Articles

Metallocene-Catalyzed Copolymerization of MMA with Anionically Synthesized Methacryloyl Macromonomers

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ABSTRACT: Well-defined graft copolymers with poly(methyl methacrylate) backbone and poly(styrene) (PS), poly(isoprene) (PI), or poly(dimethylsiloxane) (PDMS) branches were synthesized by combining anionic and metallocene catalyzed polymerization. The synthetic strategy involves the preparation of methacryloyl macromonomers of PS, PI, and PDMS by anionic polymerization, followed by copolymerization with methyl methacrylate using the highly reactive catalytic system $Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$. The macromonomers and the fractionated graft copolymers were characterized by size exclusion chromatography, low-angle laser light scattering, and ^1H NMR spectroscopy.

Introduction

Poly(methyl methacrylate) (PMMA) is among the most important commercial polymers. Blending PMMA with other polymers is a convenient procedure to change mechanical, thermal, or chemical properties, thus broadening its application spectrum.[1] Unfortunately, PMMA is not compatible with many polymers. There are generally two strategies that can be followed in order to achieve the desired compatibilization. The first has to do with the use of polymers having end functional groups that are able to interact, leading to the formation of a miscible system.[2] The other is the addition to the blend of premade block or graft copolymers.[3] The main interest of graft and block copolymers arises from their properties as interface modifiers. Therefore, the synthesis of graft copolymers of PMMA with chemically different branches is very important for the development of novel compatibilizing agents. In addition, new PMMA structures are of capital importance for designing novel materials. The objective of this paper is the synthesis of graft copolymers, consisting of PMMA backbone and poly(styrene) (PS), poly(isoprene) (PI), or poly(dimethylsiloxane) (PDMS) side arms, by combining metallocene and anionic polymerization. The metallocene catalyzed copolymerization was carried out using the three-component catalytic system $Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$.[4]

The production of graft copolymers, mainly with polyolefin backbones, via metallocene chemistry has lately been an important field of research. One route into polyolefin graft copolymers is based on the use of borane-containing polymers. These polymers were obtained by direct copolymerization of an α-olefin and a functionalized α-olefin-containing borane groups utilizing the catalytic system $Et[Ind]_2ZrCl_2/MAO$,[5] where MAO is methylaluminoxane and Ind is the indenyl group, followed by "grafting from" radical polymerization procedures.

Another method concerns the comonomer/anionic approach. Copolymers of ethylene and *p*-methylstyrene prepared with a metallocene catalyst, such as $Et[Ind]_2ZrCl_2$ or $[C_5Me_4(SiMe_2NtBu)]TiCl_2$, were lithiated at the benzyl groups and used as initiators in the anionic "graft from" polymerization of styrene, methyl methacrylate, acrylonitrile, and *p*-methylstyrene.[6]

Hawker and collaborators were able to prepare poly(propylene-*g*-styrene) using a combination of metallocene chemistry and living free radical techniques. The polydispersity of the prepared graft copolymers was rather high, varying from 1.5 to 2.9.[7]

Using the macromonomer method, Endo et al.[8] synthesized graft copolymers of poly((syndiotactic styrene)-*g*-(atactic styrene)). Copolymerization of styrene with styrene-terminated polystyrene macromonomers was performed with $CpTiCl_3$/MAO catalyst. Unfortunately, the yield of the copolymerization reaction was very low (<20%), and the molecular weight distribution of the final products was higher than 1.5.

Henschke et al.[9] reported the application of the macromonomer method to the synthesis of poly(propylene) graft copolymers. Graft copolymers of poly(propylene-*g*-styrene) have been synthesized by the copolymerization of propene with poly(styrene) macromonomers using the catalytic system $[Me_2Si(2\text{-}Me\text{-}Benzind)_2]ZrCl_2$/MAO, where Benzind is arylindenyl group. Only moderate macromonomer conversions (maximum 50%) were reported. Unfortunately, no molecular characterization results were presented in order to prove the graft structure.

Experimental Section

Materials. All manipulations were performed with high-vacuum techniques and/or Schlenk techniques. Cp_2ZrMe_2 was purchased from Aldrich or synthesized according to the literature.[10] Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was synthesized according to an improved literature procedure.[11] 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) was vacuum-distilled from calcium hydride and/or triethylaluminum ($AlEt_3$). The purification of isoprene (Aldrich, 99%), styrene (Aldrich, 99%), and solvents such as benzene (Aldrich) and tetrahydrofuran (THF, Aldrich) which were used for anionic polymerization was performed according to standard procedures required for high-vacuum techniques.[12]

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Hexamethylcyclotrisiloxane (D_3, Aldrich, 99%) was melted, stirred over finely grounded calcium hydride for ca. 12 h, and sublimed under high vacuum. The sublimed monomer was then dissolved in benzene and treated with PS^-Li^+ for further purification. The benzene was distilled from the above-mentioned mixture, the monomer was sublimed once more, and a stock solution of pure hexamethylcyclotrisiloxane in benzene was prepared. Methacryloyl chloride was prepared from an equimolar mixture of benzyl chloride (Aldrich) and methacrylic acid (Aldrich) which was refluxed for several minutes and then fractionally distilled. The fraction with bp 95−98 °C was finally collected. [3-(Methacryloxy)propyl]dimethylchlorosilane (MPDC, ABCR) was used as received without further purification. *sec*-Butyllithium (*s*-BuLi) prepared from *sec*-butyl chloride and lithium dispersion was the initiator for the anionic polymerization procedures. Ethylene oxide (EO, Kodak) was dried over calcium hydride (CaH_2) and then was distilled three times over *n*-butylithium (*n*-BuLi, Fluka) (ca. 1 h at 0 °C, each time).[13]

PS Macromonomer. In a 0.5 dm^3 Schlenk type reaction flask have been introduced, under argon atmosphere, 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, subsequently. The reaction mixture was allowed at room temperature for ca. 24 h in order to obtain quantitative yield. Then a 3-fold excess of ethylene oxide (with respect to the living polymer chains) was added in the reaction mixture (under 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, washed with methanol, dried in high vacuum until constant weight, and characterized by ^{1}H NMR spectroscopy in order to define the degree of functionalization.

PI Macromonomer. The experimental procedure was analogous to the above-mentioned preparation of PS macromonomer. The reagents used are as follows: an appropriate amount of benzene (to produce a 10% v/v monomer solution), an isoprene ampule with 220.2 mmol of freshly distilled monomer, 4.196 mmol of *s*-BuLi , a 3-fold excess of ethylene oxide; termination reagent: 3-fold excess of freshly distilled methacryloyl chloride. Finally, the resulting macromonomer was precipitated in methanol, washed with methanol, dried in high vacuum until constant weight, and characterized by ^{1}H NMR spectroscopy in order to determine the degree of functionalization.

PDMS Macromonomer. Polymerization and end-capping reactions were carried out in evacuated *n*-BuLi-washed and solvent-rinsed glass reactors. Reagents were added via break-seals, and aliquots for characterization were removed by the heat sealing of constrictions. The polymerization of hexamethylcyclotrisiloxane (D_3, 45.05 mmol) was initiated in the appropriate amount of benzene to give a 10% v/v monomer solution, using *s*-BuLi (2.130 mmol) as initiator. After 3 h, when the initiation was completed, the THF was added to produce a benzene:THF = 1:1 mixture, to promote the propagation reaction. The polymerization was allowed to proceed at room temperature for 4 h and then at −20 °C for 4 days.[14] The living polymer chains were subsequently end-capped using a 3-fold excess of [3-(methacryloxy)propyl]dimethylchlorosilane (MPDC). Finally, the resulting macromonomer was precipitated in methanol, washed with methanol, dried in high vacuum until constant weight, and characterized by ^{1}H NMR spectroscopy in order to determine the degree of functionalization.

Copolymerization Procedure. Copolymerization was carried out at 0 °C in a 0.5 dm^3 Schlenk type reaction flask. A typical copolymerization process is as follows: in the reaction flask toluene (200 mL), MMA (3 mL), and macromonomer (PDMS, 2.1 g) were added, and it was stirred in a 2-propanol bath which was kept at 0 °C. Then $ZnEt_2$ (1 mL, 97%) was injected, and the reaction mixture was left under stirring at this reduced temperature for 1 h. Afterward, 3.3 mL of a cocatalyst, $B(C_6F_5)_3$ solution in toluene (26.6 mM), and 3.0 mL of a metallocene, Cp_2ZrMe_2 solution in toluene (26.6 mM), were introduced to initiate the polymerization. The polymerization was quenched after 24 h by addition of HCl/methanol solution, and the polymer was precipitated in methanol. The polymer produced was washed with methanol, filtered, and dried in high vacuum at room temperature.

The crude products (graft copolymers) were fractionated using toluene/methanol as a solvent/nonsolvent system, except the product derived from copolymerization of MMA with PDMS macromonomer which was fractionated in a toluene: hexane (1:1)/methanol system.

The PMMA-*g*-PS copolymers, symbolized as PMMA-*g*-PS_A, PMMA-*g*-PS_B, and PMMA-*g*-PS_C, were synthesized using the same PS macromonomer but different MMA/macromonomer weight ratios. The PMMA-*g*-PI and PMMA-*g*-PDMS graft copolymers were prepared using the respective macromonomers.

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.

The copolymers were further purified by ultracentrifugation and passage through columns of silica to remove inorganic compounds (zinc oxides, catalyst, etc.).

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 10^6 to 10^3 Å. The columns were housed in an oven thermostated at 40 °C when the mobile phase was THF and at 30 °C in the case of $CHCl_3$. $CHCl_3$ and THF were used as the carrier solvents for the GPC analysis of graft copolymers, and the results were analyzed using PMMA standards. For the macromonomers THF was the carrier solvent, and the instrument was calibrated with PS, PI, and PDMS standards for the PS, PI, and PDMS macromonomers, respectively. In all cases the flow rate was 1 mL/min.

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, and both were distilled just prior their use. A Chromatix KMX-6 low-angle laser light scattering LALLS photometer at 25 °C equipped with a 2 mW He−Ne laser operating at $\lambda = 633$ nm was used. Stock solutions were prepared, followed by dilution with solvent to obtain solutions with lower concentrations. All the solutions were 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 measured with a Chromatix KMX-16 refractometer operating at 633 nm and calibrated with aqueous NaCl solutions. The d*n*/d*c* values in mL/g for the PMMA-*g*-PS_A, PMMA-*g*-PS_B, and PMMA-*g*-PS_C copolymers in DMF are 0.150, 0.090, and 0.070, respectively.

Copolymer composition and functionalization of macromonomers were determined on the basis of ^{1}H NMR spectra which were measured in chloroform-*d* at 30 °C with a Varian Unity Plus 300/54 NMR spectrometer.

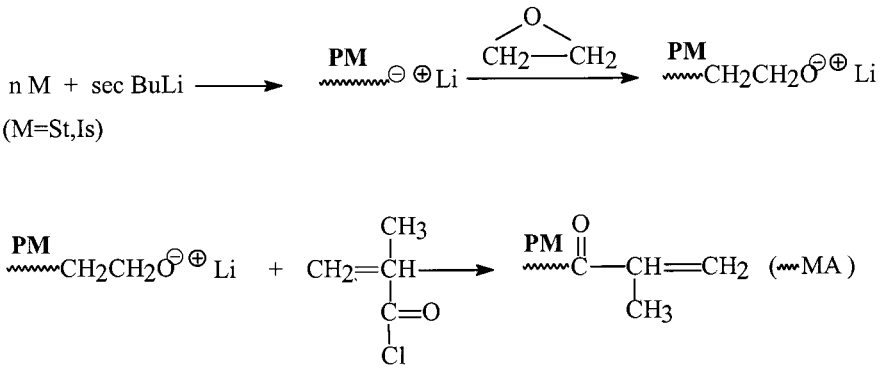
Results and Discussion

The general strategy for the synthesis of graft copolymers is given in Scheme 1.

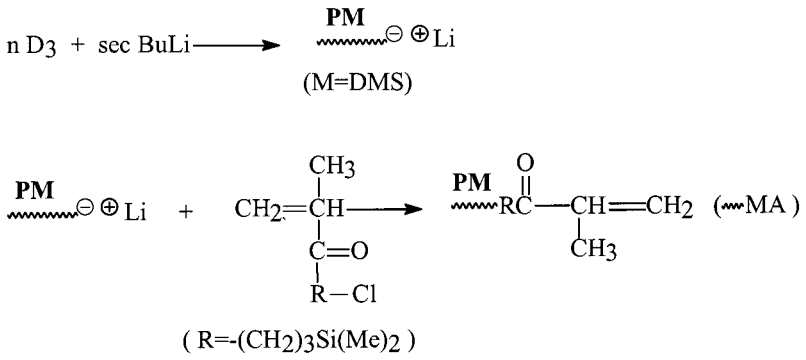
To obtain graft copolymers with uniform side chain length, the macromonomers were prepared via "living" anionic polymerization of the respective monomers using *sec*-butyllithium as initiator.[15,16] The polymerizable end group was introduced in a subsequent functionalization step by reacting the "living" chain end (−OLi) with methacryloyl chloride for PS and PI and with [3-(methacryloxy)propyl]dimethylchlorosilane (MPDC) for PDMS. The degree of functionalization, for a macromonomer with known molecular weight, was determined by comparison of the peak areas which are

Scheme 1. General Procedure for the Preparation of Graft Copolymers

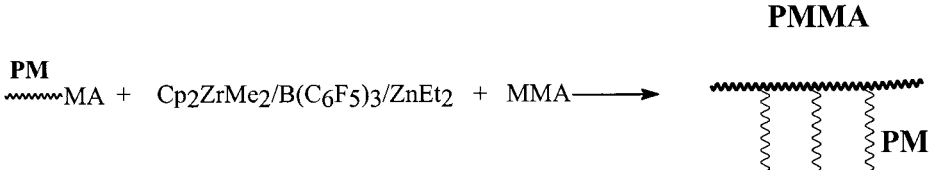
Methacryloyl-macromonomers of Styrene (St) and isoprene (Is)



Methacryloyl-macromonomers of D_3



Graft copolymers



due to double-bond protons of the functional group with the appropriate proton signals of the polymer chain. For example, in the case of the PI macromonomer this determination was made by comparing the peak areas summation at 5.5 and 6 ppm (which are due to the double-bond protons of the methacryloyl group) with the respective total peak area which is attributed to the double bonds of the polymer chain (5.2 ppm (s): one double-bond proton signal of 1,4 structure; 4.8 ppm (d): two double-bond protons signals of 3,4 structure) (Figure 1). All the macromonomers were quantitatively functionalized as was determined by ^{1}H NMR spectra using methods similar to the one described above.

The methacryloyl-terminated macromonomers were used for the copolymerization reaction with methyl methacrylate (Table 1). Representative ^{1}H NMR spectra of the graft copolymers are given in Figures 2−4. In all cases the macromonomer conversion was higher than 70% and increased with the flexibility of the macromonomer. For example, PDMS, which is the most flexible of the macromonomers used, appears to have the highest conversion observed, reaching up to 90%. It is noticeable that the conversion of the macromonomers used is extremely high compared to that in previous reports.[8,9,17]

Table 1. Copolymerization of Methacryloyl Macromonomers of PS, PI, and PDMS with Methyl Methacrylate[a]

copolymer	catalyst concn (μmol/L)	MMA concn (mmol/L)	MMA/macro-monomer (w/w)	conv % (wt)[b]
PMMA-*g*-PS_A	350	250	1:2	75
PMMA-*g*-PS_B	292	150	1:0.71	71
PMMA-*g*-PS_C	220	94	1:0.18	70
PMMA-*g*-PDMS	353	150	1:0.75	≥90
PMMA-*g*-PI	350	200	1:1.16	82

[a] Polymerization conditions: [MMA]/[$ZnEt_2$] = 4, V_{tot} = 200 mL, [$B(C_6F_5)_3$]/[Cp_2ZrMe_2] = 1.1; 24 h polymerization time. [b] By SEC in THF at 40 °C.

Another worth noting conclusion has to do with the stereochemistry of the catalyst that has been used. All previous attempts for synthesis of graft copolymers via metallocene chemistry that utilize the macromonomer approach[9,17] were based on ansa-bridged catalysts. The main idea for the use of such catalysts was that the bridge between the indenyl or cyclopentadienyl groups leads to a widening of the angle between the planes which are defined by those ligands, with the consequence that the metal center becomes less constrained. The above in terms of reactivity means that the metallic

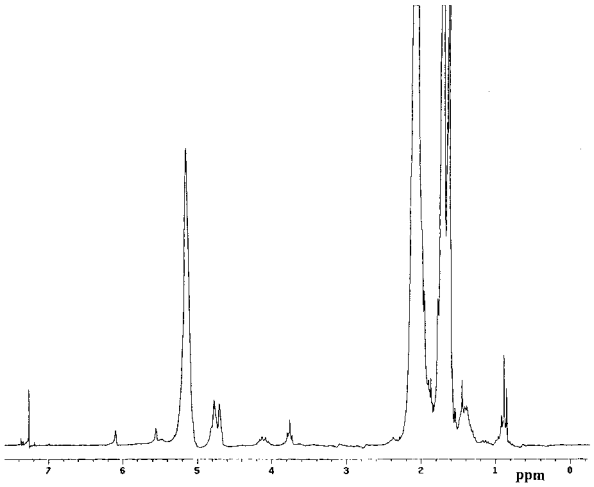


Figure 1. ^{1}H NMR spectrum of the PI macromonomer in $CDCl_3$ at 25 °C. The peaks at 5.5 and 6.1 ppm correspond to the double-bond protons of the methacryloyl end group. The peaks at 5.2 and 4.8 ppm correspond to the double-bond proton of the 1,4 structure and the two protons of the double bond of the 3,4 structures of the isoprene units, respectively.

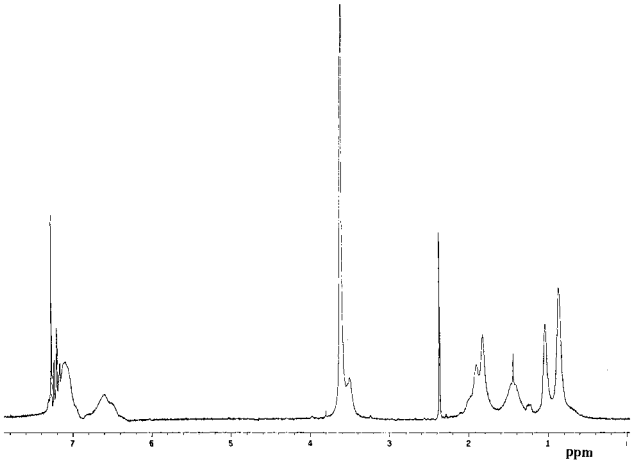


Figure 2. ^{1}H NMR spectrum of the PMMA-*g*-PS_B graft copolymer in $CDCl_3$ at 25 °C.

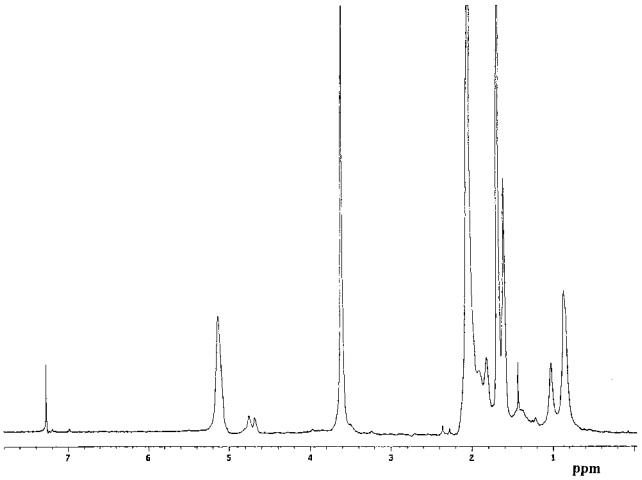


Figure 3. ^{1}H NMR spectrum of the PMMA-*g*-PI graft copolymer in $CDCl_3$ at 25 °C.

center can be approached easier from the reacting species (monomers or macromonomers). The present work demonstrates that simple unbridged catalysts can promote the copolymerization of MMA with a number of chemically different macromonomers achieving very

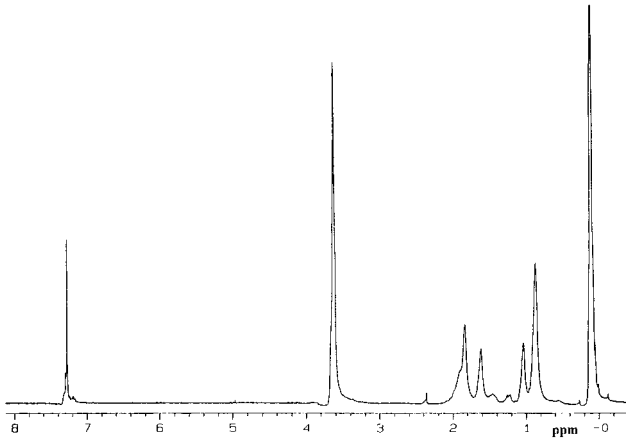


Figure 4. ^{1}H NMR spectrum of the PMMA-*g*-PDMS graft copolymer in $CDCl_3$ at 25 °C.

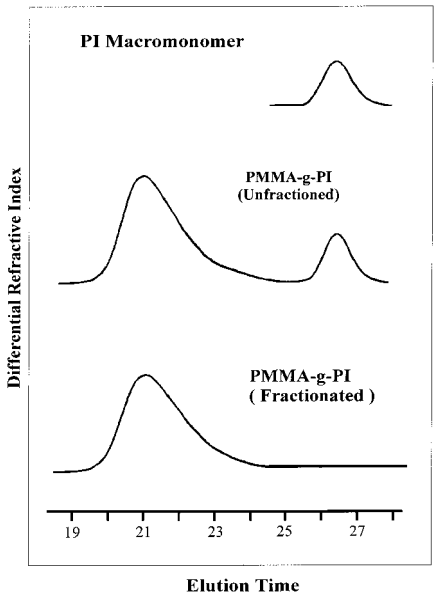


Figure 5. SEC chromatograms concerning the synthesis of the PMMA-*g*-PI graft copolymer in THF at 40 °C.

good copolymerization characteristics.

The composition of the crude product in unreacted macromonomer was determined by SEC. The PS macromonomer conversion was calculated from the comparison of the graft copolymer and the excess macromonomer peak areas using the signal of the UV detector operating at 260 nm, where only the PS component absorbs. The PI conversion was estimated from comparison of the two peak areas using the refractive index detector considering that the refractive index increments in mL/g of PI and PMMA-*g*-PI in THF are 0.130 and 0.113, respectively, as measured experimentaly. Finally, the conversion of PDMS was estimated in a similar way to PMMA-*g*-PI sample, taking into account that the d*n*/d*c* values for the PDMS macromonomer and the PMMA-*g*-PDMS graft copolymer, in mL/g, are −0.044 and 0.033, respectively. The SEC chromatograms of the PI macromonomer, the crude PMMA-*g*-PI product, and the fractionated graft copolymer are shown in Figure 5. Characteristic SEC chromatographs of the fractionated copolymers and the corresponding macromonomers are displayed in Figure 6.

The molecular characteristics of the copolymers are given in Table 2. It has to be noticed that it was very

Table 2. Molecular Characteristics of the Graft Copolymers

run	copolymer	macromonomer content[a] (wt %)	$M_{w,\,macr}{}^{b} \times 10^3$	$(M_w/M_n)_{macr}$.[b]	$M_{w,copol} \times 10^{3}$ [c]	$M_{w,copol} \times 10^3$	$(M_w/M_n)_{copol}$[c]	N_w [f]	N_w[g]
1	PMMA-*g*-PS_A	60	4.6	1.03	150	400[d]	1.26	52.2	22.8
2	PMMA-*g*-PS_B	34	4.6	1.03	100	450[e]	1.55	33.3	8.9
3	PMMA-*g*-PS_C	11	4.6	1.03	130	550[e]	1.19	13.2	3.3
4	PMMA-*g*-PDMS	42	5.4	1.04	190		1.27		13.2
5	PMMA-*g*-PI	48	4.7	1.03	180		1.32		10.6

[a] By ^{1}H NMR in $CDCl_3$ at 25 °C. [b] By SEC in THF at 40 °C. [c] By SEC in $CHCl_3$ at 30 °C. [d] By LALLS in THF at 25 °C. [e] By LALLS in DMF at 25 °C. [f] Weight-average number of grafted chains calculated from the molecular characteristics, determined by LALLS, and the composition. [g] Weight-average number of grafted chains calculated from the molecular characteristics, determined by SEC, and the composition.

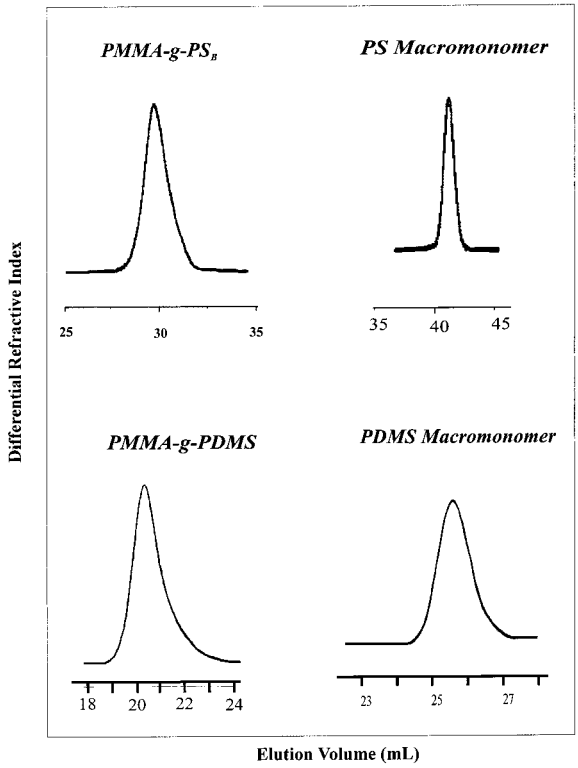


Figure 6. SEC chromatograms of the PMMA-*g*-PS_B and PMMA-*g*-PDMS graft copolymers and their corresponding macromonomers in THF at 40 °C.

difficult to perform light scattering measurements. In THF only the sample PMMA-*g*-PS_A gave reasonable results. In the other cases huge molecular weights were obtained, and the plots were not linear. A decrease in the $Kc/\Delta R_\theta$ values was initially observed followed by an increase at higher concentrations. This behavior is typical of an aggregating system and can be attributed either to traces of the catalyst which are probably chemically connected to the polymer chains or to the existence of the hydrolysis products of $ZnEt_2$ which may interact with the PMMA ester groups, forming reversible cross-links. It should be noticed that this behavior was observed despite the fact that extensive purification efforts were contacted to the final product (filtration, ultracentrifugation, silica columns). Moreover, recently zirconium traces in polyolefins prepared by zirconocene catalysts were quantitatively measured by inductive coupled plasma isotope dilution mass spectroscopy.[18] More details on this behavior will be given in a forthcoming paper.[19] To overcome this problem, DMF was used for the characterization of the PMMA-*g*-PS copolymers, since this solvent is a common good solvent for both components and polar enough to prevent the association through the solvation of metal moieties. DMF could not be used in the cases of the PMMA-*g*-PI and PMMA-*g*-PDMS graft copolymers since DMF is a nonsolvent for PI, and the d*n*/d*c* value for the last copolymer was very low to have accurate LALLS measurements. Consequently, only the SEC results are given in Table 2 as an indication of their molecular weights. The molecular weight distribution for the copolymers was found to be rather narrow (M_w/M_n = 1.2−1.3), with only the exception of PMMA-*g*-PS_B, where $M_w/M_n = 1.55$.

The weight-average number of grafts per copolymer chain, N_w, was calculated using the macromonomer content and molecular weight and the total molecular weight of the graft copolymer. Only the SEC data can be used for direct comparisons since they are available for all copolymers. Considering the three first entries in Tables 1 and 2, it seems that the MMA/macromonomer ratio is crucial for the N_w value. It is obvious that as this fraction increases, the number of grafts per copolymer chain increases. This conclusion indicates that the insertion of the macromonomers in the copolymer chain can be controlled. Comparing the molecular characteristics of the polymeric products derived from runs 2, 4, and 5 in Table 2 (samples PMMA-*g*-PS_B, PMMA-*g*-PI, and PMMA-*g*-PDMS), where the MMA/macromonomer ratio used for the synthesis is almost the same, it is obvious that the number of grafted chains increases by increasing the flexibility of the macromonomer.[20] A flexible macromonomer, defined by its low characteristic ratio, C_∞, may adopt more conformations in solution, thus facilitating the reaction of the end methacrylate group and subsequently the incorporation of the macromonomers to the graft structure. Using the absolute molecular weights, measured by LALLS for the graft copolymers with PS branches, it is obvious that the real number of branches is much higher than that determined using the SEC data for all samples. Nevertheless, the same trend is observed in both cases.

Conclusions

The motivation of the present study was the synthesis of the graft copolymers, PMMA-*g*-PS, PMMA-*g*-PI, and PMMA-*g*-PDMS by copolymerization of methyl methacrylate and a suitable macromonomer, utilizing a three-component catalytic system ($Cp_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$). Combined characterization results have shown that the synthesis of these structures was successfully ashieved. It was concluded that the insertion of the macromonomer in the chain, and the number of grafts per chain, are influenced by two main factors: the flexibility of the macromonomer and the MMA/macromonomer ratio.

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