Complex Macromolecular Architectures Utilizing Metallocene Catalysts

Christos Batis, Giorgos Karanikolopoulos, Marinos Pitsikalis, and Nikos Hadjichristidis*

Industrial Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

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ABSTRACT: Graft copolymers having poly(methyl methacrylate), PMMA, backbone and polystyrene, PS, polyisoprene, PI, poly(ethylene oxide), PEO, poly(2-methyl-1,3-pentadiene), P2MP, and PS-*b*-PI branches were prepared using the macromonomer methodology and high-vacuum techniques. The methacrylic macromonomers, mMM, were synthesized by anionic polymerization, whereas their homopolymerization and copolymerization with MMA were performed by metallocene catalysts. Relatively high macromonomer conversions were obtained in all cases. The parameters affecting the polymerization characteristics were examined. Well-defined poly(butyl methacrylate)-*b*-poly(methyl methacrylate) block copolymers were prepared for the first time by sequential addition of monomers starting from *n*-butyl methacrylate. The samples were characterized by size exclusion chromatography, SEC, ^{1}H and ^{13}C NMR spectroscopy, low-angle laser light scattering, LALLS, and differential scanning calorimetry, DSC.

Introduction

Recent advances in polymer chemistry have led to the synthesis of several complex macromolecular architectures by a variety of techniques such as anionic,[1] cationic,[2] group transfer,[3] nitroxide mediated,[4] atom transfer radical,[5] and reversible addition−fragmentation chain transfer polymerization.[6] These developments stimulated tremendous efforts to study the structure−properties relationships and opened a new era in material science, introducing macromolecular architecture as one of the most important parameters influencing materials properties.[7]

Among the different polymerization techniques, metallocene and related transition metal catalyzed polymerizations have attracted a continuously growing academic interest leading to numerous industrial applications.[8] Most of the efforts are dedicated to the polymerization of olefins,[9] but increasing interest has been developed in the past decade in the synthesis of polymethacrylates,[10] especially after the appearance of the mechanistic studies reported by Collins.[11]

Several efforts for the synthesis of complex architectures utilizing metallocene catalysts have been previously reported in the literature. Chung and collaborators developed a route for the synthesis of block and graft copolymers of olefinic monomers with methyl methacrylate, MMA, using borane chemistry.[12] Copolymerization of ethylene and 5-hexenyl-9-BBN was performed using $Et(Ind)_2ZrCl_2$/MAO, Cp_2ZrCl_2/MAO, or $TiCl_3$/$EtAlCl_2$ to yield a linear polyethylene, PE, chain having borane side groups. By selective oxidation of the borane groups, free radical centers were created along the chain from which the polymerization of MMA was initiated to afford PE-*g*-PMMA graft copolymers.[13] Polypropylene, PP, having a vinyl end group was prepared using $Et(Ind)_2ZrCl_2$/MAO as the catalyst system through the termination of the polymerization by β-hydrogen elimination. The olefinic chain end was hydroborated by 9-BBN, and the borane end group was then transformed by oxidation to a polymeric radical, which was used as a macroinitiator to polymerize MMA, thus leading to the synthesis of PP-*b*-PMMA diblock copolymers.[14]

Waymouth and Hawker et al. combined metallocene chemistry and nitroxide mediated living radical polymerization to synthesize PP-*g*-PS and PE-*g*-PS as well as PE-*g*-(PS-*b*-PBd), PE-*g*-(PBd-*b*-PS), PE-*g*-(PS-*b*-PBuA), and PE-*g*-(PBuA-*b*-PBd) graft copolymers where PS is polystyrene, PBuA poly(butyl acrylate), and PBd polybutadiene.[15] The procedure involves the copolymerization of olefins with monomers containing nitroxide functions able to initiate the radical polymerization of styrene or other monomers leading to the formation of the graft structures. Products with broad molecular weight or bimodal distributions were obtained from this method.

Henschke et al. prepared PP-*g*-PS graft copolymers by the copolymerization of propene with allyl-terminated PS macromonomers using the $[Me_2Si(2\text{-Me-Benzind})_2]ZrCl_2$/MAO system.[16] The macromonomers were prepared by anionic polymerization through the termination of living polystyryllithium with allyl bromide at −78 °C. Moderate macromonomer conversions up to 50% were reported for macromonomers having molecular weights ranging from 4000 to 41000.

Shiono and collaborators prepared atactic PP macromonomers through the polymerization of propene with bis(pentamethylcyclopentadienyl)zirconium dichloride/MAO, $Cp_2^*ZrCl_2$/MAO, and termination by β-hydrogen elimination.[17] The PP macromonomers were copolymerized with propene using *rac*-$[Me_2Si(2\text{-Me-Benzind})_2]ZrCl_2$/MAO as the catalytic system to produce atactic PP-*g*-isotactic PP stereo-comb polymers.

The macromonomer method was also employed by Endo et al. to prepare syndiotactic PS-*g*-atactic PS stereo-combs.[18] Anionic polymerization was used to prepare vinylbenzyl-terminated PS macromonomers, which were subsequently copolymerized with styrene using $CpTiCl_3$/MAO as the catalyst. Low copolymerization yields (<20%) were obtained in this study.

ω-Allyl, ω-undecenyl, and ω-vinylbenzyl PS macromonomers were homopolymerized by Lutz et al. using $CpTiCl_3$/MAO or Cp^*TiCl_3/MAO as the catalyst system, with the last macromonomer being the most reactive one.[19] Relatively low conversions (<62%) were obtained for the synthesis of polymacromonomers.

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Höcker et al. have reported the synthesis of PE-*b*-PMMA block copolymer by sequential polymerization of monomers starting from ethylene and using $Me_2C(Cp)(Ind)ZrMe_2/B(C_6F_5)_3$ as the catalytic system.[20] Solubility tests and NMR spectroscopy were used to confirm the success of the synthetic procedure. The size exclusion chromatograms (SEC) of the final products were compared with the SEC chromatograms of PE homopolymers, prepared under identical conditions with those used for the synthesis of the PE blocks of the block copolymers. The polydispersity indices ranged between 2.4 and 2.6, and the MMA conversion was close to 77%.

PP-*b*-PMMA diblock copolymers were prepared by sequential monomer addition.[21] When *rac*-$Et(Ind)_2ZrCl_2$ was used as catalyst both blocks were isotactic, whereas with $Me_2Si(C_5Me_4)(tBuN)TiMe_2$ as the catalyst the PP block was atactic and the PMMA block was syndiotactic. Contamination of the block structures with homopolymers was reported.

Rare earth metal complexes [Sm(II), Y(III), Sm(III)] were employed by Yasuda and collaborators for the synthesis of block copolymers of several polymethacrylates with poly(1-hexene), poly(1-pentene), polycaprolactone, and PE. Well-defined copolymers of the A−B, A−B−A, and A−B−C type were prepared in most cases.[22]

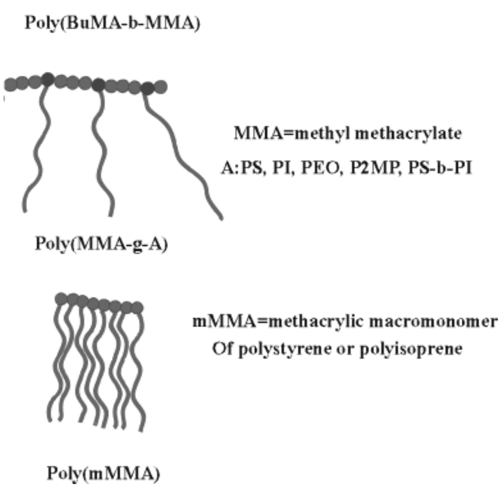
The synthesis of graft copolymers having PMMA backbones and PS, PI, or PDMS branches, where PI is polyisoprene and PDMS is poly(dimethylsiloxane), was reported using the macromonomer method.[23] The macromonomers were prepared by anionic polymerization and were subsequently copolymerized with MMA using the three-component catalytic system $Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ to synthesize the graft copolymers.

In the present study we report the synthesis of graft co- and terpolymers of the type PMMA-*g*-PS, PMMA-*g*-PI, PMMA-*g*-PEO, PMMA-g−P2MP, and PMMA-*g*-(PS-*b*-PI) [PEO is poly(ethylene oxide) and P2MP is poly(2-methyl-1,3-pentadiene)] by metallocene-catalyzed copolymerization of methacrylic macromonomers, mMM and MMA. We also report the homopolymerization of mMM leading to PS and PI polymacromonomers as well as the sequential polymerization of BuMA with MMA. The catalytic systems used for the synthesis of the graft co- and terpolymers were $Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (1), *rac*-$Et(Ind)_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (2), and *rac*-$Et(Ind)_2ZrMe_2/[Me_2NHPh]^+[B(C_6F_5)_3]^-/ZnEt_2$ (3). The structures synthesized are given in Scheme 1.

Experimental Section

Materials. All manipulations were performed using high vacuum and/or Schlenk techniques. Cp_2ZrMe_2 and *rac*-$Et(Ind)_2ZrMe_2$ were purchased from Aldrich and Strem Chemicals or synthesized according to the literature.[24] Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was prepared according to literature procedures.[25] Tetrakis(pentafluorophenyl)borate dimethylanilinium salt, $[B(C_6F_5)_4]^-[Me_2NHPh]^+$, was synthesized or donated by ExxonMobil.[25a] Diethylzinc ($ZnEt_2$, 97%) was purchased from Fluka. Toluene (Aldrich) was dried and vacuum-distilled from calcium hydride (CaH_2) and metallic sodium, subsequently. Methyl methacrylate (MMA, Merck) and butyl methacrylate (BuMA, Merck) were vacuum-distilled from calcium hydride and/or triethylaluminum ($AlEt_3$). The purification of isoprene (Aldrich, 99%), styrene (Aldrich, 99%), ethylene oxide (EO, Kodak), 2-methyl-1,3-pentadiene (Aldrich), and solvents such as benzene (Aldrich), tetrahydrofuran (THF, Aldrich), pentane (Aldrich), hexane (Aldrich), and diethyl ether (Aldrich), which were used for anionic polymerization, was performed according to standard procedures required for high-vacuum techniques.[26] Methacryloyl chloride was prepared by refluxing an equimolar mixture of benzyl chloride (Aldrich) and methacrylic acid (Aldrich) for several minutes and then collecting the fraction with bp 95−98 °C by fractional distillation. *sec*-Butyllithium (*s*-BuLi) prepared from *sec*-butyl chloride and lithium dispersion was the initiator for the anionic polymerization procedures. Benzyl potassium, prepared under vacuum following literature procedures, was the initiator for the polymerization of ethylene oxide.[27]

Scheme 1



PS Macromonomer. In a 0.5 dm^3 Schlenk type reaction flask, under an argon atmosphere, were subsequently introduced 87.3 mmol of styrene, the appropriate amount of benzene in order to obtain a 10% v/v monomer solution, and 2.725 mmol of *s*-BuLi. The reaction mixture was allowed to stand at room temperature for ca. 24 h, and then a 3-fold excess of ethylene oxide, over the living anionic chains, was added, under an argon atmosphere, via a proper ampule with break-seal. After a few hours a 3-fold excess of freshly distilled methacryloyl chloride (with respect to the living polymer chains) was added to the reaction mixture to terminate the polymerization. The resulting macromonomer was precipitated in methanol, filtered and washed with methanol, dried under high vacuum until constant weight, and characterized by ^1H NMR spectroscopy in order to define the degree of functionalization.

*PI Macromonomer***.** The experimental procedure was analogous to the one reported for the synthesis of the PS macromonomer. The reagents used are an appropriate amount of benzene (to produce a 10% v/v monomer solution), isoprene ampule with 220.2 mmol of freshly distilled monomer, 4.196 mmol of *s*-BuLi, a 3-fold excess of ethylene oxide, and a 3-fold excess of freshly distilled methacryloyl chloride. The resulting macromonomer was precipitated in methanol, filtered and washed with methanol, dried in high vacuum until constant weight, and characterized by ^1H NMR spectroscopy.

PS-b-PI Macromonomer. A procedure similar to the one used for the synthesis of the PS and PI macromonomers was employed, except that the living polymer chain was prepared by the sequential anionic polymerization of styrene and isoprene. 2.4 mmol of *sec*-BuLi, 56.7 mmol of styrene, and 85 mmol of isoprene were used.

PEO Macromonomer. In a 0.5 dm^3 Schlenk type reaction flask, under an argon atmosphere, 193 mmol of EO, the appropriate amount of benzene in order to obtain a 10% v/v monomer solution, and 1.5 mmol of benzyl potassium were subsequently introduced. The polymerization was allowed to proceed for 24 h at room temperature. After that, a 3-fold excess of freshly distilled methacryloyl chloride (with respect to the living polymer chains) was added to the reaction mixture to terminate the polymerization. The macromonomer was precipitated in hexane, filtered, washed, and dried under vacuum.

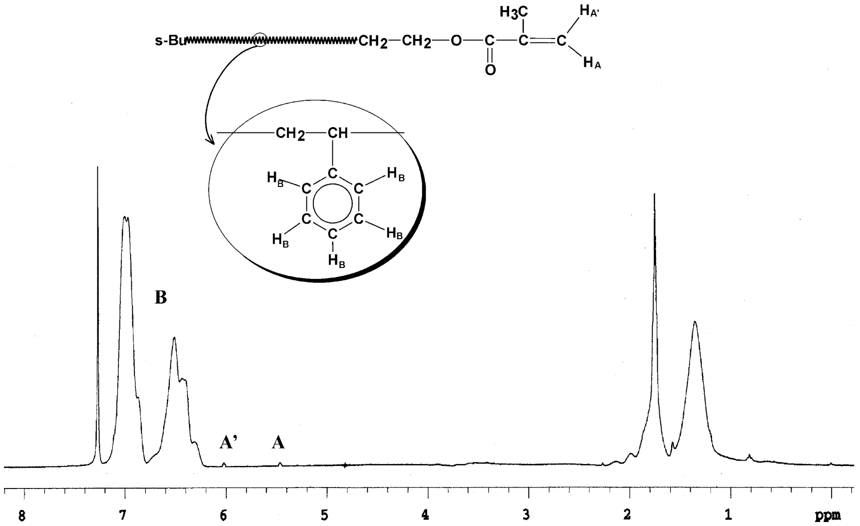


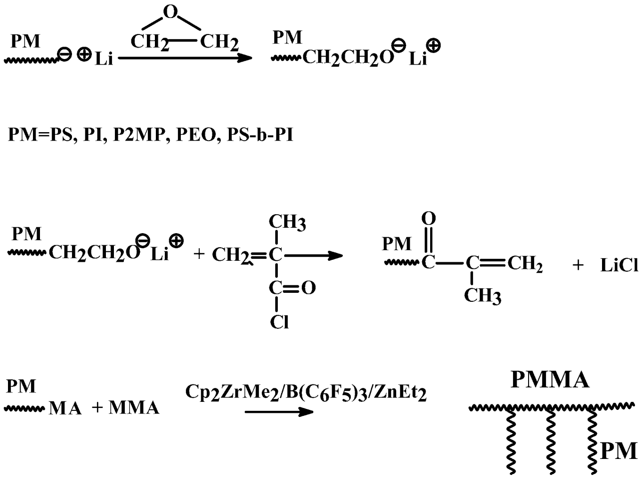
Figure 1. 300 MHz ^{1}H NMR spectrum of the PS macromonomer with M_w = 50 000 in CDCl$_3$ at 25 °C.

Table 1. Synthesis of Graft Co- and Terpolymers of Methyl Methacrylate (MMA), Styrene (S), Isoprene (I), Ethylene Oxide (EO), and 2-Methyl-1,3-pentadiene (2MP)

graft copolymer or terpolymer[a]	catalyst concn (μmol/L)	MMA concn (mmol/L)	MMA/macromonomer (w/w)	macromonomer conversion (%)[b]
PMMA-*g*-PS$_{Cp1}$	300	150	1:0.1	100
PMMA-*g*-PS$_{Cp2}$	750	352	1:0.35	70
PMMA-*g*-PS$_{Cp3}$	980	352	1:1	52
PMMA-*g*-PI$_{Cp1}$[c]	350	200	1:1.16	82
PMMA-*g*-PS$_{Rac1}$[d]	900	350	1:1.3	80
PMMA-*g*-PI$_{Rac1}$[d]	1000	350	1:1.3	80
PMMA-*g*-PEO[e]	1500	340	1:0.56	26[g]
PMMA-g−P2MP[f]	600	280	1:1.1	40
PMMA-*g*-(PS-*b*-PI)$_1$	980	350	1:1	75
PMMA-*g*-(PS-*b*-PI)$_2$	980	80	1:4	50

[a] Polymerization conditions: [MMA]/[ZnEt$_2$] = 4, V_{total} = 60−80 mL, [B(C$_6$F$_5$)$_3$]/[Cp$_2$ZrMe$_2$] = 1.1; polymerization time 24 h at 0 °C. [b] By SEC in THF at 40 °C. [c] Catalyst: Cp$_2$ZrMe$_2$. [d] Catalyst: *rac*-EtInd$_2$ZrMe$_2$. [e] Polymerization time 70 h at 17 °C. [f] Polymerization time 32 h at 0 °C. [g] By SEC in CHCl$_3$ at 40 °C.

Scheme 2



P2MP Macromonomer. The polymerization of 2MP was performed under vacuum at 40 °C for 3 weeks using *sec*-BuLi as initiator (10 g of monomer and 1.39 mmol of initiator), according to literature procedures.[28] The living polymer was terminated after reaction with an excess of methacryloyl chloride, the macromonomer was then precipitated in methanol, filtered and dried under vacuum.

Synthesis of Graft Copolymers and Terpolymers. Copolymerization was carried out at 0 °C except in the case of PEO macromonomer, where the reaction took place at 17 °C, in a 0.5 dm^3 Schlenk type reaction flask. A typical copolymerization process is as follows: in the reaction flask toluene, MMA, and macromonomer were added and were stirred in a 2-propanol bath which was kept at 0 °C. ZnEt$_2$ (mol of Zn/mol of MMA = 1/4) was then injected, and the reaction mixture was left under stirring at 0 °C for 1 h. Afterward, solutions of the boron cocatalyst and the metallocene catalyst were introduced to initiate the polymerization. The polymerization was quenched after 24 h by addition of HCl/methanol ∼ 1/10 solution, and the polymer was precipitated in methanol. The polymer produced was washed with methanol, filtered, and dried under high vacuum at room temperature. The crude products (graft copolymers) were fractionated using toluene/methanol as solvent/nonsolvent system.

Synthesis of Polymacromonomers. A procedure similar to the one reported above was followed for the homopolymerization of macromonomers leading to the synthesis of polymacromonomers. The reaction was allowed to proceed for 68 h prior to termination with HCl/methanol.

Synthesis of Block Copolymers. The copolymerization procedure was carried out at 0 °C in a 0.5 dm^3 Schlenk type reaction flask. A typical polymerization process is as follows: in the reaction flask, toluene and BuMA were added. The mixture was stirred in a 2-propanol bath, which was kept at 0 °C. ZnEt$_2$ (mol of Zn/mol of BuMA = 1/4) was injected, and the reaction mixture was left under stirring at this reduced temperature for 1 h. After this aging period, the appropriate amounts of the metallocene solution in toluene and the cocatalyst solution in toluene were introduced to initiate the polymerization. Upon completion of the polymerization of the first monomer (3−5 h depending on the concentrations of the reaction mixture), MMA, preaged in ZnEt$_2$ (mol Zn/mol MMA = 1/4) for 1 h, was added to the reaction flask, and the polymerization was quenched after 24 h by addition of HCl/

Table 2. Molecular Characteristics of the Graft Co- and Terpolymers of Methyl Methacrylate (MMA), Styrene (S), Isoprene (I), Ethylene Oxide (EO), and 2-Methyl-1,3-pentadiene (2MP)

graft copolymer or terpolymer	macromonomer content[a] (mol %)	$M_{w,macr}{}^{b}$ × 10^{-3}	$M_w/M_{n,macr}{}^{b}$	$M_{w,copol}$ × $10^{-3\,b}$	$M_{w,copol}$ × $10^{-3\,c}$	$M_w/M_{n\ copol}{}^{b}$	no. of branches[d]
PMMA-*g*-PS$_{Cp1}$	34	4.6	1.03	100	450	1.22	33
PMMA-*g*-PS$_{Cp2}$	34	16	1.18	100		1.21	
PMMA-*g*-PS$_{Cp3}$	16	50	1.05	360	600	1.13	2
PMMA-*g*-PI$_{Cp1}$	48	4.7	1.03	180		1.32	
PMMA-*g*-PS$_{Rac1}$	47	4.6	1.03	145		1.22	
PMMA-*g*-PI$_{Rac1}$	42	4.7	1.03	190		1.24	
PMMA-*g*-PEO	14	4.1[e]	1.10[e]	490[e]		1.74[e]	
PMMA-g−P2MP	36	8.5	1.09	25		1.31	
PMMA-*g*-(PS-*b*-PI)$_1$	67	4.6	1.04	110	670	1.34	97
PMMA-*g*-(PS-*b*-PI)$_2$	77	4.6	1.04	73		1.27	

[a] By ^{1}H NMR in $CDCl_3$ at 25 °C. [b] By SEC in THF at 40 °C. [c] By LALLS in THF at 25 °C. [d] Calculated by the molecular characteristics and the composition. [e] By SEC in $CHCl_3$ at 40 °C.

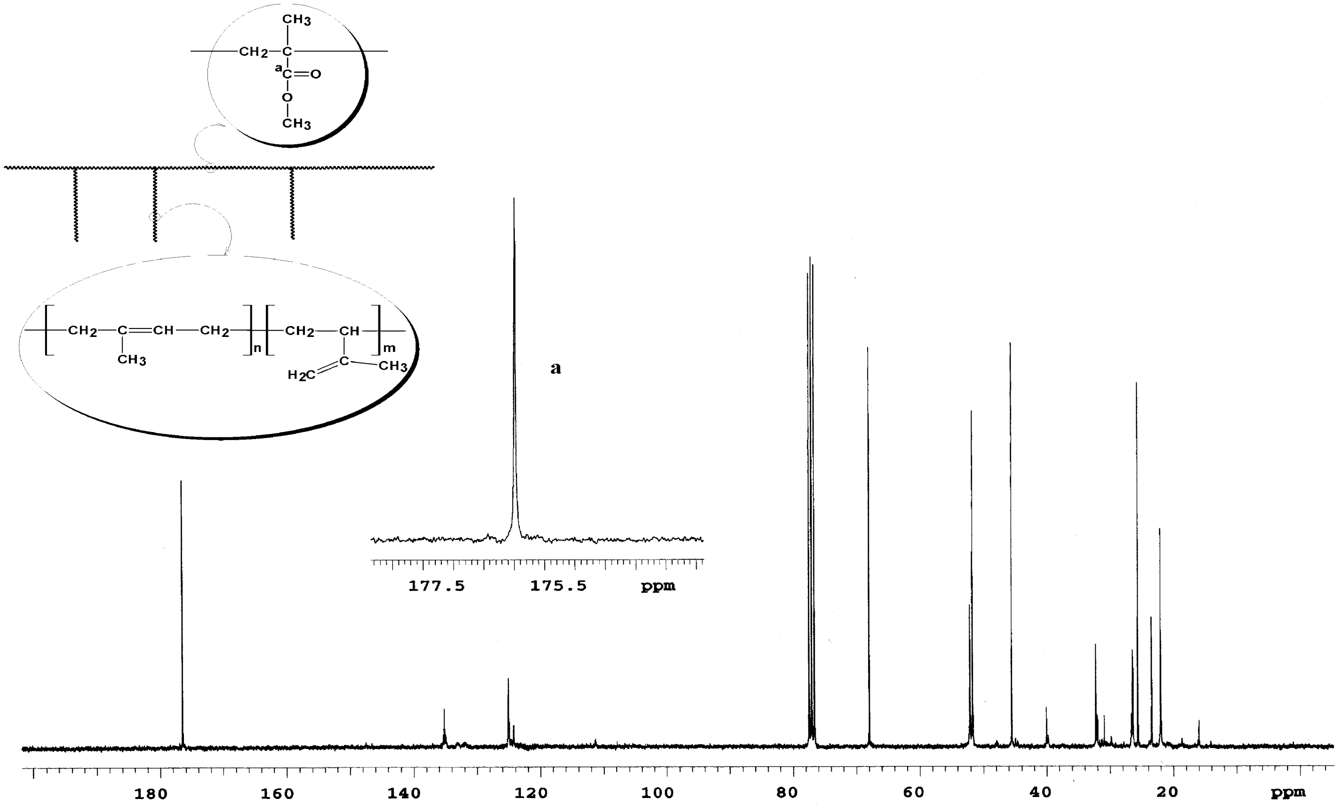


Figure 2. 50 MHz ^{13}C NMR spectrum of the PMMA-*g*-PI$_{Rac1}$ graft copolymer in $CDCl_3$ at 25 °C.

methanol. The block copolymer was precipitated in methanol, washed with methanol, filtered, and dried under high vacuum at room temperature.

All the synthesized polymers were purified by ultracentrifugation and passage through silica column to remove residual inorganic compounds (zinc oxides, catalyst, etc.).

Characterization Techniques. The macromonomers and the fractionated graft copolymers were characterized by size exclusion chromatography (SEC), low-angle laser light scattering (LALLS), and ^{1}H NMR spectroscopy.

SEC experiments were carried out using a modular instrument consisting of a Waters model 510 pump, a Waters model U6K sample injector, a Waters model 401 differential refractometer, and a set of 4 μ-Styragel columns with a continuous porosity range from 10^3 to 10^6 Å. The columns were housed in an oven thermostated at 40 °C. THF was used as the carrier solvent at a flow rate of 1 mL/min. The SEC results were analyzed using PMMA standards. The instrument was calibrated with PS, PI, and PEO standards for the PS, PI, and PEO macromonomers, respectively.

Static light scattering measurements were performed in THF or dimethylformamide (DMF). THF was refluxed over Na metal, whereas DMF was stirred overnight over anhydrous $MgSO_4$ and refluxed over KOH. Both solvents were distilled just prior their use. A Chromatix KMX-6 low-angle laser light scattering LALLS photometer equipped with a 2 mW He−Ne laser operating at $\lambda = 633$ nm was used at 25 °C. Stock solutions were prepared, followed by dilution with solvent to obtain solutions with lower concentrations. All the solutions were optically clarified by filtering through 0.22 μm pore size nylon filters directly into the scattering cell.

Refractive index increments, d*n*/d*c*, at 25 °C were determined using a Chromatix KMX-16 refractometer operating at 633 nm and calibrated with aqueous NaCl solutions.

Copolymer composition, functionalization of macromonomers, and tacticity of the PMMA polymer chains were determined from the ^{1}H and ^{13}C NMR spectra obtained in chloroform-*d* at 30 °C with a Varian Unity Plus 300/54 NMR spectrometer.

Results and Discussion

Synthesis of Graft Copolymers and Terpolymers. The macromonomer methodology, shown in Scheme 2, was adopted for the synthesis of the graft co- and terpolymers.

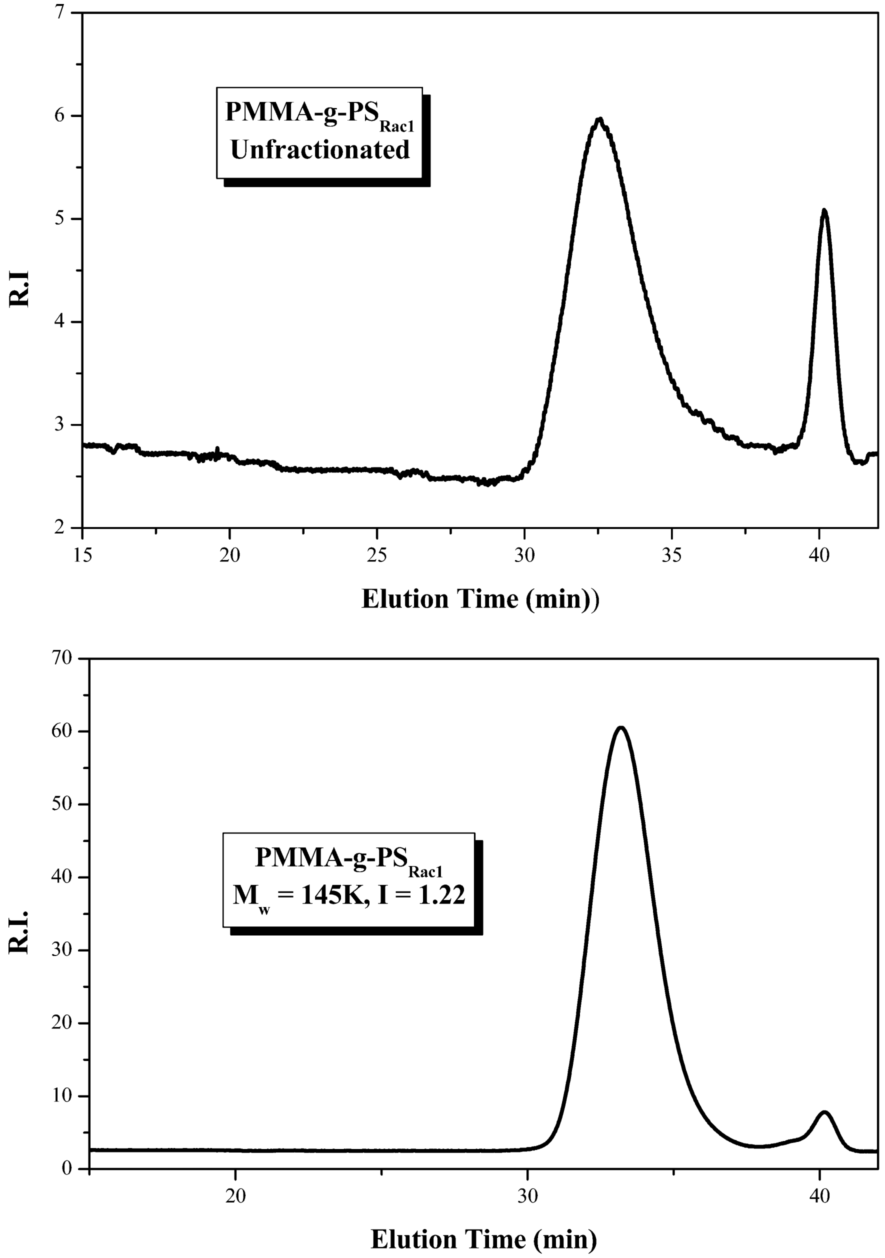


Figure 3. SEC chromatograms of the PMMA-*g*-PS_{Rac1} graft copolymer: (a) crude product (up), (b) fractionated sample (down).

Anionic polymerization was used to produce macromonomers with predetermined molecular weights, narrow molecular weight distributions, and quantitative yields of end-functionalization, according to well-established procedures.[29] The degree of functionalization was checked by ^1H NMR spectroscopy by comparing the area under the signals attributed to the double bonds of the methacryloyl end group (5.5 and 6 ppm) with the appropriate signals of the polymer chain. A characteristic ^1H NMR spectrum is given in Figure 1. Quantitative functionalization yields were obtained in all cases. However, in the case of the macromonomers of higher molecular weights (PS macromonomers with $M_n >$ 23 000) the small contribution of the end group to the overall molecular weight introduced large uncertainties in the determination of the degree of functionalization.

The macromonomers were copolymerized with MMA to prepare the graft copolymers. For the copolymerization reaction three different catalytic systems were used: $Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (1), *rac*-$Et(Ind)_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (2), and *rac*-$Et(Ind)_2ZrMe_2$ /$[Me_2NHPh]^+$-$[B(C_6F_5)_3]^-/ZnEt_2$ (3). In a previous study the catalytic system (1) was utilized for the synthesis of graft copolymers having PMMA backbones and PS, PI, or

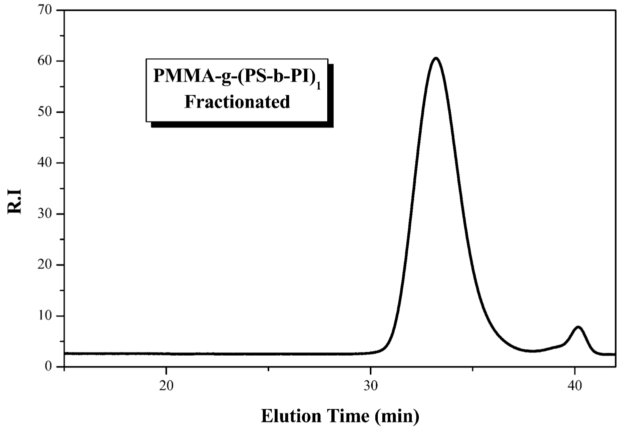


Figure 4. SEC chromatogram of the fractionated PMMA-*g*-(PS-*b*-PI)$_1$ graft terpolymer.

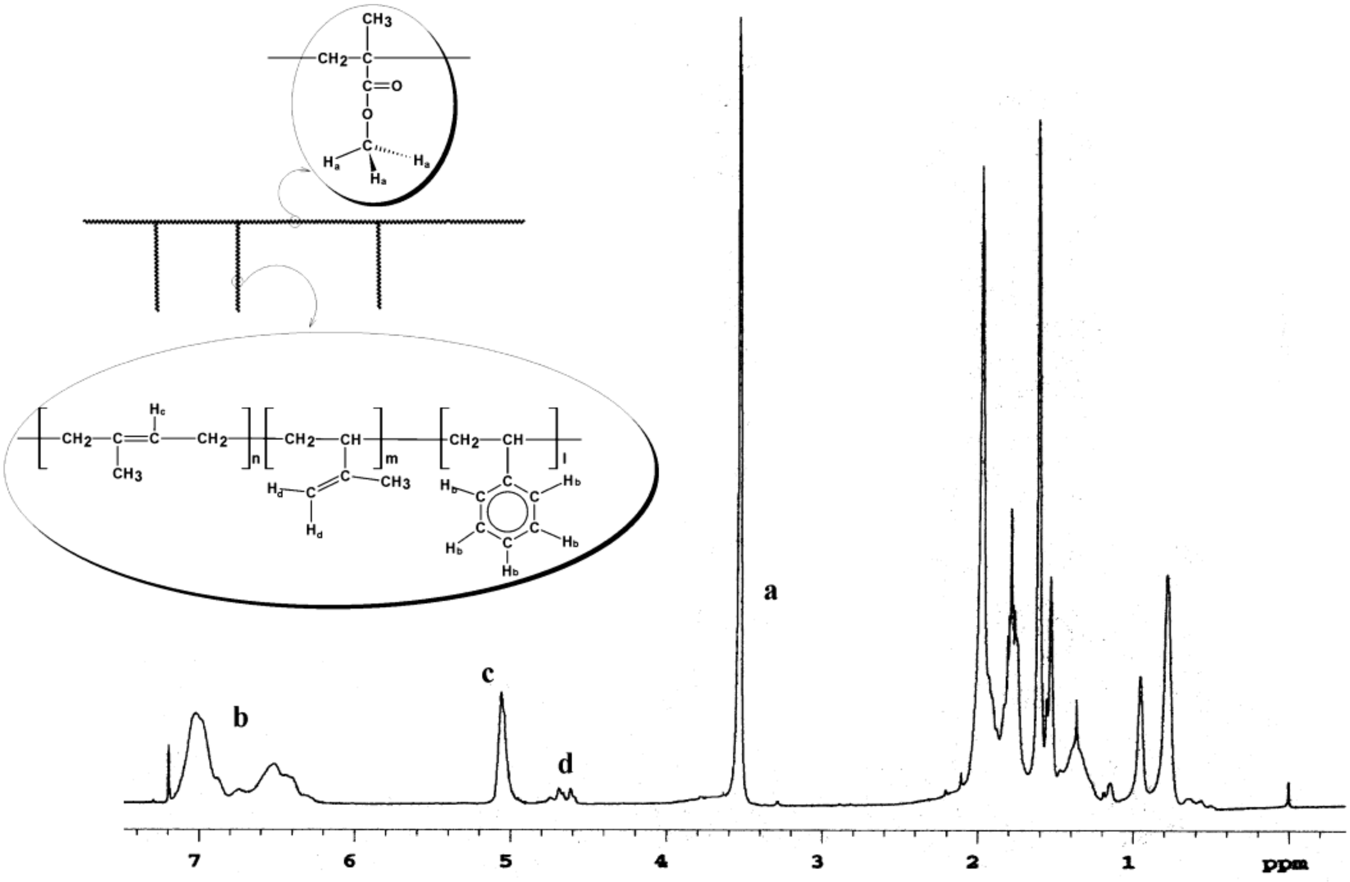


Figure 5. 300 MHz ^{1}H NMR spectrum of the PMMA-*g*-(PS-*b*-PI)$_1$ graft terpolymer in CDCl$_3$ at 25 °C.

PDMS side chains. It was concluded that both the flexibility of the macromonomer and the MMA/macromonomer ratio affect the degree of macromonomer insertion in the graft structure.

In the present study PS macromonomers having high molecular weights were prepared with the catalytic system (1) in order to study the effect of the macromonomers' molecular weight on the copolymerization characteristics. For comparison, the results of a low molecular weight PS macromonomer are presented. The data are reported in Tables 1 and 2 (entries 1−3). It is evident that increasing the molecular weight of the macromonomer results in decreasing macromonomer conversions and number of grafted chains for the same MMA/macromonomer molar ratio. This conclusion is in agreement with previous studies concerning the synthesis of graft copolymers using the macromonomer method.[30] The reactivity of the macromonomer is reduced with the increase of its molecular weight. However, even in the case of the PS macromonomer with the highest molecular weight, the conversion was higher than 52%. This is direct evidence that the catalyst is very reactive for the polymerization of the methacryloyl end groups. The relatively narrow molecular weight distributions of the graft copolymers show that the termination reactions are minimized and that the polymerization proceeds in a controlled manner.

The effect of the nature of the catalytic system was examined using the system (2) for the synthesis of PMMA-*g*-PS and PMMA-*g*-PI graft copolymers utilizing macromonomers of low molecular weights, as shown in Tables 1 and 2 (entries 5 and 6). In previous studies catalysts bearing bridges between the cyclopentadiene groups or the indenyl and the cyclopentadiene group were used.[31] This bridging leads to a widening of the angle between the planes which are defined by the Cp or their derivatives ligands, so that the metal center becomes less constrained and more available for the complexation of the coming monomers and the growing polymer chain. In our previous study it was shown that the catalytic system (2) compared to (1) polymerizes MMA slower but in a more controlled fashion, leading to products of narrow molecular weight distribution.[31] In addition, the PMMA produced by (2) is almost 100% isotactic, whereas the PMMA produced by (1) is mainly syndiotactic. The results idicate that the conversion of both PS and PI macromonomers is similar using the catalytic system (2) for the same MMA/macromonomer ratio, whereas as was reported for system (1) the conversion increases with the flexibility of the macromonomer. The different behaviors of the two systems are a manifestation of their different stereochemistries. Catalyst (1) has a higher ligand mobility compared with catalyst (2), where the indenyl ligands are fixed with the ethyl bridge. Consequently, in the latter case the

Table 3. Synthesis of Poly(methacrylic macromonomers) of Polystyrene (PS) and Polyisoprene (PI)[a]

polymacromonomer	catalyst concn (mmol/L)	macromonomer concn (mmol/L)	macromonomer conversion (%)[b]
PPS$_{Cp}$[c]	1.98	11	63
PPI$_{Cp}$[c]	1.98	7.3	90
PPI$_{Rac}$[d]	1.33	7.3	30

[a] Polymerization conditions: [MMA]/[ZnEt$_2$] = 4, V_{total} = 60 mL, [B(C$_6$F$_5$)$_3$]/[catalyst] = 1.1; polymerization time 68 h at 0 °C. [b] By SEC in THF at 40 °C. [c] Catalyst: Cp$_2$ZrMe$_2$. [d] Catalyst: *rac*-EtInd$_2$ZrMe$_2$.

Table 4. Molecular Characteristics of the Poly(methacrylic macromonomers) of Polystyrene (PS) and Polyisoprene (PI)

polymacromonomer	$M_{\mathrm{w,macr}}{}^{a} \times 10^{-3}$	$M_w/M_{\mathrm{n,macr}}{}^{a}$	$M_{\mathrm{w,comb}}{}^{a} \times 10^{-3}$	$M_{\mathrm{w,comb}}{}^{b} \times 10^{-3}$	$M_w/M_{\mathrm{n,comb}}{}^{a}$	no. of branches[c]
$\mathrm{PPS_{Cp}}$	3.1	1.03	39	88	1.09	28
$\mathrm{PPI_{Cp}}$	4.8	1.15	29.5		1.05	
$\mathrm{PPI_{Rac}}$	4.8	1.15	30.5		1.03	

[a] By SEC in THF at 40 °C. [b] By LALLS in THF at 25 °C. [c] Calculated by the molecular characteristics.

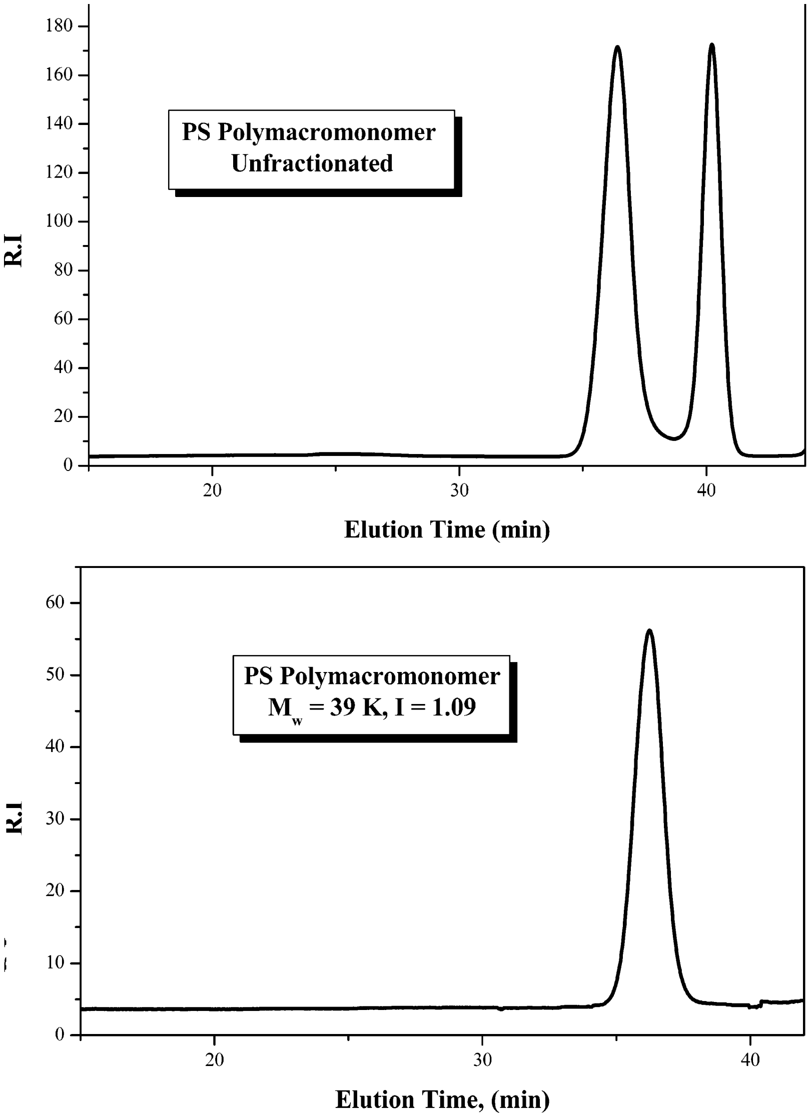


Figure 6. SEC chromatograms of the PS polymacromonomer: (a) crude product (up); (b) fractionated sample (down).

stereochemistry of the active catalytic center plays the most important role in combination with the nature of the polymerizable end group, for either a PS or a PI macromonomer. As expected, the catalytic system (2) produced graft copolymers with an isotactic PMMA backbone, as was determined from the ^{13}C NMR spectra. An example of the PMMA-*g*-$\mathrm{PI_{Rac1}}$ graft copolymer is given in Figure 2. The SEC chromatogram of the sample PMMA-*g*-$\mathrm{PS_{Rac1}}$ before and after the fractionation is displayed in Figure 3.

To further explore the effect of the nature of the macromonomer on the copolymerization behavior with metallocene catalysts, PEO and P2MP macromonomers with methacryloyl end groups were prepared by anionic polymerization (Tables 1 and 2, entries 7 and 8). PEO is a flexible polymer but crystallizes at 10 °C. For this reason the copolymerization took place at 17 °C. It was found that performing the polymerization of MMA at higher temperatures leads to lower molecular weights, broader molecular weight distributions, and lower yields due to the acceleration of the termination side reactions along with the propagation reaction.[32] Furthermore, PEO carries oxygen atoms along the chain that may compete with the carbonylic oxygens of the methacrylate monomers for complexation with the active metal center. Having these data in our hands, it was reasonable to understand the low macromonomer conversion and the broad molecular weight distribution of the PMMA-*g*-PEO graft copolymer.

P2MP ($c_\infty = 5.5^{33}$) has an extra methyl group compared with PI ($c_\infty = 5.1^{34}$) and consequently is less flexible. On the basis of the results obtained with the catalytic system (1), it is possible to explain the lower macromonomer conversion (40%) compared with the corresponding PI macromonomers (82%). However, the conversion is somewhat lower than that obtained with

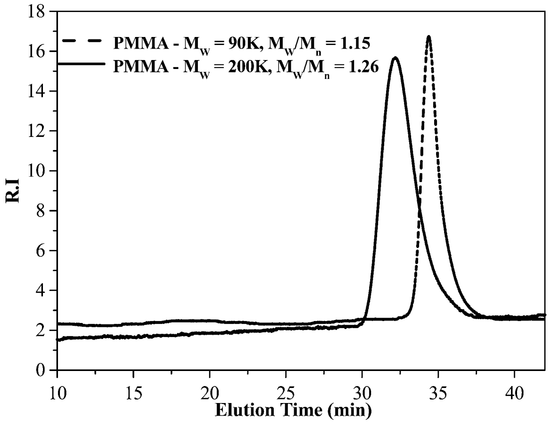


Figure 7. SEC chromatograms concerning a reinitiation experiment of the polymerization of MMA: (a) initial PMMA (dashed line); (b) polymer produced after the addition of a new quantity of MMA to the reaction mixture (solid line).

the PS macromonomers, despite the fact that PS is less flexible than P2MP. Further experiments are needed to verify this conclusion. The molecular weight distribution of the PMMA-*g*-P2MP graft copolymer is almost the same with the corresponding PMMA-*g*-PI samples, meaning that P2MP macromonomer does not introduce any extra termination reactions, due to the similarity with the PI chains.

A more complex architecture was obtained by the copolymerization of PS-*b*-PI macromonomers carrying the methacryloyl end group at the PI chain end, which is more flexible than the PS block, with MMA leading to the synthesis of PMMA-*g*-(PI-*b*-PS) graft block terpolymers. The results are displayed in Tables 1 and 2 (entries 9 and 10), whereas a characteristic SEC chromatogram and ^{1}H NMR spectrum are given in Figures 4 and 5, respectively. The conversion is similar to that obtained in the case of the PI macromonomers for similar MMA/macromonomer ratios. It is characteristic that even in the case where the MMA/macromonomer ratio is 1:4, the macromonomer conversion is 50%. These results show that the flexibility of the PI block, where the polymerizable end group is attached, determines the kinetic behavior of the macromonomer.

Synthesis of Polymacromonomers. The synthesis of polymacromonomers has been a long-term challenge for polymer chemists. Many efforts have been made using a variety of methods and techniques. Depending on the number of the macromonomers that are incorporated in the final structure and the relative molecular weights of the macromonomer and the backbone, a plethora of different architectures can be prepared, such as stars, molecular brushes, combs, etc.[29a,30]

To explore the possibility of using metallocene catalysts for the synthesis of polymacromonomers, PS and PI macromonomers of low molecular weight were homopolymerized using the catalytic systems (1) and (2). The results are tabulated in Tables 3 and 4. Previous studies concerning the homopolymerization of vinylbenzyl-terminated PS macromonomers using $CpTiCl_3$/MAO or Cp^*TiCl_3/MAO as catalytic systems showed that the conversions were generally lower than 50% and the molecular weight distributions in the range 1.17−1.4, whereas the number of branches incorporated in the comb structure was in the range 7−21. Similar efforts have not been published using zirconocene catalysts for the polymerization of macromonomers with methacryloyl end functions. However, from the data concerning the polymerization of stearyl methacrylate, a monomer having a side chain of 18 carbon atoms, it was concluded that the rate of polymerization is reduced compared to the MMA polymerization rate; the yield is not quantitative even after 72 h (about 80%), and the molecular weight distributions were in the same range as with PMMA samples.[31] These results indicate the effect of the steric hindrance exercised by the bulky side group of the monomer for the complexation on the active catalytic center, in agreement with the group transfer mechanism proposed by Collins.[11]

With these results, the homopolymerization of the PS and PI macromonomers was conducted for 68 h to achieve the maximum possible yield. The results concerning the polymerization of the PS and PI macromonomers with the catalytic system (1) show that the conversion is 63% and 90%, respectively, meaning that despite the steric hindrance effects the catalyst is very active. The higher conversion of the PI macromonomer is attributed to the higher flexibility of PI compared to that of PS, in agreement with previous conclusions.[23] The catalytic system (2) was also employed in order to study the effect of the catalyst's symmetry on the

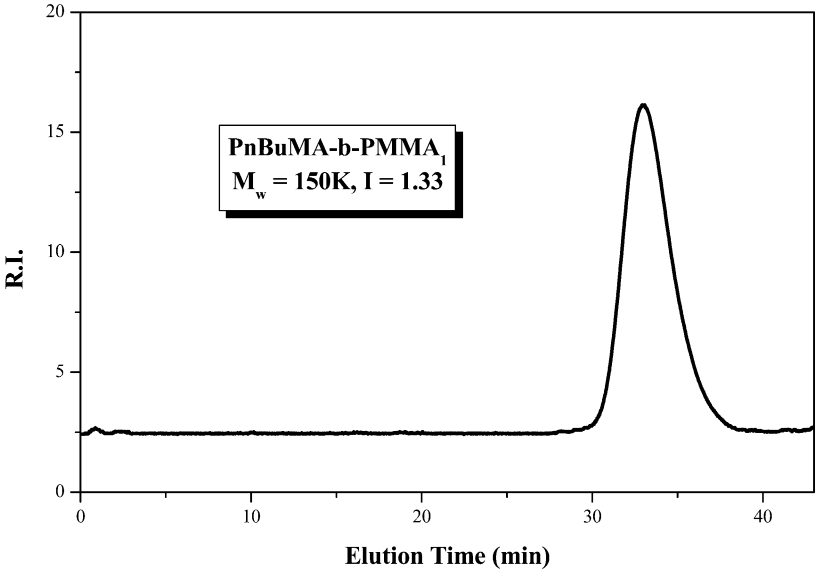


Figure 8. SEC chromatogram of the sample PnBuMA-*b*-PMMA$_1$.

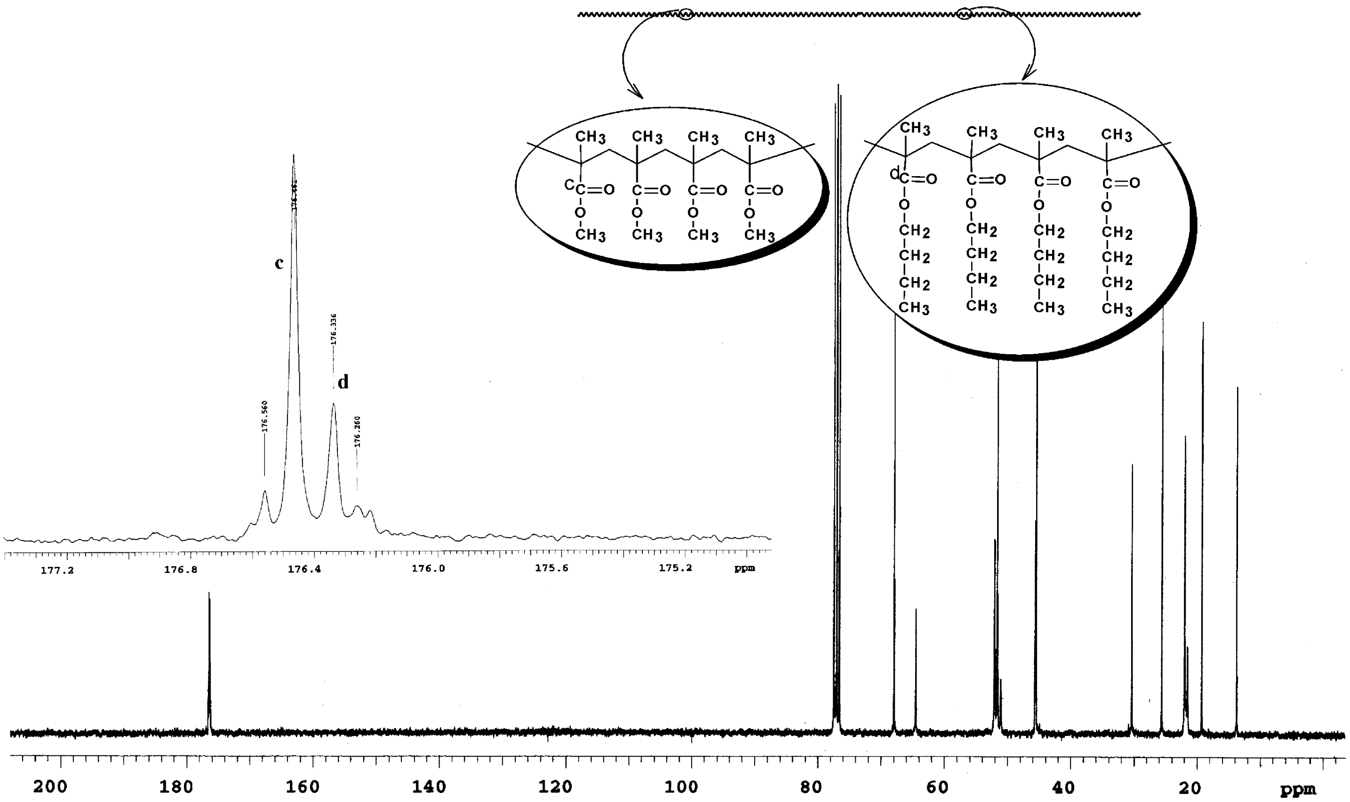


Figure 9. 300 MHz ^{1}H NMR spectrum of the sample PnBuMA-*b*-PMMA$_3$ in CDCl$_3$ at 25 °C.

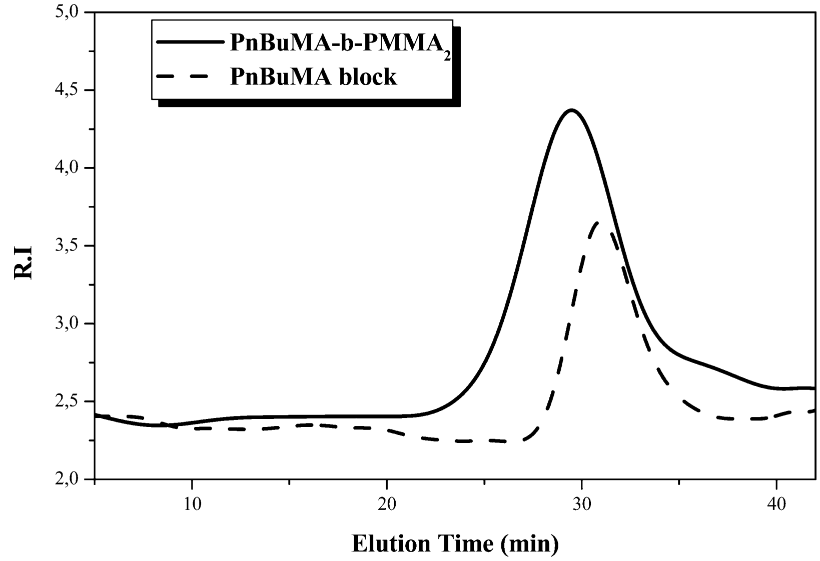


Figure 10. SEC chromatograms concerning the synthesis of PnBuMA-*b*-PMMA$_2$: (a) PnBuMA block (dashed line); (b) PnBuMA-*b*-PMMA$_2$ block copolymer.

polymerization characteristics and to prepare polymacromonomers with isotactic PMMA backbones. The more flexible PI macromonomer was used in this case, and the conversion was 30%, much lower than that obtained with the catalytic system (1). This is attributed to the much slower polymerization rate that is obtained with this isospecific catalyst. However, the molecular weight distributions are very narrow in all cases, meaning that the polymerization is well controlled and that the termination reactions are greatly suppressed. A characteristic SEC chromatogram is given in Figure 6.

It has to be depicted that the above-mentioned results underline the critical perspectives for the polymerization of polar monomers with catalytic systems of IVA group elements. Moreover, this is the first report of very efficient homopolymerization of macromonomers utilizing transition-metal catalysts.

Synthesis of Block Copolymers. Zirconocene catalysts have been used so far for the synthesis of block copolymers of polyolefins and PMMA. However, unambiguous results for the successful synthesis of the block copolymers have not been provided. In the case of the PE-*b*-PMMA block copolymers, SEC analysis was performed on the final product and on a PE sample, prepared under conditions identical with those used for the synthesis of the copolymer's PE block.[20] However sampling from the reactor was not performed to obtain the PE block chromatogram. No homopolymers were

Table 5. Synthesis of Block Copolymers of *n*BuMA and MMA[a]

block copolymer	catalyst concn (μmol/L)	total monomers concn (mmol/L)	*n*BuMA:MMA feed molar ratio	*n*BuMA:MMA molar ratio in copolymer[b]	$M_w \times 10^{-3}$ [c]	M_w/M_n[c]
PnBuMA-*b*-PMMA$_1$[d]	1200	1600	1:1.5	1:1.5	150	1.33
PnBuMA-*b*-PMMA$_2$[d]	300	1600	1:1.5	1:1.4	900	1.35
PnBuMA-*b*-PMMA$_3$[d]	1100	800	1:3.7	1:3.9	85	1.33
PnBuMA-*b*-PMMA$_4$[e]	1170	650	1:3.0	1:2.1	130	1.09
PnBuMA-*b*-PMMA$_5$[f]	875	650	1:3.0	1:3.5	150	1.10

[a] Polymerization conditions: [MMA] + [*n*BuMA]/[ZnEt$_2$] = 4, V_{total} = 80 mL, [cocatalyst]/[catalyst] = 1,1; polymerization time 24 h at 0 °C. [b] By ^{1}H NMR. [c] By SEC in THF at 40 °C. [d] Catalyst: Cp$_2$ZrMe$_2$, cocatalyst: B(C$_6$F$_5$)$_3$. [e] Catalyst: *rac*-EtInd$_2$ZrMe$_2$; cocatalyst: B(C$_6$F$_5$)$_3$. [f] Catalyst: *rac*-EtInd$_2$ZrMe$_2$; cocatalyst: [Me$_2$NHPh]$^+$[B(C$_6$F$_5$)$_4$]$^-$.

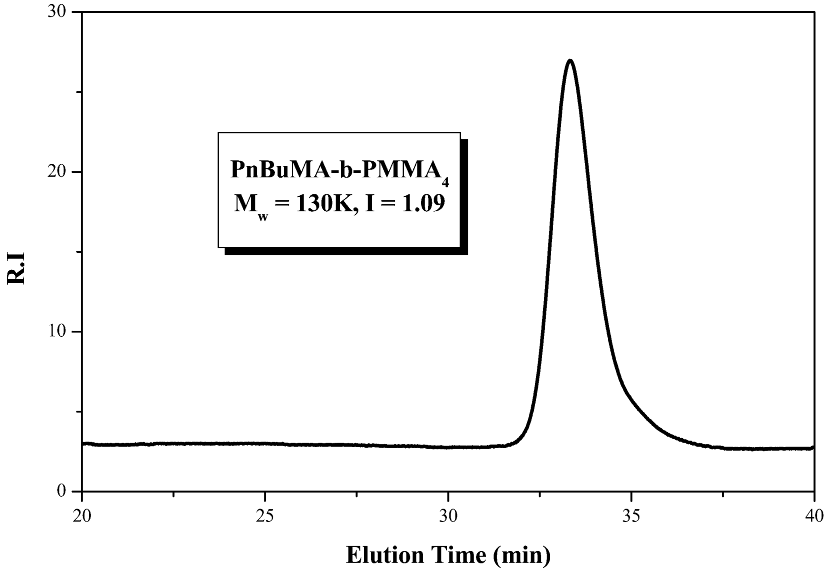


Figure 11. SEC chromatogram of the sample PnBuMA-*b*-PMMA$_4$.

found after extraction with selective solvents, and the NMR spectra revealed the presence of both PE and PMMA at the final product. However, the possibility of the formation of a random sequence of the different monomer units between the two pure blocks, due to the incomplete polymerization of the first monomer prior the addition of the second, cannot be ruled out. In the case of the PP-*b*-PMMA copolymers SEC analysis was not performed, and the presence of homopolymers was reported after extractions with selective solvents.[21]

Block copolymers of different polymethacrylates have not been prepared so far using zirconocenes. However, Collins et al. have tried successfully to reinitiate the polymerization of MMA after the polymerization of a first quantity of MMA.[10] Bearing these results in mind, a similar reinitiation experiment was performed using the catalytic system (1). A quantity of MMA was polymerized, and then a new quantity was added in the reaction system. The SEC profiles are given in Figure 7. It is obvious that an increase of the molecular weight takes place, meaning that in the specific time frame of the experiment the system is “living”.

A series of experiments were subsequently conducted with the sequential addition of monomers starting from MMA and continuing with BuMA. The SEC profiles showed the existence of two or three peaks. The NMR spectra of these products showed that both MMA and BuMA units were present. It is assumed that during the addition of BuMA part of the active catalytic centers are terminated, leading to the formation of PMMA homopolymer and PMMA-*b*-PBuMA block copolymers, or the first block is terminated and the polymerization of the second monomer is initiated leading to the formation of a mixture of homopolymers. A third possibility is that both procedures may take place simultaneously, which probably explains the formation of three peaks at the chromatogram. A possible reason for this behavior is that the polymerization of BuMA proceeds much slower than that of MMA, giving the opportunity for side reactions to take place. Gibson et al. failed to prepare PMMA-*b*-PBuMA copolymers due to their attempt to initiate the procedure from the polymerization of MMA,[10b] in agreement with the results of the present study. Only a mixture of the two homopolymers was observed. The polymerizations were conducted using Cp$_2$ZrMe$_2$ and B(C$_6$F$_5$)$_3$ as the catalytic system in CH$_2$Cl$_2$, which was the solvent. ZnEt$_2$ was not used in these experiments.

When the order of addition was reversed, i.e., BuMA was polymerized first followed by the addition of MMA, single peak chromatograms were obtained, as shown in Figure 8, and the ^{1}H NMR spectra revealed the existence of both blocks, as displayed in Figure 9. Upon completion of the PBuMA block polymerization, sampling from the reactor was conducted, and the chromatogram was compared with that of the final diblock. From these results, displayed in Figure 10, it is obvious that the block copolymer was prepared without any appreciable termination of the first block. The success of the synthetic procedure is based on the fact that our kinetic measurements, concerning the polymerization of both BuMA and MMA have been taken into account.[31] Therefore, the time needed for the completion of the polymerization of each block was known under the specific experimental conditions used (temperature, nature of catalytic system, monomer, catalyst, and

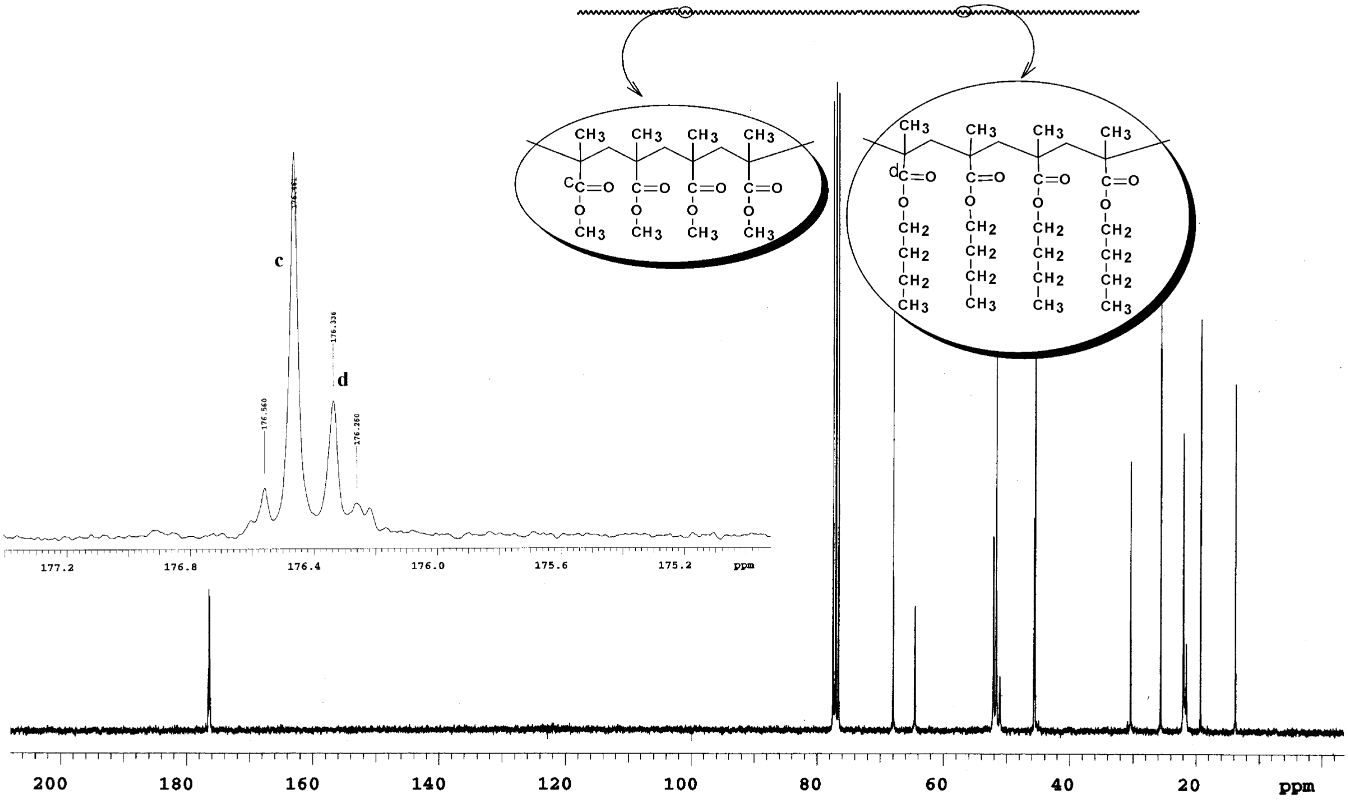


Figure 12. 50 MHz ^{13}C NMR spectrum of the PnBuMA-*b*-PMMA$_4$ block copolymer in CDCl$_3$ at 25 °C.

cocatalyst concentrations, etc.). This was necessary in order to find the optimum duration of the experiment without having the danger of incomplete polymerization of the blocks and at the same time preventing the side reactions from taking place. The results are tabulated in Table 5. It is obvious from these results that the molar ratio of the two monomer units in the block structure is the same, in the frame of the experimental error, as the molar feed ratio. The molecular weight of the diblocks prepared varies between 85 000 and 900 000, whereas the molecular weight distribution is reasonably narrow, in the range obtained for the specific catalytic system.

Experiments were also conducted using the catalytic systems (2) and (3), with the knowledge that these systems promote a better controlled polymerization and provide isotactic chains. The data displayed in Table 5 (entries 4 and 5) indicate that narrow molecular weight distribution diblocks ($M_w/M_n \sim 1.10$) were prepared. As an example, the chromatogram shown in Figure 11 has a single and narrow peak, indicating that a well-defined diblock has been synthesized. Furthermore, the ^{13}C NMR spectrum shown in Figure 12 revealed the formation of isotactic polymeric chains. It has to be noticed that analogous results, regarding the narrow molecular weight distribution and the large M_w values, have been previously reported only for rare earth catalysts.[22]

Table 6. DSC Results from the PBuMA-*b*-PMMA Block Copolymers

sample	$(T_g)_{PBuMA}$ (°C)	$(T_g)_{PMMA}$ (°C)
syndio-PMMA[a]		117
iso-PMMA[a]		52
syndio-PBuMA[a]	21	
iso-PBuMA[a]	−18	
PBuMA-*b*-PMMA$_1$	11.6	115.2
PBuMA-*b*-PMMA$_2$	10.3	120.0
PBuMA-*b*-PMMA$_3$	2.7	110.2
PBuMA-*b*-PMMA$_4$	−11.4	50.8
PBuMA-*b*-PMMA$_5$	−18.8	50.4

[a] Data from *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999.

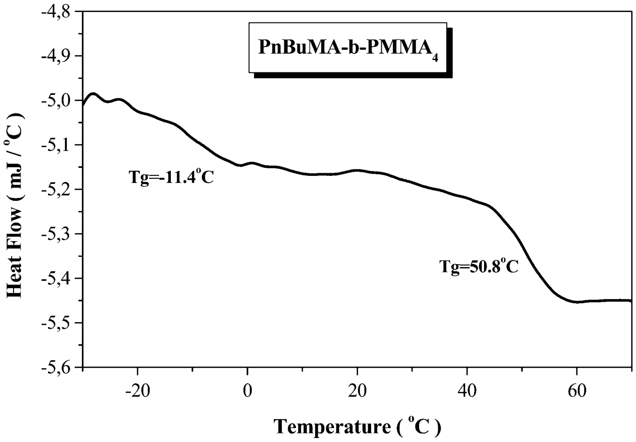


Figure 13. DSC thermogram of the sample PnBuMA-*b*-PMMA$_4$.

To check whether a random sequence of the different monomer units exists between the two pure blocks instead of a simple junction point, DSC experiments were conducted for these diblock copolymers. The results are displayed in Table 6. In all cases two clearly distinguished glass transition temperatures, T_gs, are observed, as shown for example in Figure 13, meaning that two different phases exist. The absence of a third T_g reveals the absence of an appreciable interface due to a random placement of the two monomer units. Furthermore, the two T_gs are close to the values obtained for the two homopolymers, prepared under identical conditions, as shown in Table 6. Small deviations from the T_g values of the homopolymers can be attributed to differences in the tacticity and the molecular weight between the samples. This is direct evidence that well-defined block copolymers have been prepared with the use of the suitable metallocene catalyst.

Conclusions

Graft copolymers and terpolymers having PMMA backbone and PS, PI, PEO, P2MP, and PS-*b*-PI branches were synthesized by copolymerization of MMA with the corresponding methacrylic macromonomers, mMM, prepared by anionic polymerization. $Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (1) and *rac*-$Et(Ind)_2ZrMe_2$ /$B(C_6F_5)_3/ZnEt_2$ (2) were used as the catalytic systems for the copolymerization reaction. The flexibility, the structure, and the molecular weight of the macromonomer along with the nature of the catalytic system were found to affect the copolymerization behavior. PS and PI mMM were homopolymerized using the catalytic systems (1) and (2). High macromonomer conversions were obtained with (1), whereas with (2) the conversion was lower, due to the lower polymerization rate adopted with this system. Block copolymers PBuMA-*b*-PMMA were also prepared, for the first time, by sequential addition of monomers starting from the polymerization of BuMA. Catalytic systems (1), (2), and *rac*-$Et(Ind)_2ZrMe_2/[Me_2NHPh]^+[B(C_6F_5)_3]^-/ZnEt_2$ (3) were employed. Well-defined block copolymers, especially using (2) and (3), were obtained as was revealed by SEC, NMR, and DSC measurements.

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