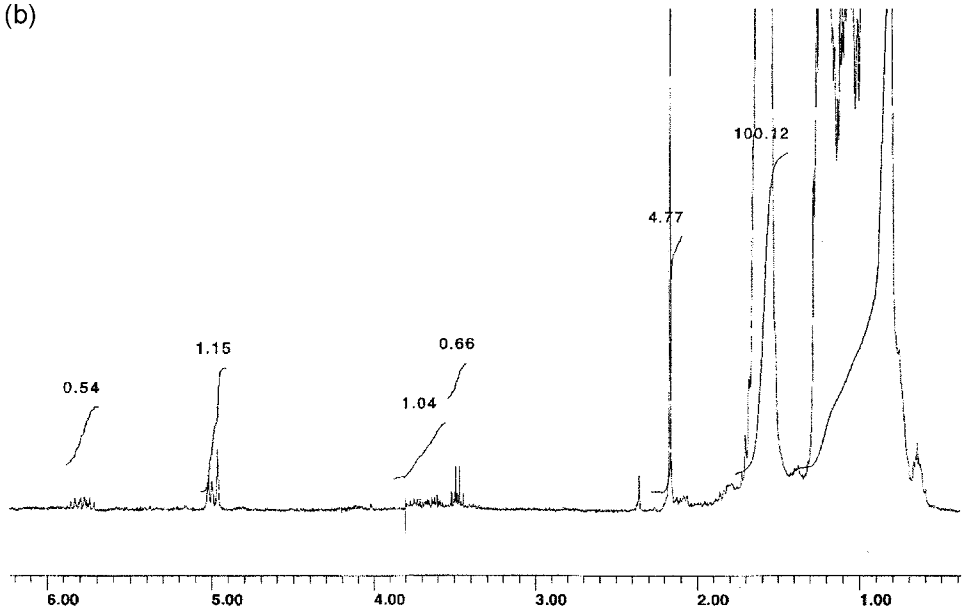
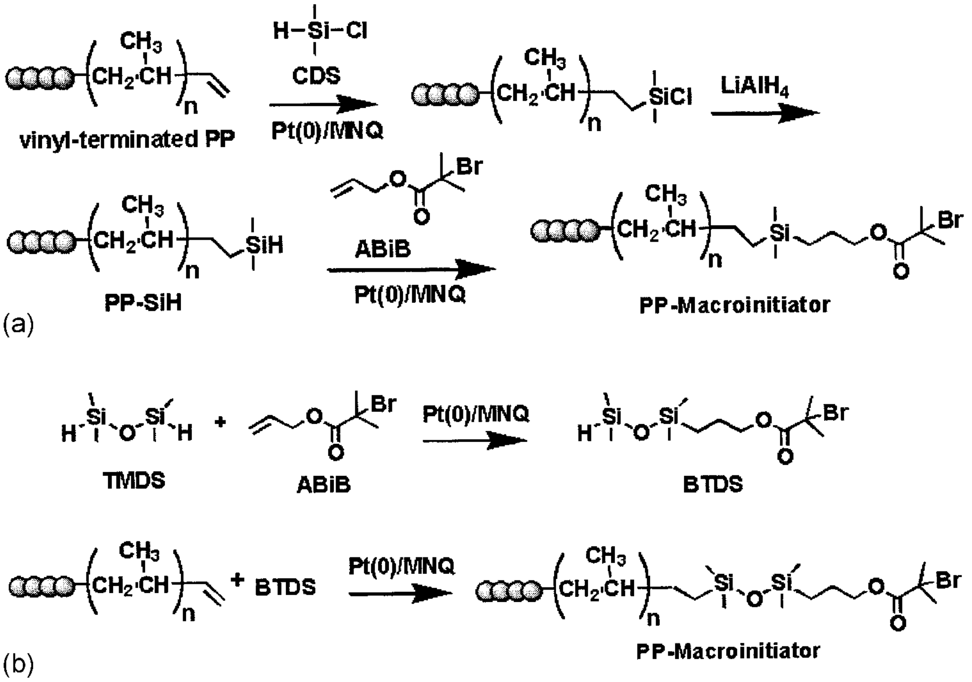


Figure 1. Continued.



Scheme 1. (a) Synthesis of 2-bromoisobutyrate functional PP macroinitiator by hydrosilation of vinyl terminated PP, reduction of silane functional PP and second hydrosilation reaction with allyl 2-bromoisobutyrate; (b) Synthesis of PP macroinitiator via synthesis of 1-(2-bromoisobutyryloxy)propyltetramethylsiloxane followed by hydrosilation with vinyl terminated PP.

Of the two approaches to prepare PP macroinitiators, the second route (Sch. 1b) was more successful. Difficulties were encountered in the first route to prepare the macroinitiator due to low yields for reactions with PP. While the first hydrosilation reaction of vinyl teriminated PP with chlorodimethylsilane (CDS) proceeded to completion, the reduction step to transform the chlorosilyl group (Si-Cl) to the silane (Si-H) was difficult to optimize, resulting in yields less than 80%. For this reason, a difunctional silane (BTDS, Sch. 1) was first prepared by the hydrosilation of 1,1,3,3-tetramethyldisiloxane (TMDS) with ABiB in the presence of Karsedt's catalyst and 4-methylnapthylquionone (MNQ) [22]. The hydrosilation reaction apparently proceeded to high conversion (>95%) as determined from ^{1}H NMR. The second hydrosilation step of BTDS with vinyl terminated PP was then performed and complete consumption of vinylic protons from PP at $\delta = 5.8$ and 5.0 ppm was also observed from ^{1} H NMR (Fig. 2).

ATRP of Methyl Methacrylate Using PP Macroinitiators

To incorporate polar segments to the PP macroinitiator, the ATRP of MMA was conducted. To maximize the efficiency of blocking, the halogen exchange technique via ATRP was employed where the 2-bromoisobutyrate

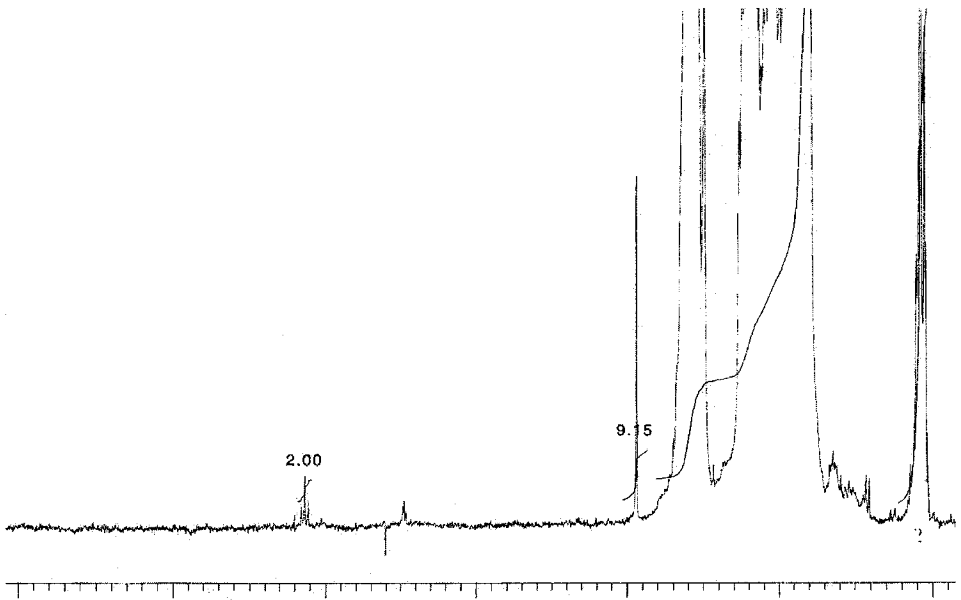


Figure 2. ^{1}H NMR of 2-bromoisobutyrate functional PP macroinitiator synthesized by hydrosilation of vinyl terminated PP and BTDS.

functional macroinitiator was chain extended with MMA using a copper(I) chloride (Cu(I)Cl) based catalyst system. To insure proper activity and homogeneity, 2 molar equivalents of 4,4′-di(5nonyl)-2,2′-bipyridine (dNbpy) relative to Cu(I)Cl was added to solubilize the complex.

After 30 h at 90°C, the polymerization mixture remained dark red and homogeneous throughout the process. Monomer conversion was determined to be 81% (^{1}H NMR and GC) and molar mass was analyzed using SEC ($M_n = 6{,}770$; $M_w/M_n = 2.30$). SEC traces (see Fig. 3) of various kinetic samples taken during the chain extension of PP progressively shifted toward higher molecular weight with increasing conversion. However, a low molar mass peak was observed in the chromatogram due to unreacted PP. The significant amount of residual macroinitiator was attributed to a low degree of functionality of PP with 2-bromoisobutyrate groups. Elemental analysis of the PP macroinitiator revealed that the content of bromine was 1.16 wt%, indicating that less than the half of the polypropylene chains were end-functionalized with a Br-based initiating group before performing ATRP. This could be due to incomplete functionalization of PP in the initial preparation of vinyl-terminated PP, as the subsequent hydrosilation step to attach 2-bromoisobutyrate groups appeared to reach full conversion.

Despite the presence of unreacted PP in the final PP-*b*-PMMA product, isolation of the pure block copolymer was attained by selective extraction of

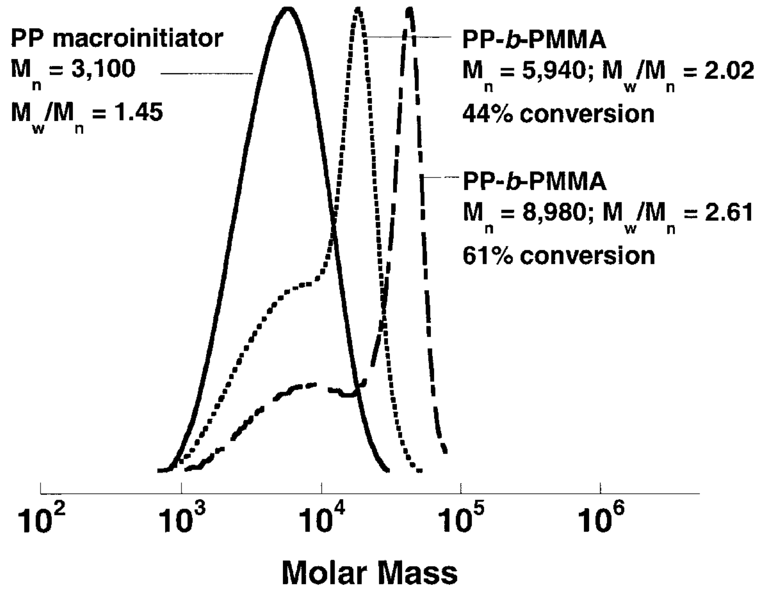


Figure 3. SEC chromatograms of block copolymers prepared by the ATRP of MMA from 2-bromoisobutyrate functional PP.

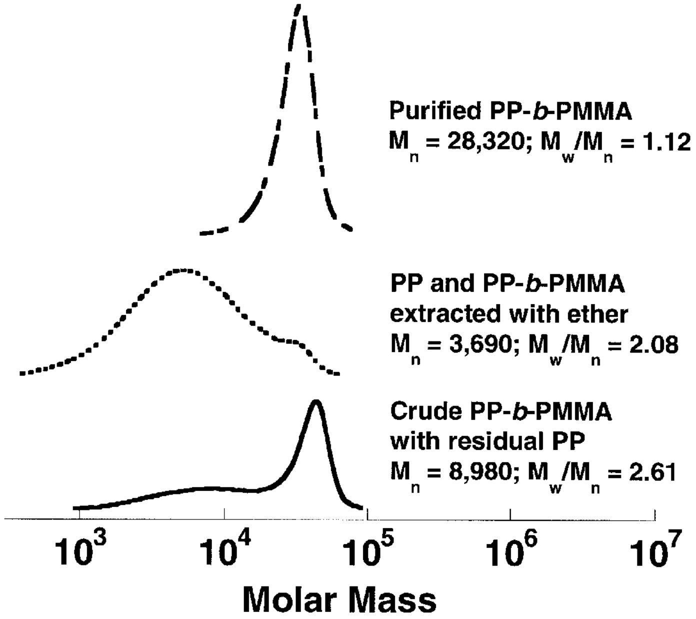


Figure 4. SEC chromatograms of crude PP-*b*-PMMA ($M_n = 6{,}770$; $M_w/M_n = 2.30$) with unreacted PP ($M_n = 3{,}100$; $M_w/M_n = 1.45$). After washing of the crude product with diethyl ether, residual PP extracted away from PP-*b*-PMMA ($M_n = 22{,}200$; $M_w/M_n = 1.14$).

residual homopolymer using diethyl ether. SEC of the product before and after extraction clearly demonstrate the ability to purify the block copolymer using this approach (Fig. 4). Polydispersity of the final PP-*b*-PMMA ($M_n = 22{,}200$) was as low as $M_w/M_n = 1.14$, confirming that the control over the polymerization was present despite inefficient blocking.^{1}H NMR analysis of the fractionated block copolymer also confirmed the presence of both PP (25 mol%) and PMMA (75 mol%) segments (Fig. 5).

ATRP of *n*-Butyl Acrylate Using PP Macrointiator

Polyacrylate segments were also incorporated into PP by the ATRP of *n*-butyl acrylate (BA). Unlike the ATRP of MMA from the 2-bromoisobutyrate functional PP, a copper(I)bromide (Cu(I)Br) based catalyst was used in conjunction with dNbpy. In this case, the halogen exchange process was not necessary due to favorable matching of tertiary alkyl halides as initiators (e.g., α-halo esters) for the ATRP of acrylate monomers [25–27].

After 48 h, a monomer conversion of 61% was observed in the polymerization and SEC of the final product revealed a molar mass of $M_n = 4{,}530$; $M_w/M_n = 2.08$. As for the ATRP of MMA, SEC of PP-*b*-PBA revealed bimodality corresponding to both extended block copolymer and

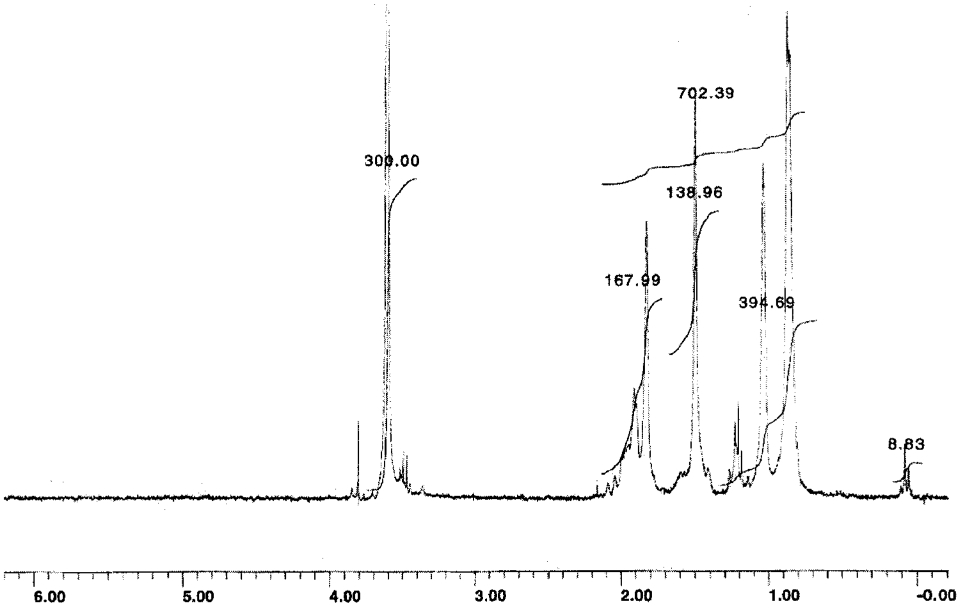


Figure 5. ^{1}H NMR of purified PP-*b*-PMMA ($M_n = 22{,}200$; $M_w/M_n = 1.14$).

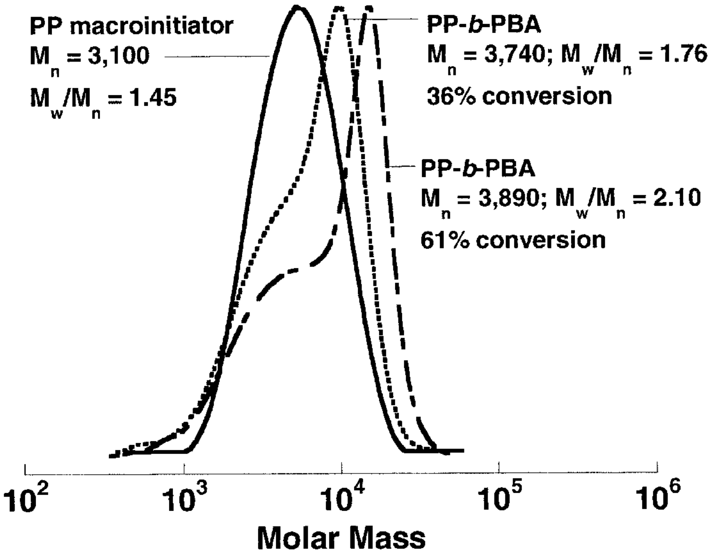


Figure 6. SEC chromatograms of PP-*b*-PBA prepared by the ATRP of BA from 2-bromoisobutyrate PP macroinitiator.

unreacted macroinitiator (Fig. 6). Selective extraction of residual PP was not possible as for the PP-*b*-PMMA copolymers due to comparable solubilities of low molar mass PP and PBA containing polymers. However, the clear shift of M_{peak} towards high values indicate that functionalized chains did grow to higher molar mass, enabling incorporation of the polar PBA segment to the material. This observation is consistent with previous reports that 2-bromoisobutyrate functional polymers can initiate the ATRP of both acrylate and methacrylate monomers to prepare block copolymers.[22]

CONCLUSION

The synthesis of polypropylene block copolymers containing polar poly(meth)acrylates was conducted. By the hydrosilation of vinyl terminated PP with silanes containing 2-bromoisobutyrate groups, polyolefins macroinitiators for ATRP were prepared. This approach enables a wide range of polar (meth)acrylate monomers to be incorporated to nonpolar macroinitiators in a versatile fashion. In particular, the ability to synthesize both PP-*b*-PMMA and PP-*b*-PBA was demonstrated.

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REFERENCES

1. Boffa, L.S.; Novak, B.M. Chem. Rev. **2000**, *100*, 1479–1493.
2. Chung, T.C. Prog. Polym. Sci. **2001**, *27*, 39–85.
3. Brintzinger, H.H.; Fischer, D.; Muelhaupt, R.; Rieger, B.; Waymouth, R.M. Angew. Chem., Int. Ed. Engl. **1995**, *34*, 1143–1170.
4. Coates, G.W. Chem. Rev. **2000**, *100*, 1223–1252.
5. Ittel, S.D.; Johnson, L.K.; Brookhart, M. Chem. Rev. **2000**, *100*, 1169–1203.
6. Matyjaszewski, K. *Controlled Radical Polymerization*; American Chemical Society: Washington, DC, 1997; Vol. 685.
7. Matyjaszewski, K. *Controlled/Living Radical Polymerization*; American Chemical Society: Washington, DC, 2000; Vol. 768.
8. Boerner, H.; Matyjaszewski, K. Macromol. Symp. **2002**, *177*, 1–15.
9. Davis, K.; Matyjaszewski, K. Adv. Pol. Sci. **2002**, *159*, 1–169.
10. Wang, J.-S.; Matyjaszewski, K.J. Am. Chem. Soc. **1995**, *117*, 5614–15.
11. Coca, S.; Matyjaszewski, K.J. Polym. Sci. Part A: Polym. Chem. **1997**, *35*, 3595–3601.

12. Hong, S.C.; Pakula, T.; Matyjaszewski, K. Macromol. Chem. Phys. **2001**, *202*, 3392–3402.
13. Matyjaszewski, K.; Xia, J. Chem. Rev. **2001**, *101*, 2921–2990.
14. Matyjaszewski, K.; Teodorescu, M.; Miller, P.J.; Peterson, M.L. J. Polym. Sci., Part A: Polym. Chem. **2000**, *38*, 2440–2448.
15. Liu, S.; Sen, A. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **2000**, *41*, 1573–1574.
16. Schellekens, M.A.J.; Klumperman, B.; van der Linde, R. Macromol. Chem. Phys. **2001**, *202*, 1595–1601.
17. Stehling, U.M.; Malmstroem, E.E.; Waymouth, R.M.; Hawker, C.J. Macromolecules **1998**, *31*, 4396–4398.
18. Fox, P.A.; Waymouth, R.M.; Hawker, C.J. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **1999**, *40*, 872–873.
19. Chung, T.C.; Lu, H.L.; Janvikul, W. Polymer **1997**, *38*, 1495–1502.
20. Chung, T.C.; Xu, G.; Lu, Y.; Hu, Y. Macromolecules **2001**, *34*, 8040–8050.
21. Nakagawa, Y.; Miller, P.J.; Matyjaszewski, K. Polymer **1998**, *39*, 5163–5170.
22. Miller, P.J.; Matyjaszewski, K. Macromolecules **1999**, *32*, 8760–8767.
23. Lehmus, P.; Kokko, E.; Leino, R.; Luttikhedde, H.J.G.; Rieger, B.; Seppaelae, J.V. Macromolecules **2000**, *33*, 8534–8540.
24. Matyjaszewski, K.; Patten, T.E.; Xia, J. J. Am. Chem. Soc. **1997**, *119*, 674–680.
25. Grimaud, T.; Matyjaszewski, K. Macromolecules **1997**, *30*, 2216–2218.
26. Wang, J.-L.; Grimaud, T.; Matyjaszewski, K. Macromolecules **1997**, *30*, 6507–6512.
27. Matyjaszewski, K.; Shipp, D.A.; Wang, J.-L.; Grimaud, T.; Patten, T.E. Macromolecules **1998**, *31*, 6836–6840.

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