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Synthesis and Characterization of Complex Macromolecular Architectures Based on Poly(α-olefins) Utilizing a C_s-Symmetry Hafnium Metallocene Catalyst in Combination with Atom Transfer Radical Polymerization (ATRP)

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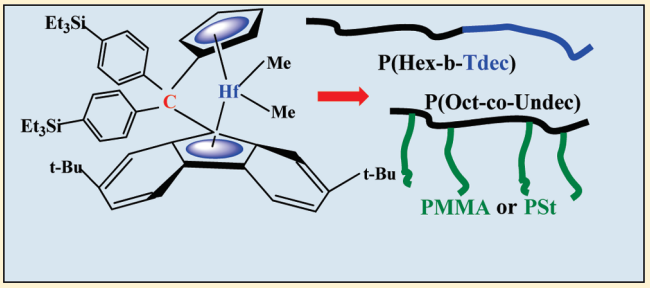
Supporting Information

ABSTRACT: Herein we describe the synthesis of block and graft copolymers made from several higher α-olefins, and in some cases styrene and methyl methacrylate, through the use of metallocene catalysts as well as the combination of metallocene and atom transfer radical polymerization (ATRP). The C_s-symmetry hafnium metallocene catalyst $[(p\text{-}Et_3Si)Ph]_2C$-(2,7-di-*tert*-BuFlu)(Cp)$Hf(CH_3)_2$ with tetrakis(pentafluorophenyl) borate dimethylanilinium salt, $([B(C_6F_5)_4]^-[Me_2NHPh]^+)$, as cocatalyst, in the presence of trioctylaluminum has been used for the synthesis of the following diblock copolymers and triblock terpolymers by sequential polymerization: poly[(hexene-1)-*b*-(tetradecene-1)], poly[(octene-1)-*b*-(tetradecene-1)], poly[(hexene-1)-*b*-(methyl methacrylate)], poly[(octene-1)-*b*-(methyl methacrylate)], poly[(hexene-1)-*b*-(octene-1)-*b*-(tetradecene-1)], poly[(hexene-1)-*b*-(octene-1)-*b*-(decene-1)], and poly[(hexene-1)-*b*-(octene-1)-*b*-(methyl methacrylate)]. By combining the above metallocene catalyzed polymerization and ATRP, graft and block−graft copolymers having either poly(tetradecene-1) or poly(octene-1) backbones and poly(methyl methacrylate) or polystyrene branches were synthesized. All samples were thoroughly characterized by size exclusion chromatography, SEC, ^1H and ^{13}C NMR spectroscopy, and low angle laser light scattering, LALLS, as well as differential scanning calorimetry, DSC.



INTRODUCTION

The synthesis of novel products based on polyolefins remains a topic of great interest in polymer chemistry. These products can be used in a wide variety of applications, since polyolefins provide excellent mechanical properties, chemical resistance and processability at low cost.[1] Several synthetic approaches have been developed for the controlled polymerization of olefins regarding molecular weight, molecular weight distribution and stereochemistry.[2] The discovery of Ziegler−Natta catalysts[3] initiated a new era in polymer chemistry allowing for the synthesis of polyolefins with good catalyst activity and controlled stereochemistry. Later on the development of homogeneous catalytic species based on group 4 metallocene complexes allowed for even higher productivity and increased control over the molecular and structural characteristics of the products.[4] More recently there have been significant developments in several areas: group 3 and 5 metallocenes; half-metallocenes bearing amine, alkoxide, amide groups as well;[5] late transition metal complexes based mainly on cationic α-diimine palladium and nickel complexes;[6] and finally early transition metals bearing non-Cp ligands, such as diamido, alkylthio, and amine−phenolate ligands.[7]

Most of the efforts have been devoted to the polymerization of ethylene and propylene and relatively little attention has been given for the polymerization of higher α-olefins, due to the low catalytic activities and low molecular weights produced from these monomers.[8] In general, as the length of the monomer increases, the polymerization rate decreases due to increasing steric requirements. However, ansa metallocene catalysts have been developed for the homogeneous polymerization of higher α-olefins in order to obtain products of high molecular weight and high rates of polymerization.[9] It was observed that zirconocenes lead to poly(α-olefin)s bearing lower molecular weights

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but with higher catalytic activities than the corresponding hafnocenes.[10] The nature of the catalytic system and the monomer, the temperature of the polymerization and the concentrations of the catalyst and the monomer are the major parameters influencing the kinetics of the polymerization and the microstructure of the produced polymers.[11]

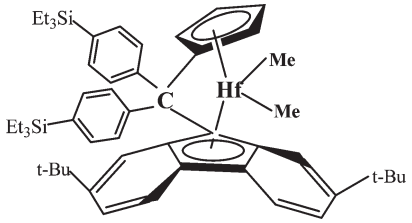
Statistical copolymers can be made through the simultaneous polymerization of two or more olefin monomers in a continuous stirred tank reactor system, and in fact such copolymers are of enormous practical importance. The addition of a second, or even a third, comonomer allows for the manipulation of basic properties such as crystallizability,[12] degree of entanglement,[13] and miscibility,[14] which provides a useful method to control the processing and performance of such materials. As a result, most olefin polymers produced today are copolymers, since this allows an affordable way to design the optimal material for many applications.

In the past, very extensive studies have been devoted to the random copolymerization of ethylene with higher α-olefins leading to linear low density polyethylenes having controlled density and crystallinity depending on the amount and the nature of the α-olefin.[15] Early attempts in catalytic metallocene polymerization have allowed the realization of polymerization of several monomers such as ethylene, propylene and α-olefins to produce relatively well-defined copolymers with interesting properties.[16]

On the other hand, block and graft copolymers of olefins are much less common commercially. Despite the many advantages that such well-controlled architecture can provide,[17] the expense and difficulty in preparing olefin block and graft copolymers have limited their use.[18] Special care has been devoted to the synthesis of block copolymers of ethylene and propylene by sequential addition of the monomers.[19] Hlatky and Turner[20] prepared diblock copolymers of ethylene and propylene using Cp_2HfMe_2 as the catalyst and $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ as the cocatalyst. Fukui and co-workers[21] reported the synthesis of diblock copolymers of ethylene and propylene using Cp_2HfMe_2 activated with $B(C_6F_5)_3$ and employing $Al(n\text{-}Oct)_3$ as a scavenger. Coates[22] and Fujita[23] have independently reported that titanium catalysts with phenoxyimine ligands are capable synthesizing polypropylene−polyethylene−polypropylene block copolymers. Furthermore, multiblock polymers with isotactic and atactic PP were reported by Sita,[24] Busico,[25] and Coates[26] using group 4 metallocenes catalysts. On the other hand, late transition metal complexes, based on nickel and palladium, have been employed as the catalytic species promoting the block copolymerization of olefins.[27]

Block copolymers of polyolefins, especially PE and PP, with PMMA have been reported in the literature using lanthanocenes, such as $Cp^*_2SmMe(THF)$ and $[Cp^*_2SmH_2]$,[28] half-lanthanocenes, such as $Cp^*La[CH\text{-}(SiMe_3)_2]_2(THF)$[29] and group 4 metallocenes, such as $Me_2(Cp)(Ind)ZrMe^+MeB(C_6F_5)_3^-$.[30] The synthesis of copolymers with higher α-olefins is less common. For example binuclear hydrido samarocene and yttrocene complexes have been used for the synthesis of block copolymers of pentene-1 and hexene-1 with MMA.[31] The synthesis of more complex structures has been realized by combination of coordination polymerization with other polymerization techniques.[32] Copolymers with isotactic polypropylene side chains grafted onto an ethylene-propylene backbone have been made by several routes.[33] More recently, Arriola et al.[34] have developed means to produce blocky olefin copolymers using two catalyst centers that produce different copolymer compositions in the same reactor environment along with so-called shuttle agents that move the growing chain between these catalytic centers multiple times during the growth of each chain.

Scheme 1



In previous reports from this group the polymerization of higher α-olefins (from hexene-1 to hexadecene-1) using the C_s-symmetry hafnium metallocene catalyst $[(p\text{-}Et_3Si)Ph]_2C(2,7\text{-di-}tert\text{-}BuFlu)(Cp)Hf(CH_3)_2$, (Scheme 1) was studied[35] and the synthesis of functionalized polyolefins coming from the copolymerization of octene-1 and tetradecene-1 with silyl-protected 10-undecen-1-ol (1-*tert*-butyldimethylsilyloxy-10-undecene)[36] was reported. Emphasis was given on the kinetics of the polymerization, the control over the molecular characteristics and the microstructure of the polyolefins.

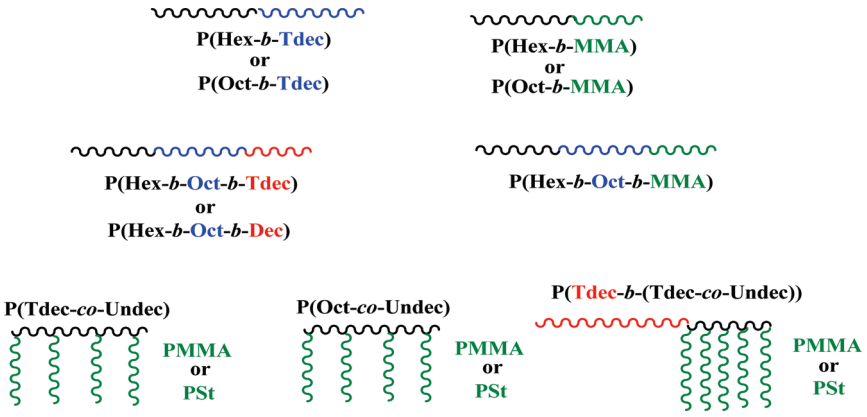
In the present study, the same catalytic system is employed for the synthesis of several types of well-defined block and graft copolymers. These include diblock copolymers and triblock terpolymers of higher α-olefins; block copolymers of higher α-olefins and poly(methyl methacrylate) (PMMA); and graft and block−graft copolymers having a polyolefin backbone and either PMMA or polystyrene (PSt) branches (Scheme 2).

EXPERIMENTAL SECTION

Materials. All manipulations were performed using high-vacuum and/or Schlenk techniques. The hafnium catalyst $[(p\text{-}Et_3Si)Ph]_2C(2,7\text{-ditert-BuFlu})(Cp)Hf(CH_3)_2$, (Scheme 1) was donated by ExxonMobil.[37] Tetrakis(pentafluorophenyl) borate dimethylanilinium salt ($[B(C_6F_5)_4]^-[Me_2NHPh]^+$) was synthesized[38] or purchased from Strem Chemicals. Trioctylaluminium (TOA, 25 wt % in hexane) was purchased from Aldrich. Toluene (Aldrich) was dried and vacuum-distilled from calcium hydride (CaH_2), metallic sodium, and polystyryllithium. Methylene chloride (CH_2Cl_2, Aldrich) was dried and vacuum-distilled from calcium hydride. The monomers hexene-1 (Hex), octene-1 (Oct), decene-1 (Dec), and tetradecene-1 (Tdec), (Aldrich), were vacuum-distilled from calcium hydride under vacuum. MMA (Merck) was vacuum-distilled from calcium hydride. 10-undecen-1-ol (Undec), (Aldrich) was vacuum-distilled from magnesium sulfate ($MgSO_4$). Styrene (St), (Aldrich) was vacuum-distilled from calcium hydride and dibutylmagnesium. *tert*-Butyldimethylsilyl chloride (Strem Chemicals), imidazol (Fluka), triethylamine (99.5%, Aldrich), 2-bromoisobutyryl bromide (98%, Aldrich), copper(I) chloride (Aldrich) and (*N,N,N′,N′,N″,N″*-hexamethyltriethylenetetramine), HMTETA (Aldrich) were used as received.

Synthesis of block copolymers of Hexene-1 or Octene-1 with Tetradecene-1. Block copolymerization of Hex or Oct with Tdec was carried out at 0 °C in a 0.1-dm^3 Schlenk-type reaction flask. A typical polymerization process was the following: Toluene (5 mL), the hafnium catalyst (final concentration, c = 8.32 mM) with the borane cocatalyst (final concentration, c = 8.32 mM), and TOA (molar ratio Al/Hf = 5/1) in toluene, were added to the reaction flask to provide the catalytic system. The mixture was stirred at 0 °C, followed by the addition of Hex or

Scheme 2



Oct (1.5 mL). The polymerization was allowed to proceed for 2 min. The unreacted monomer was eliminated by distillation under vacuum. This procedure led to the reduction of the solution's volume to about 3 mL. Then Tdec (1.5 mL) with 5 mL of toluene were added to the reaction flask and the polymerization was continued for 2 min. The polymerization was quenched by the addition of acidified methanol and the polymer was precipitated in methanol, washed with methanol, filtered, and dried in high vacuum at room temperature.

Synthesis of Block Copolymers of Hexene-1 or Octene-1 with Methyl Methacrylate. The block copolymerization of Hex or Oct with MMA was carried out in a 0.1-dm^3 Schlenk-type reaction flask. A typical polymerization process was the following: Toluene (5 mL) and the hafnium catalyst (final concentration, c = 6.2 mM) with the borane cocatalyst (final concentration, c = 6.2 mM) were added to the reaction flask to provide the active catalytic system. The mixture was stirred at 0 °C, followed by the addition of Hex or Oct (1.5 mL). The polymerization was allowed to proceed for 30 and 20 min, respectively. The unreacted monomer was eliminated by distillation under vacuum, leading to a reduction of the solution volume to about 3 mL. Then MMA (1.5 mL) was added to the reaction flask and the polymerization was continued for 20 h at 110 °C. The polymerization was quenched by the addition of acidified methanol, and the polymer was precipitated in methanol, washed with methanol, filtered, and dried in high vacuum at room temperature.

Synthesis of Triblock Terpolymers of Hexene-1 and Octene-1 with Decene-1 or Tetradecene-1. The synthesis of the triblock terpolymers of Hex and Oct with Tdec or Dec was carried out at 0 °C in a 0.1-dm^3 Schlenk-type reaction flask. A typical example is the following: Toluene (5 mL), the hafnium catalyst (final concentration, c = 8.32 mM) with the borane cocatalyst (final concentration, c = 8.32 mM), and TOA (molar ratio Al/Hf = 5/1) in toluene, were added to the reaction flask to provide the active catalyst. The mixture was stirred at 0 °C, followed by the addition of Hex (1.5 mL). The polymerization was allowed to proceed for 5 min. The unreacted monomer was eliminated by distillation under vacuum. Subsequently, Oct (1.5 mL) with 5 mL of toluene was added to the reaction flask and the polymerization was continued for 20 min. The unreacted monomer was again eliminated by distillation under vacuum. After the completion of the polymerization, Tdec (1.5 mL) or Dec (1.5 mL) and 10 mL of toluene were added and the polymerization was extended for 30 min The polymerization was quenched by the addition of acidified methanol, and the polymer was precipitated in methanol, washed with methanol, filtered, and dried in high vacuum at room temperature.

Synthesis of 1-*tert*-Butyldimethylsilyloxy-10-undecene. A solution of *tert*-butyldimethylsilyl chloride (3.9 g, 26.0 mmol) in 40 mL of methylene chloride was added dropwise to a stirred solution of 10-undecen-1-ol (3.0 g, 17.0 mmol) and imidazol (1.8 g, 26.0 mmol) in 50 mL of methylene chloride at 0 °C under argon atmosphere. After the addition was completed, the reaction mixture was stirred overnight at room temperature and then filtered. The organic layer was treated with water and brine, separated, and the aqueous layer was extracted three times with 50 mL of methylene chloride. The combined organic portions were dried over $MgSO_4$, filtered, and vacuum-distilled (yield 85%). This was examined by ^1H NMR in $CDCl_3$ with the following peak assignments: δ = 0.0 (s,6H, -Si$(CH_3)_2$-), 0.966 (s, 9H, $-C(CH_3)_3$), 0.8−1.8 (m, 16H, $-CH_2-CH_2-O-$), 3.45−3.50 (t, 2H, $-CH_2-O-$), 4.78−4.92 (m, 2H, $-CH=CH_2$), 5.59−5.79 (m, 1H, $-CH=CH_2$).

Synthesis of Poly(α-olefin) Multifunctional Macroinitiator (POct and PTdec). The copolymerization of α-olefin and the silyl protected 10-undecen-1-ol was carried out at 0 °C in a 0.1-dm^3 Schlenk-type reaction flask. A typical polymerization process was the following: Toluene (5 mL), α-olefin, and silyl protected 10-undecen-1-ol were added to the reaction flask and the mixture was stirred at 0 °C. This was followed by the addition of 5.0 mL of the hafnium catalyst solution (final concentration, c = 8.32 mM) with the borane cocatalyst (final concentration, c = 8.32 mM) and TOA (molar ratio Al/Hf = 5/1) in toluene, for the initiation of the polymerization. The polymerization was quenched with acidified methanol, and the polymer was precipitated in methanol, washed with methanol, filtered, and dried in high vacuum at room temperature. The protective *tert*-butyldimethylsilyl group was partly removed by treatment of the polymer solution in THF with methanol, which was acidified with HCl.

The unprotected poly(α-olefin-*co*-10-undecen-1-ol) along with triethylamine, and THF were added to a 500 mL glass flask equipped with a mechanical stirrer. The mixture was cooled to 0 °C and stirred, and the solution of 2-bromoisobutyryl bromide in THF was added dropwise to the reaction flask. The mixture was warmed at room temperature and stirred overnight. The resulting salt was removed by filtration, the polymer was collected by condensation of the filtrate, dissolved in CH_2Cl_2 and washed successively with distilled water/$NaHCO_3$. The organic phase was dried over $MgSO_4$, condensed and the macroinitiator was dried under vacuum. The poly(α-olefin) multifunctional macroinitiator was obtained in almost quantitative yield.

Synthesis of Graft Copolymers. A typical ATRP experiment was performed using standard Schlenk techniques as follows. The poly(α-olefin) multifunctional macroinitiator was placed in a 25 mL Schlenk flask with toluene as the solvent, followed by the addition of CuCl and HMTETA. The reaction mixture was warmed to the desired temperature and the monomer was added. After the desired polymerization time, the polymerization was terminated, and the resulting graft copolymer

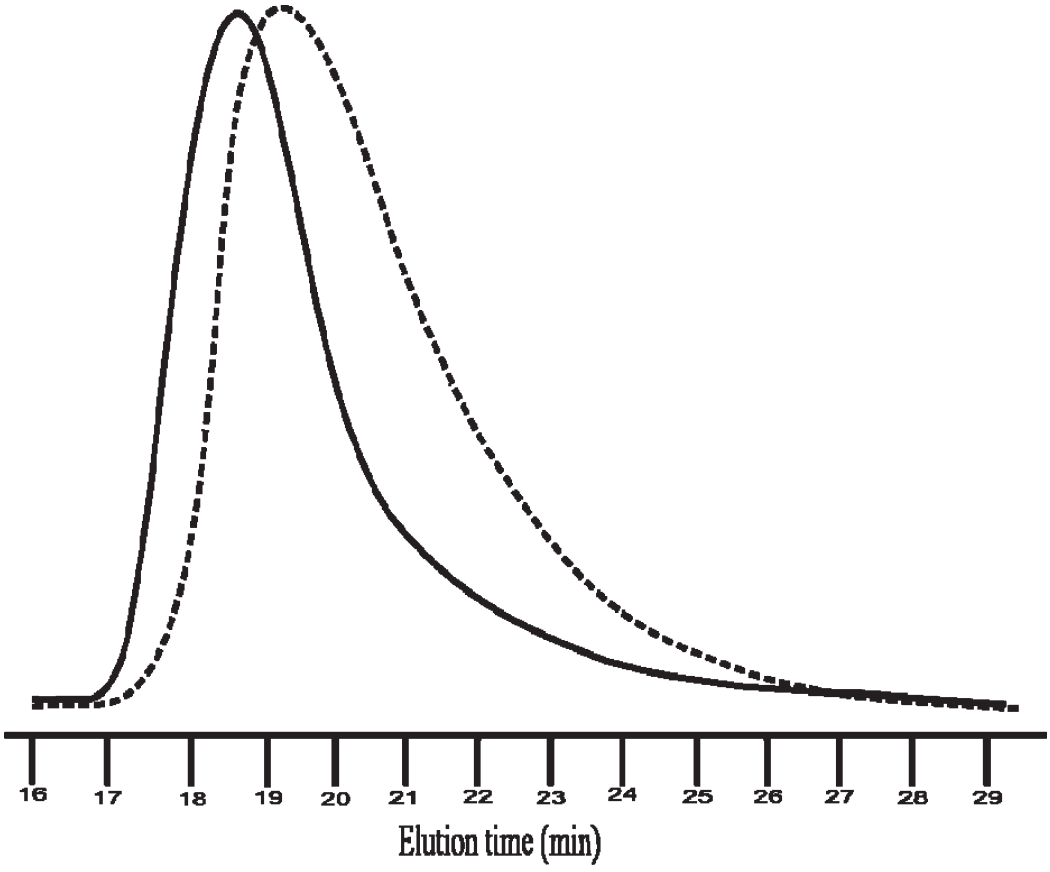


Figure 1. Monitoring the synthesis of P(Hex-*b*-Tdec) by SEC: (---) PHex block and (—) P(Hex-*b*-Tdec) block copolymer (sample 1, Table 1).

was precipitated in excess methanol. The graft copolymer was filtered, washed with methanol, and dried under vacuum.

Synthesis of Poly(α-olefin) Multifunctional Macroinitiator P[Tdec-*b*-(Tdec-*co*-10-undecen-1-ol)]. Block copolymerization of Tdec and Tdec along with the silyl protected 10-undecen-1-ol was carried out at 0 °C in a 0.1-dm^3 Schlenk-type reaction flask. A typical polymerization process was the following: the hafnium catalyst (final concentration, c = 8.32 mM) with the borane cocatalyst (final concentration, c = 8.32 mM) and TOA (molar ratio Al/Hf = 5/1) were added in toluene (5 mL). The mixture was stirred at 0 °C. Tdec (1.5 mL) was then added and the polymerization was allowed to proceed for 3 min, followed by the addition of silyl protected 10-undecen-1-ol and a new amount of Tdec. The polymerization was allowed to proceed for a few seconds and was then quenched by the addition of acidified methanol. The polymer was precipitated in methanol, washed with methanol, filtered, and dried in high vacuum at room temperature.

Poly[Tdec-*b*-(Tdec-*co*-10-undecen-1-ol)], triethylamine, and THF were added to a 500 mL glass flask equipped with a mechanical stirrer. The mixture was cooled to 0 °C, stirred and the solution of 2-bromoisobutyryl bromide in THF was added dropwise to the reaction flask. The mixture was warmed at room temperature and stirred overnight. The resulting salt was removed by filtration, the polymer was collected by condensation of the filtrate, dissolved in CH_2Cl_2 and washed successively with distilled water/$NaHCO_3$. The organic phase was dried over $MgSO_4$, condensed and the macroinitiator was dried under vacuum. The poly(α-olefin) multifunctional macroinitiator was obtained in almost quantitative yield.

Synthesis of Block−Graft Copolymers. A typical ATRP experiment was performed using standard Schlenk techniques as follows. The poly(α-olefin) multifunctional macroinitiator was placed in a 25 mL Schlenk flask with toluene as the solvent, followed by the addition of CuCl and HMTETA. The reaction mixture was warmed to the desired temperature and the monomer was added. After the desired polymerization time, the polymerization was stopped, and the resulting block−graft copolymer was precipitated in excess methanol. The block−graft copolymer was filtered, washed with methanol, and dried under vacuum.

Characterization Techniques. Size exclusion chromatography (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 four μ-styragel columns with a continuous porosity range of 10^6-10^3 Å. The columns were housed in an oven thermostated at 40 °C. Tetrahydrofuran was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with polystyrene (PSt) standards (six samples covering a molecular weight range of 10 to 900 kg/mol).

The polymer composition was determined from ^{1}H NMR spectra, which were recorded in chloroform-d at 30 °C with a Varian Unity Plus 300/54 NMR spectrometer. Furthermore, the polymer composition was determined from ^{13}C NMR spectra, which were recorded in chloroform-*d* at 25 °C using a Varian 600 MHz NMR spectrometer utilizing the inverse gated proton decoupling sequence incorporated in the library of the 600 MHz Varian NMR spectrometer which eliminates the NOE. The time delay used was 20 s and was established running T_1 experiments (delay time used was >5 T_1 of the longest relaxing nucleus). The 90° pulse applied was 6.7 μs while the number of transients was 2500.

The copolymers were further characterized by low-angle laser light scattering (LALLS). Static light scattering measurements were performed in THF. THF was refluxed over Na metal. A Chromatix KMX-6 low-angle laser light scattering LALLS photometer at 25 °C equipped with a 2 mW He−Ne laser operating at λ = 633 nm was used. Stock solutions were prepared, followed by dilution with solvent to

Table 1. Molecular Characteristics of the Block Copolymers of α-Olefins

				M_n (kg/mol)		M_w/M_n[e]	
sample	copolymers[a]	[Hf] (mM)	% w/w[b]	$M_{n(a\ block)}$ (kg/mol)[c]	$M_{n(Copolym.)}$ (kg/mol)[d]	$M_w/M_{n(a\ block)}$	$M_w/M_{n(Copolym.)}$
1	P(Hex-*b*-Tdec)	8.32	67:33	295	455	1.39	1.32
2	P(Hex-*b*-Tdec)	8.32	63:37	280	460	1.37	1.33
1	P(Oct-*b*-Tdec)	5.2	50:50	260	490	1.54	1.42
2	P(Oct-*b*-Tdec)	8.32	62:38	250	425	1.55	1.45
1	P(Hex-*b*-MMA)	6.20	80:20	260	325	1.47	1.44
2	P(Hex-*b*-MMA)	6.20	83:17	290	345	1.51	1.37
1	P(Oct-*b*-MMA)	6.20	77:23	280	390	1.35	1.28
2	P(Oct-*b*-MMA)	6.20	81:19	220	280	1.24	1.26

[a] Polymerization time for hexene-1 and octene-1 $t = 2$ min, tetradecene-1 $t = 20$ min and MMA $t = 20$ h, $T_p = 0$ °C for the α-olefins and $T_p = 110$ °C for MMA, [B] = [Hf] (mM) Al/Hf = 5/1. [b] By ^{13}C or ^{1}H NMR in $CDCl_3$. [c] By LALLS in THF and the M_w/M_n values by SEC. [d] By the M_n values of the first block and the composition by NMR. [e] By SEC in THF.

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 PHex, POct, PDec, and PTdec homopolymers in THF are 0.069, 0.071, 0.073, and 0.070 respectively.

DSC experiments were performed with a 2910 Modulated DSC model from TA Instruments. The samples were heated or cooled at a rate of 10 °C/min. The second heating results were recorded.

RESULTS AND DISCUSSION

Diblock Copolymers of Hexene-1 or Octene-1 with Tetradecene-1 and MMA. The catalytic system based on the C_s-symmetry hafnium catalyst $[(p\text{-}Et_3Si)Ph]_2C(2,7\text{-di-}tert\text{-BuFlu})(C_p)Hf(CH_3)_2$, and the borate cocatalyst ($[B(C_6F_5)_4]^-[Me_2NHPh]^+$) in the presence of TOA was employed for the preparation of block copolymers of Hex or Oct with Tdec, P(Hex-*b*-Tdec), and P(Oct-*b*-Tdec), respectively. The synthesis was performed by sequential addition of monomers starting from the polymerization of the lower boiling point monomer either Hex or Oct. It was found that the polymerization of both Hex and Oct proceeds to high yields (up to 90%) but it is not quantitative.[36] Therefore, after the polymerization of the first block the unreacted monomer was eliminated by distillation under vacuum before the addition of the second monomer, Tdec. If some amount of Hex or Oct remained in the flask when the Tdec was added, a random copolymerization with Tdec would result, leading to structurally ill-defined block copolymers. The copolymerization took place in the presence of a suitable amount of TOA (molar ratio Al/Hf = 5/1). It was found that TOA greatly accelerates the polymerization of α-olefins so that it can be completed in a few minutes instead of several hours.[36] The reaction was monitored by SEC, showing that there was a clear shift of the chromatogram corresponding to the first block to higher molecular weight species. An example referring to the synthesis of a P(Hex-*b*-Tdec) copolymer is given in Figure 1. In addition, there was no evidence of termination reactions after the addition of the second monomer, since SEC analysis showed that the first block was completely consumed during the crossover reaction, leading to the synthesis of rather well-defined block copolymers.

The molecular characteristics of the block copolymers are given in Table 1. It is obvious that the samples had moderately narrow and similar molecular weight distributions both for the first block and for the final block copolymer. The composition of the copolymers was calculated from the ^{13}C NMR spectra in $CDCl_3$. Characteristic spectra are given in Figures 2 and 3. For the block copolymers P(Hex-*b*-Tdec) the composition was obtained from the signals at 23.45 ppm, corresponding to the C5 of Hex and at 22.95 ppm, corresponding to the C13 of Tdec (Figure 2). In the case of the block copolymers P(Oct-*b*-Tdec) the composition was calculated from the signals at 29.6 ppm, attributed to the C7 of Tdec compared to other signals attributed to both monomers (Figure 3). Furthermore, the overall polymerization yield was as high as 90%. All of these data indicate that this synthetic approach was well controlled and efficient for the synthesis of block copolymers.

A similar approach was also adopted for the synthesis of block copolymers of Hex or Oct with MMA. The sequence of monomer addition is crucial for the efficient synthesis of such copolymers. A procedure involving the initial polymerization of MMA followed by the addition of the olefin was unsuccessful. In this case SEC and ^{1}H NMR analysis revealed that the only product was PMMA homopolymer. Consequently, the active chain end of the growing PMMA chain is not able to initiate the polymerization of the olefin for the synthesis of the block copolymer. However, the reverse mode of monomer addition is an efficient method for the synthesis of the desired structures. In the experiment described here, the polymerization of the olefin was conducted first under the conditions reported above. Any amount of unreacted monomer was eliminated by distillation under vacuum followed by the addition of MMA. The molecular characteristics of the samples are given in Table 1, where the reaction sequence was monitored by SEC. A characteristic example is given in Figure 4. It is obvious that the polyolefin trace shifts to higher molecular weights after the polymerization of MMA and that both peaks have relatively low polydispersity. Furthermore, the first block was quantitatively consumed during the crossover reaction indicating the absence of termination reactions. The successful synthesis of the diblocks was further confirmed by the ^{1}H NMR spectra. Characteristic examples are given in Figures 5 and 6. Furthermore, the yield of the polymerization of both monomers was near quantitative. All of these results point to the same conclusion that the polymerization was very well controlled.

The block copolymerization of the α-olefins with MMA can only be done by polymerizing the olefin first, due to mechanistic incompatibility (i.e., migration insertion in olefin polymerization vs conjugate addition in MMA polymerization). According to the

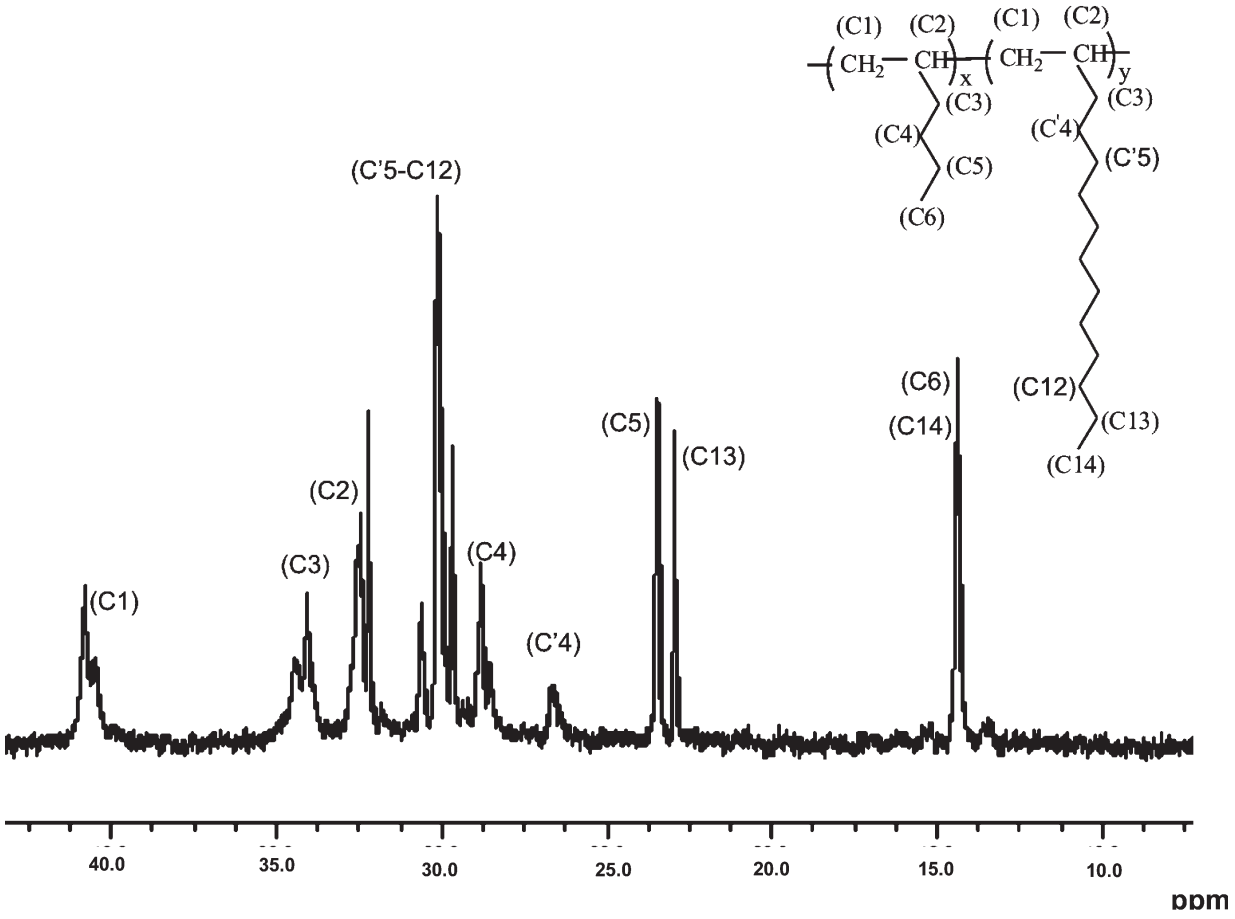


Figure 2. 150.86 MHz ^{13}C NMR spectrum of P(Hex-*b*-Tdec) block copolymer, (sample 1) in $CDCl_3$ at 25 °C.

literature,[39] the mechanism of the polymerization of MMA involves either a monometallic or a bimetallic approach. In both approaches the end methacrylate unit is attached to the hafnium metal as an enol ester. The monometallic mechanism involves the presence of cationically charged metal species, whereas the bimetallic mechanism assumes the presence of both neutral and cationically charged catalyst species. In the later case, the growing PMMA chain is connected to the neutral hafnium moiety, whereas the new coming monomer approaches the cationic metal center through the carbonyl group. The growing polymer chain is transferred from the neutral to the cationically charged species upon addition of the new monomer unit. During this procedure the cationic complexes become neutral and the neutral complexes become cationically charged. In both mechanisms the polymer chain grows through the Michael addition of the incoming monomer to the enol ester of the growing polymer chain. These active PMMA catalytic species are not able to initiate the polymerization of olefins. According to the monometallic mechanism the olefin may form a π-complex with the cationically charged metal species. However, the chain growth is hindered by the fact that the monomer has to be introduced to the rather strong Hf−O bond for the subsequent formation of the σ-complex instead of an Hf−C bond, which is usually the case for olefin polymerization. According to the bimetallic mechanism the neutral species carrying the PMMA chain cannot interact with the olefins, since the hafnium complex has no vacant site available for interaction with the olefin. The reverse procedure allows for the efficient block copolymerization, since the polyolefin chain plays the role of the alkyl ligand of the active catalytic species that are available for the polymerization of MMA. These mechanistic considerations are displayed in Scheme 3. Yasuda et al. reported the synthesis of P(Hex-*b*-MMA) block copolymers using bridged organolanthanide complexes.[31] They also concluded that the only efficient way to prepare the desired copolymers was the polymerization of Hex first followed by the addition of MMA.

Differential scanning calorimetry, DSC, was employed to study the thermal properties of the produced block copolymers. The results are displayed in Table 2. The polymers produced by the specific catalytic system are predominantly syndiotactic. The T_g values of PHex and POct homopolymers prepared by the same catalytic system were found to be equal to −32.7 and −59.0 °C, respectively.[36] PTdec, on the other hand, is a semicrystalline polymer due to the presence of the long side chains, which can form crystalline domains (side chain crystallinity). The T_m value measured for PTdec prepared by the same catalytic species was found to be equal to 7.1 °C. For the syndiotactic PMMA the T_g value reported in the literature was equal to 108 °C.[40] For all samples two distinct transitions were observed corresponding to the respective transition of each block. The T_g and T_m values were in very close agreement with those reported for the corresponding homopolymers indicating that the copolymers are microphase separated.

Triblock terpolymers of Hex and Oct with Tdec, Dec or MMA. The synthesis of the triblock terpolymers P(Hex-*b*-Oct-*b*-Tdec), P(Hex-*b*-Oct-*b*-Dec), and P(Hex-*b*-Oct-*b*-MMA) was

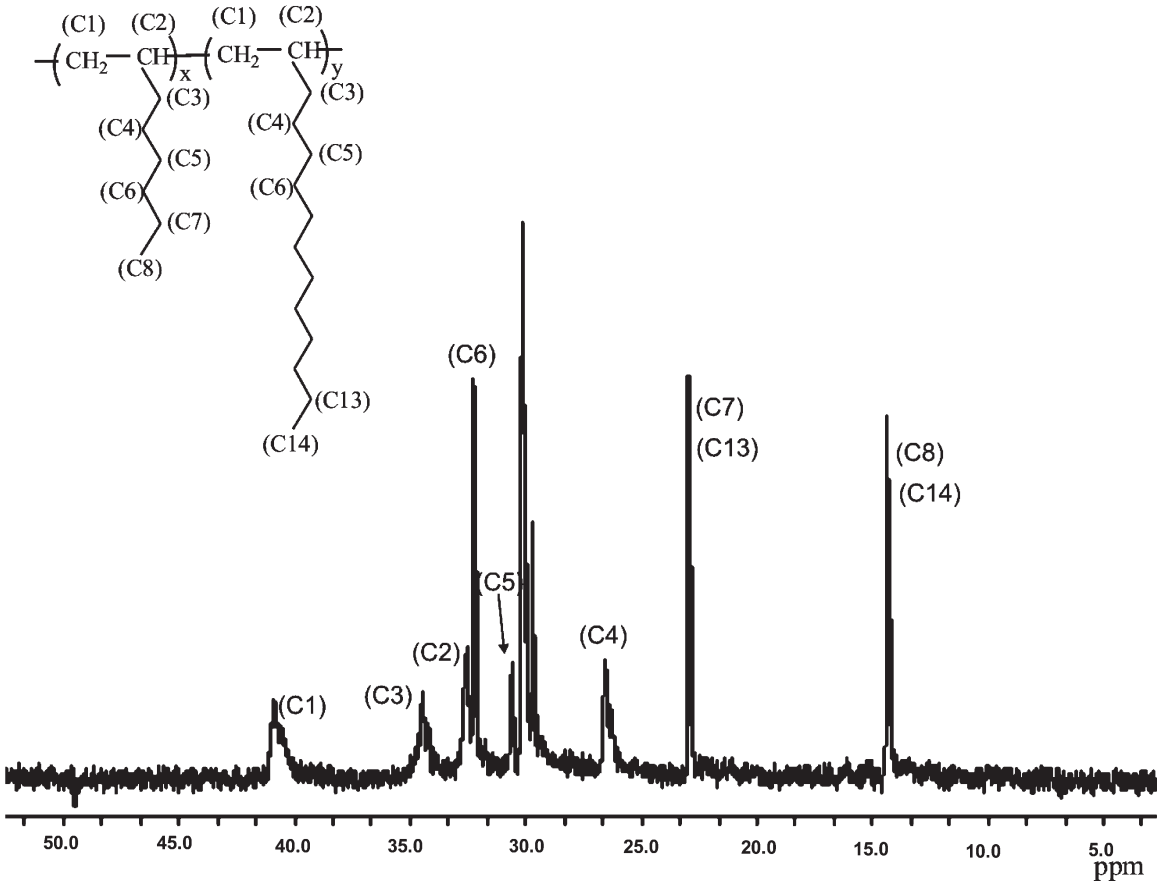


Figure 3. 150.86 MHz ^{13}C NMR spectrum of P(Oct-*b*-Tdec) block copolymer, (sample 2) in $CDCl_3$ at 25 °C.

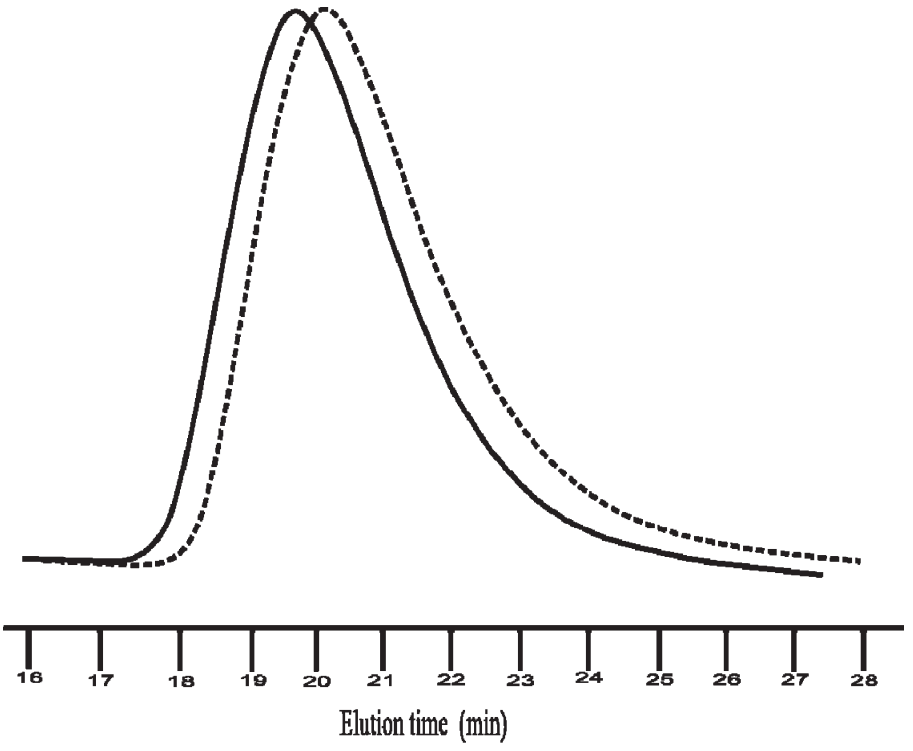


Figure 4. Monitoring the synthesis of P(Oct-*b*-MMA) by SEC: (---) POct block and (—) P(Oct-*b*-MMA) block copolymer (sample 2, Table 1).

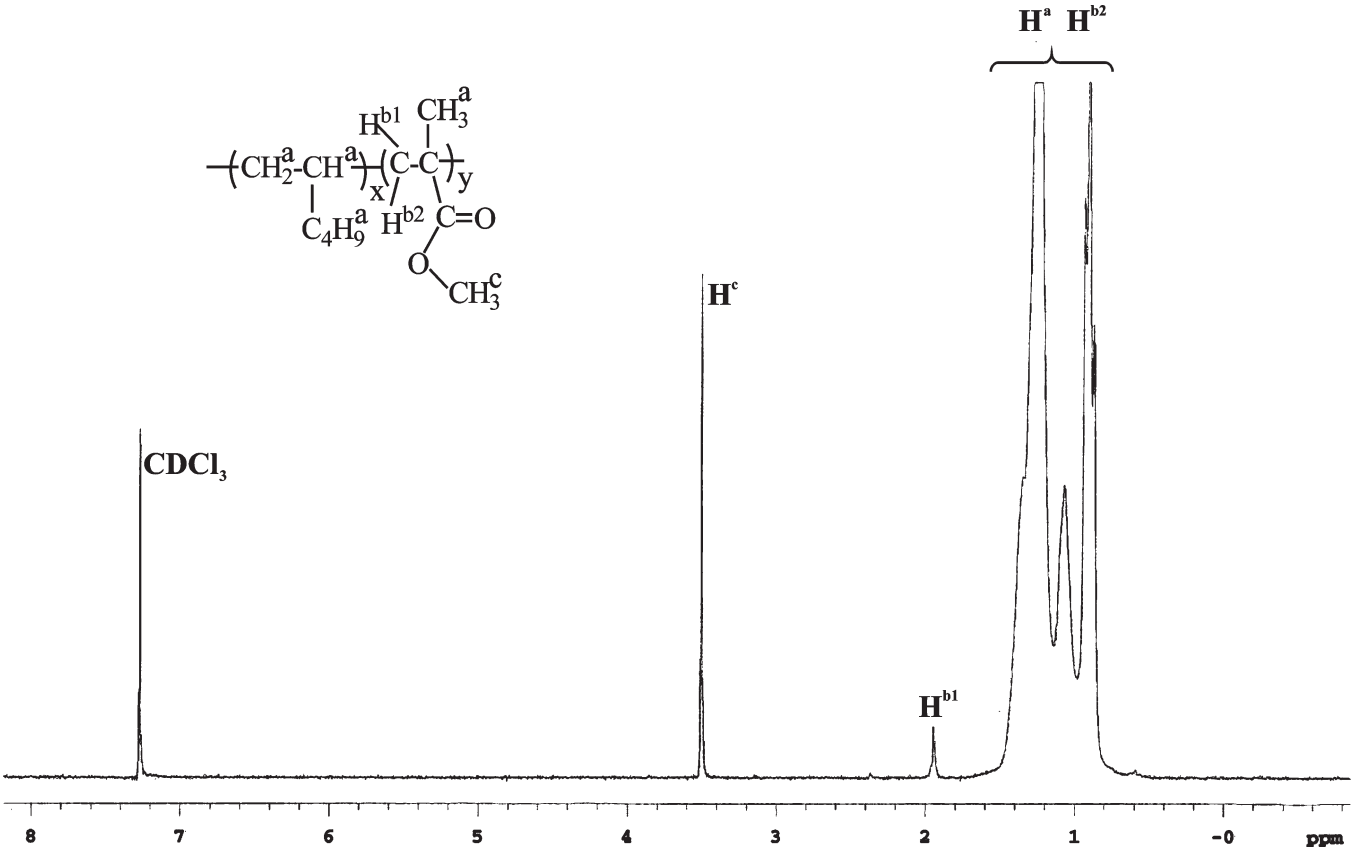


Figure 5. 300 MHz ^{1}H NMR spectrum of P(Hex-*b*-MMA) block copolymer, (sample 1, Table 1) in $CDCl_3$ at 25 °C.

also achieved using the methods reported above for the synthesis of the diblock copolymers. The order of monomer sequence addition was determined by the order of increase of the monomers' boiling point. Since the polymerization yield was not quantitative for the olefins and in order to avoid statistical copolymerization, it was necessary to eliminate the excess of unreacted monomer by distillation prior the addition of the next one. This was facilitated by starting with the polymerization of the lowest boiling point monomer and then proceeding with monomers of higher boiling points. The polymerization took place in the presence of TOA in order to accelerate the reaction. For the synthesis of the P(Hex-*b*-Oct-*b*-MMA) triblock terpolymers MMA was polymerized last for reasons explained earlier in the case of the corresponding diblock copolymers. The molecular characteristics of the samples are given in Table 3. The copolymerization reactions were monitored by SEC. Characteristic chromatograms regarding the synthesis of the triblock terpolymers are given in Figure 7.

SEC analysis unambiguously shows that the polymerization of the different blocks proceeds without appreciable chain termination leading to products of relatively narrow molecular weight distributions. The composition of the P(Hex-*b*-Oct-*b*-Tdec) terpolymers was calculated from the ^{13}C NMR spectra in $CDCl_3$. A characteristic example is shown in Figure 8. The composition was obtained from the characteristic signals, corresponding to the specific carbons of the polyolefins: the signal at 23.45 ppm, corresponding to the C5 of Hex, the signal at 29.6 ppm, corresponding to the C7 of Tdec and the signals at 22.9 ppm, which corresponds to the C7 of Oct and C13 of Tdec. The composition of the P(Hex-*b*-Oct-*b*-MMA) triblock terpolymers was obtained by combination of the ^{1}H NMR and ^{13}C NMR spectra.

The thermal behavior of the triblock terpolymers was examined by DSC experiments. The results are given in Table 4. In two cases distinct thermal transitions were observed. For the amorphous P(Hex-*b*-Oct-*b*-MMA) triblock terpolymer the three T_g values obtained were very close to those of the corresponding homopolymers.[36] The same behavior was also observed for the T_g values of the amorphous blocks of the P(Hex-*b*-Oct-*b*-Tdec) triblock terpolymers. However, the melting temperature of the PTdec block was slightly lower than the one measured for the corresponding homopolymer. This effect can be attributed to the presence of the amorphous blocks of PHex and POct, which induced constraints on the organization of the PTdec blocks to crystalline domains. These results clearly indicate that the terpolymers are microphase separated. For the P(Hex-*b*-Oct-*b*-Dec) copolymer two Tg values were obtained. This can be attributed either to the non resolved transitions of the POct and PDec blocks (the Tg values are −59.0 and −66.1 °C, respectively[36]) or to possible mixing of the two phases.

Synthesis of Graft Copolymers Having PTdec or POct Backbones and PMMA or PSt Branches. In a previous report[35] it was shown that the direct copolymerization of Tdec and Oct with 10-undecen-1-ol using the same catalytic system, employed in this work, in the presence of TOA failed to provide controlled copolymerization, due to problems induced by the presence of the hydroxyl groups. Therefore, the functional group was protected by reaction with *tert*-butyldimethylsilyl chloride. Consequently, statistical copolymers of these α-olefins with 1-*tert*-butyldimethylsilyloxy-10-undecene were synthesized employing

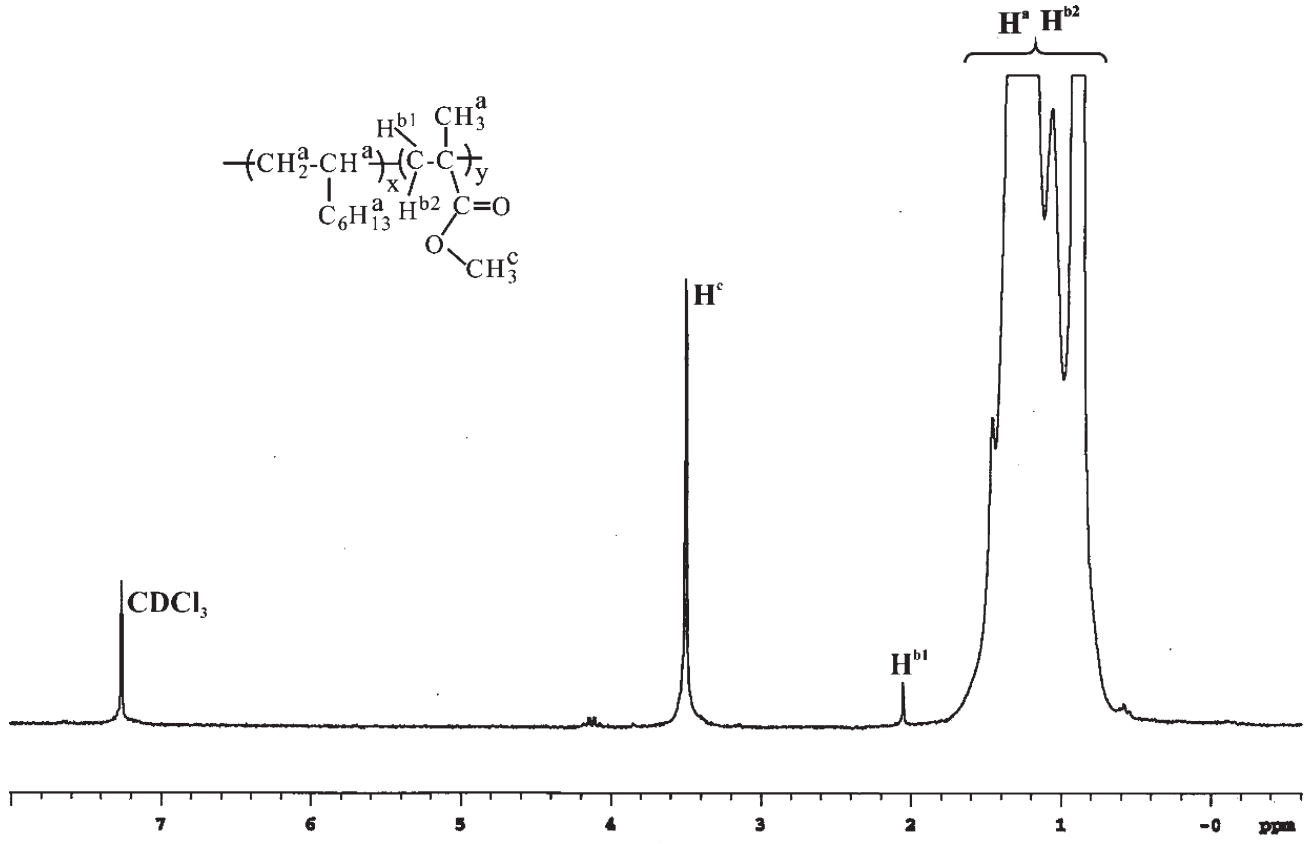


Figure 6. 300 MHz ^{1}H NMR spectrum of P(Oct-*b*-MMA) block copolymer, (sample 2, Table 1) in $CDCl_3$ at 25 °C.

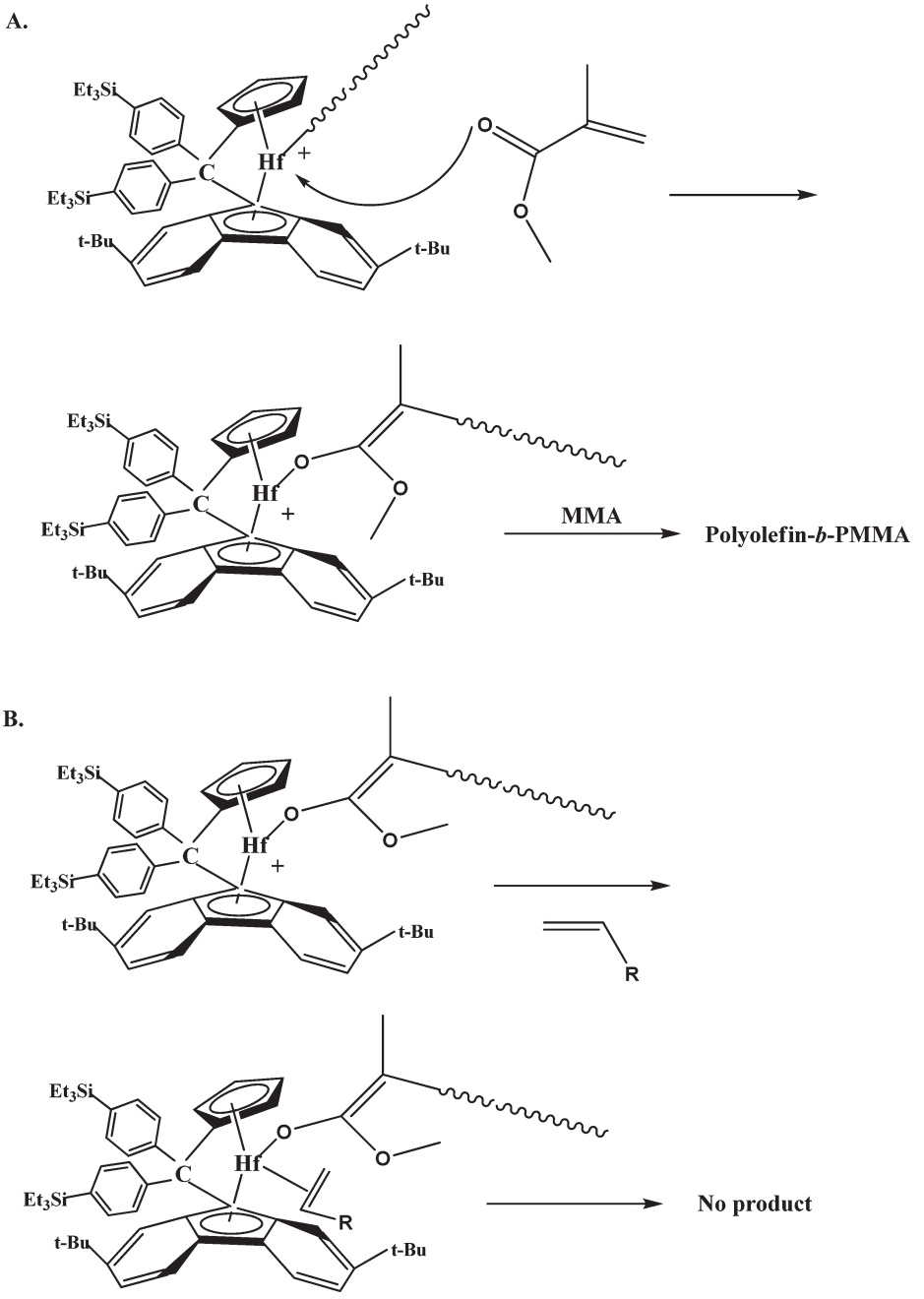
the same catalytic system. Copolymers of high molecular weights and relatively narrow molecular weight distributions were obtained. The reactivity ratios of the monomers were measured using several graphical methods. It was concluded that the polymerization rate of the α-olefins was much higher that that of the protected 10-undecen-1-ol. In the case of the P(Tdec-*co*-Undec) copolymers there was a tendency to obtain a highly alternating structure, whereas in the case of the P(Oct-*co*-Undec) copolymers multiblock copolymers with longer sequences of the unfunctionalized polyolefin were formed.

These statistical copolymers can be further employed for the synthesis of graft copolymers bearing PTdec or POct backbones and PMMA or PSt branches. The reaction sequence is given in Scheme 4. The protective *tert*-butyldimethylsilyl group was partly removed under mild acidic conditions leading to polyolefins having hydroxyl groups along the chains. These groups were then esterified by reaction with 2-bromoisobutyryl bromide in the presence of triethylamine affording a multifunctional macroinitiator bearing initiation sites for ATRP. From these initiation sites the polymerization of either MMA or St was conducted leading to the synthesis of the desired graft copolymers. The partial deprotection of the *tert*-butyldimethylsilyl groups assures that all the ATRP initiation sites (formed after the esterification of the hydroxyl groups) will be efficiently used for the polymerization of MMA or St. Otherwise, the steric crowding from the huge number of initiation sites may prevent their efficiency, leading to nonwell-defined graft copolymers with a wide distribution of branches.

The reaction sequence was monitored by ^{1}H NMR spectroscopy and SEC. A representative example showing the ^{1}H NMR spectra of the partly deprotected P(Tdec-*co*-Undec) statistical copolymers prior to and after the esterification reaction is reported in the Supporting Information (SI9a and SI9b). The signal attributed to the methylene protons next to the hydroxyl group ($-CH_2OH$, δ = 3.5 ppm) disappeared after the esterification reaction and a singlet appeared, attributed to the methyl protons of the ester groups ($-CH_2OCOC-(CH_3)_2Br$, δ = 1.8 ppm), indicating the quantitative conversion of the hydroxyl groups.

The number of initiating sites, calculated by the NMR spectra, was equal to 105 and 230 per PTdec and POct chain, respectively. The radical grafting from copolymerization usually leads to radical−radical coupling termination reactions leading to cross-linked products. Therefore, in order to avoid these side reactions the copolymerization was conducted in rather dilute solutions. The ATRP of MMA and St was performed using CuBr as the catalyst and HMTETA as the cocatalyst in toluene solutions at 80 and 110 °C respectively. The reaction was monitored by SEC. A characteristic example is shown in Figure 9 (see also Figure SI10, Supporting Information). It is evident that the macroinitiator was quantitatively consumed and that the final product had a monodisperse and symmetric peak of relatively narrow molecular weight distribution, despite the fact that the number of branches was quite high in all cases. This is one of the advantages of the grafting "from" procedure, adopted in this work.[41] Similar grafting "from" approaches in combination with ATRP techniques have been employed in the past for the synthesis of polymer brushes.[42] The ^{1}H NMR spectra further support the formation of the graft copolymers. A characteristic example is given in Figure 10 (see also Figure SI11, Supporting Information). The copolymers with MMA showed a signal at

Scheme 3



3.6 ppm, which is attributed to the ester hydrogens, $COOCH_3$, of the MMA units, whereas the copolymers with St showed the characteristic signals of the aromatic protons in the range between 6 and 7 ppm. The molecular characteristics of the samples are given in Table 5.

The thermal properties of the P[(Tdec-*co*-Undec)-*g*-MMA] and P[(Tdec-*co*-Undec)-*g*-St] graft copolymers were studied by DSC. The results are given in Table 6. The melting temperature and the melting enthalpy of the PTdec backbone considerably decreased compared to the corresponding linear chains. This behavior is attributed to the constraints imposed by the PMMA and PSt side chains, which restrict the organization of the PTdec backbone to crystalline domains. The T_g values of the PMMA and PSt side chains were increased compared to the corresponding linear chains and taking into account their low molecular weight.

Table 2. DSC Results of the Block Copolymers of α-Olefins[a]

copolymers	M_n (kg/mol)	M_w/M_n	ΔH_m (J/g)	T_g (°C)	T_m/T_{g2} (°C)
P(Hex-*b*-Tdec)	455	1.32	27.20	−31.8	5.2
P(Oct-*b*-Tdec)	425	1.45	28.32	−59.5	6.2
P(Hex-*b*-MMA)	325	1.47	-	−33.1	108.4
P(Oct-*b*-MMA)	390	1.35	-	−58.8	104.1

[a] Characteristic thermograms are given in the Supporting Information.

Table 3. Molecular Characteristics of the Triblock Terpolymers of α-Olefins

				M_n (kg/mol)			M_w/M_n[e]		
sample	copolymers[a]	[Hf] (mM)	% w/w[b]	M_n(kg/mol)[c]$_{(first\ block)}$	M_n(kg/mol)[d]$_{(Diblock)}$	M_n (kg/mol)[d]$_{(Triblock)}$	$M_w/M_{n(first\ block)}$	$M_w/M_{n(Diblock)}$	$M_w/M_{n(Triblock)}$
1	P(Hex-*b*-Oct-*b*-Tdec)	8.32	56:34:10	190	310	370	1.60	1.45	1.38
2	P(Hex-*b*-Oct-*b*-Tdec)	8.32	50:42:8	340	625	680	1.52	1.51	1.40
3	P(Hex-*b*-Oct-*b*-Dec)	8.32	54:36:10	335	556	656	1.48	1.46	1.30
4	P(Hex-*b*-Oct-*b*-MMA)	8.32	53:36:11	375	600	720	1.60	1.54	1.48
5	P(Hex-*b*-Oct-*b*-MMA)	8.32	50:20:30	380	530	760	1.52	1.49	1.45

[a] Polymerization time for hexene-1, t = 5 min, and octene-1, t = 20 min, tetradecene-1 or decene-1, t = 30 min, and MMA t = 20 h, T_p = 0 °C for the α-olefins and T_p = 110 °C for MMA, [B] = [Hf] (mM) Al/Hf = 5/1. [b] By ^{1}H and ^{13}C NMR in $CDCl_3$. [c] By LALLS in THF and the M_w/M_n values by SEC. [d] By the M_n values of the first block and the composition by NMR. [e] By SEC in THF.

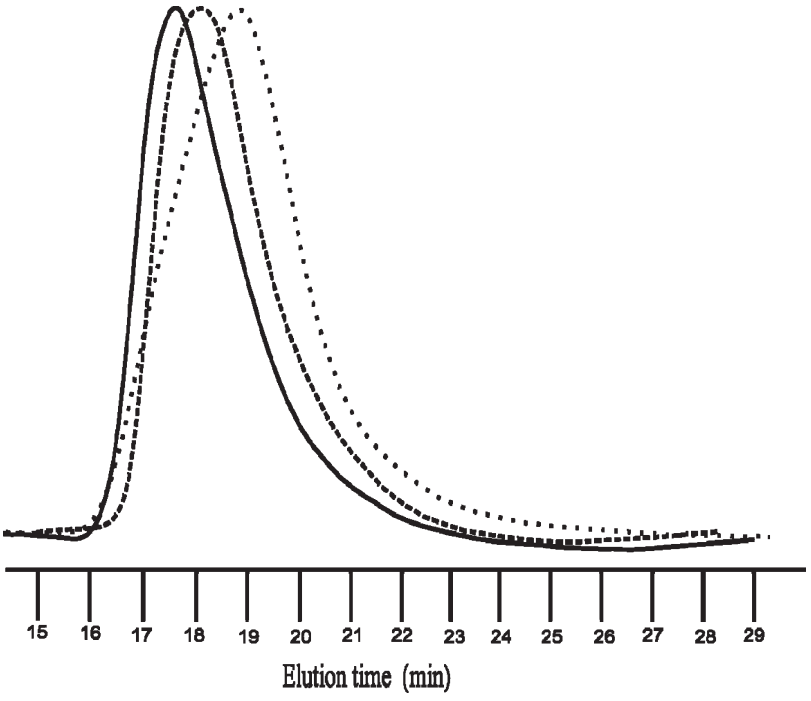


Figure 7. Monitoring the synthesis of P(Hex-*b*-Oct-*b*-Tdec) triblock terpolymer by SEC: (···) PHex block, (---) P(Hex-*b*-Oct) diblock copolymer and (—) P(Hex-*b*-Oct-*b*-Tdec) triblock terpolymer, (sample 2, Table 3).

This result reflects the high grafting density of the side chains, which causes extension of these chains and restrictions to their mobility. Similar behavior was observed for the P[(Oct-*co*-Undec)-*g*-MMA] and P[Oct-*co*-Undec)-*g*-St] graft copolymers (Table 6). Increased T_g values were obtained for both the backbone and side chains for reasons reported previously.

Synthesis of Block−Graft Copolymers with PTdec-*b*-(PTdec-*co*-Undec) Backbone and PMMA or PSt branches. The same approach was adopted for the synthesis of the PTdec-*b*-[(PTdec-*co*-Undec)-*g*-PMMA] and PTdec-*b*-[(PTdec-*co*-Undec)-*g*-PSt] block−graft copolymers, as shown in Scheme 5. Tdec was polymerized as previously reported in the presence of TOA. When the polymerization was completed a mixture of a fresh amount of Tdec and silyl protected Undec was added to the reaction mixture leading to the synthesis of a PTdec-*b*-(PTdec-*co*-Undec) diblock copolymer, where the first block was a PTdec homopolymer and the second a random copolymer consisting of Tdec and Undec monomer units. The *tert*-butyldimethylsilyl protective groups were removed and the remaining hydroxyl moieties were subsequently esterified by reaction with 2-bromoisobutyryl bromide, following the same approach as discussed previously. The ^{1}H NMR spectra of both the PTdec-*b*-(PTdec-*co*-Undec) block copolymer and the resulting multifunctional macroinitiator are given in the Supporting Information (Figure SI12, parts a and b). The spectra show the presence of a triplet attributed to the methylene protons being next to the hydroxyl group ($-CH_2OH$, δ = 3.5 ppm) and a singlet attributed to the methyl protons of the ester group ($-CH_2OCOC-(CH_3)_2Br$, δ = 1.8 ppm). After the esterification reaction the triplet disappeared, indicating efficient conversion of the hydroxyl group to the ester group. NMR analysis revealed that there are 42 bromoisobutyryl moieties along the backbone.

The bromoisobutyryl functions served as initiators for the ATRP of either MMA or St, leading to the synthesis of the

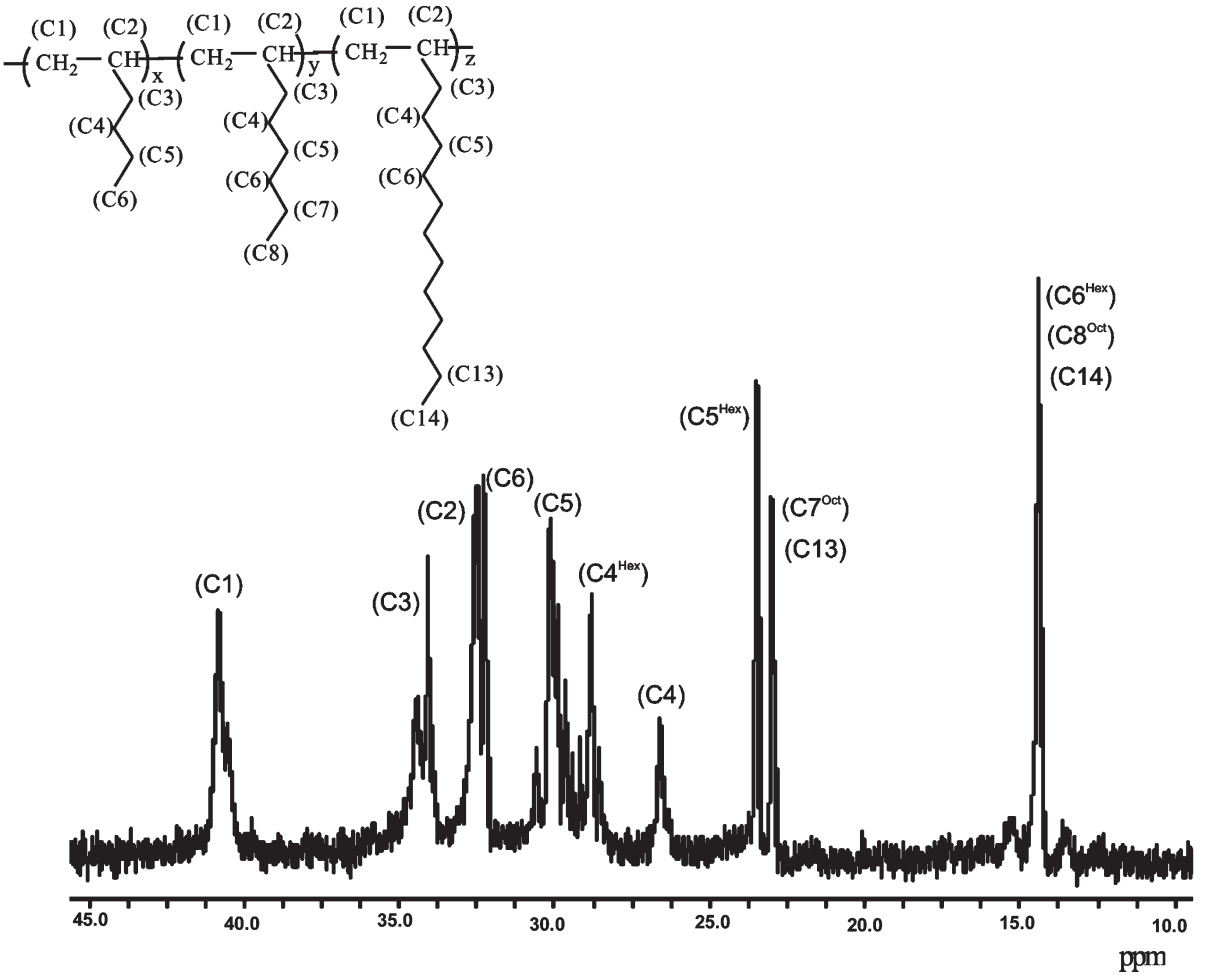


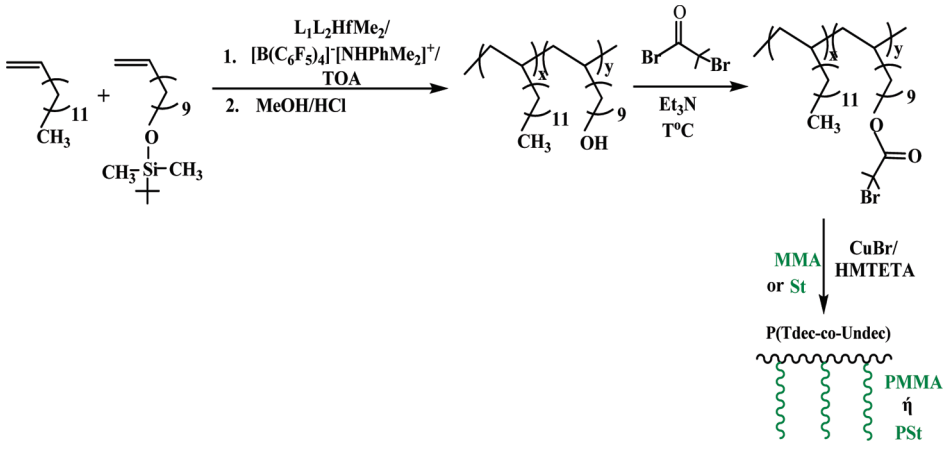
Figure 8. 150.86 MHz ^{13}C NMR spectrum of P(Hex-*b*-Oct-*b*-Tdec) triblock terpolymer, (sample 2, Table 3) in $CDCl_3$ at 25 °C.

Table 4. DSC Results of the Triblock Terpolymers of α-Olefins[a]

copolymers	M_n (kg/mol)	M_w/M_n	ΔH_f (J/g)	T_{g1} (°C)	T_{g2} (°C)	T_m/T_{g3} (°C)
P(Hex-*b*-Oct-*b*-Tdec)	370	1.38	20.13	−31.1	−59.2	5.4
P(Hex-*b*-Oct-*b*-Dec)	656	1.30	-	−31.9	−60.1	-
P(Hex-*b*-Oct-*b*-MMA)	760	1.45	-	−33.9	−52.5	108.4

[a] Characteristic thermograms are given in the Supporting Information.

Scheme 4



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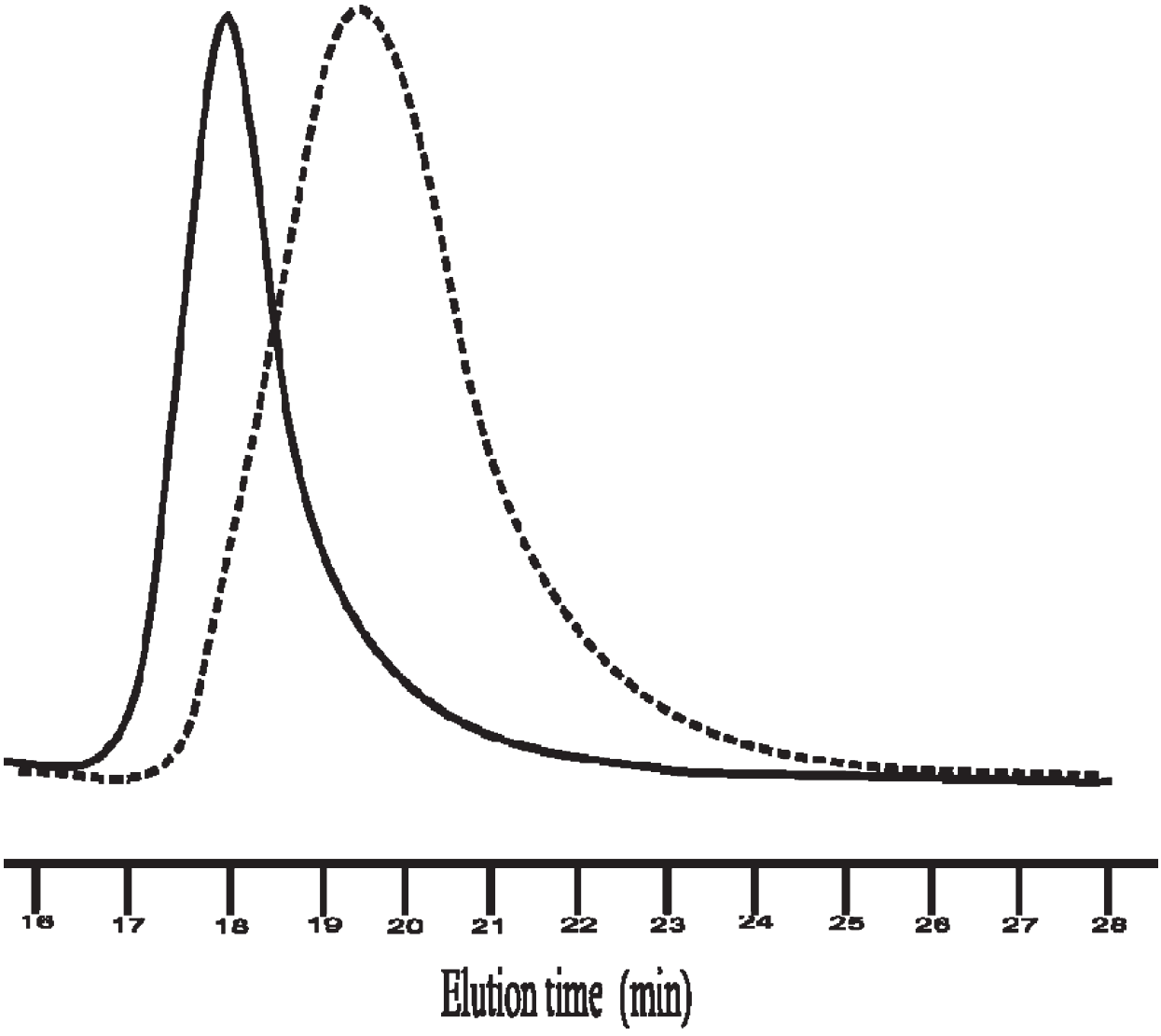


Figure 9. Monitoring the synthesis of P[(Tdec-*co*-Undec)-*g*-MMA] graft copolymer by SEC: (---) P(Tdec-*co*-Undec) random copolymer and (—) P[(Tdec-*co*-Undec)-*g*-MMA] graft copolymer, (sample 2, Table 5).

Table 5. Molecular Characteristics of the Graft Copolymers Consisting of PTdec or POct Backbone and PMMA or PS Side Chains

sample	copolymers[a]	time (min)	$(M_n)_{Macroin.}$ (kg/mol)[b]	$(M_n)_{Graft}$ (kg/mol)[c]	$(M_w/M_n)_{Macroin.}$[d]	$(M_w/M_n)_{Graft}$[d]	% w/w[e] MMA or St	$(M_n)_{branch}$ (kg/mol)[f]	N[g]
1	(P(Tdec-*co*-Undec)-*g*-MMA)	60	390	2260	1.33	1.10	83	17.5	105
2	(P(Tdec-*co*-Undec)-*g*-MMA)	30	390	830	1.33	1.22	53	4.2	105
3	(P(Tdec-*co*-Undec)-*g*-MMA)	20	390	820	1.33	1.25	52	4.1	105
1	(P(Tdec-*co*-Undec)-*g*-St)	1200	390	690	1.33	1.35	43	2.9	105
1	P((Oct-*co*-Undec)-*g*-MMA)	5	315	630	1.31	1.38	50	1.4	230
2	P((Oct-*co*-Undec)-*g*-MMA)	7	315	1050	1.31	1.35	70	3.2	230
1	P((Oct-*co*-Undec)-*g*-St)	20	315	1260	1.31	1.28	75	4.1	230
2	P((Oct-*co*-Undec)-*g*-St)	20	315	890	1.31	1.30	65	2.5	230

[a] T_p for MMA 80 °C and 110 °C for styrene. [b] By LALLS in THF and the M_w/M_n values by SEC. [c] By the M_n of macroinitiator and the composition by ^{1}H NMR in $CDCl_3$. [d] By SEC in THF. [e] By ^{1}H NMR spectroscopy. [f] By the number of branches and the molecular characteristics. [g] *N*: number of branches measured by ^{1}H NMR in $CDCl_3$ of the P(Tdec-*co*-Undec) or P(Oct-*co*-Undec) macroinitiator.

desired products. The reactions were monitored by SEC. A characteristic example is given in Figure 11. The PTdec and PTdec-*b*-(PTdec-*co*-Undec) chromatograms had rather broad molecular weight distributions but are symmetric. A small but

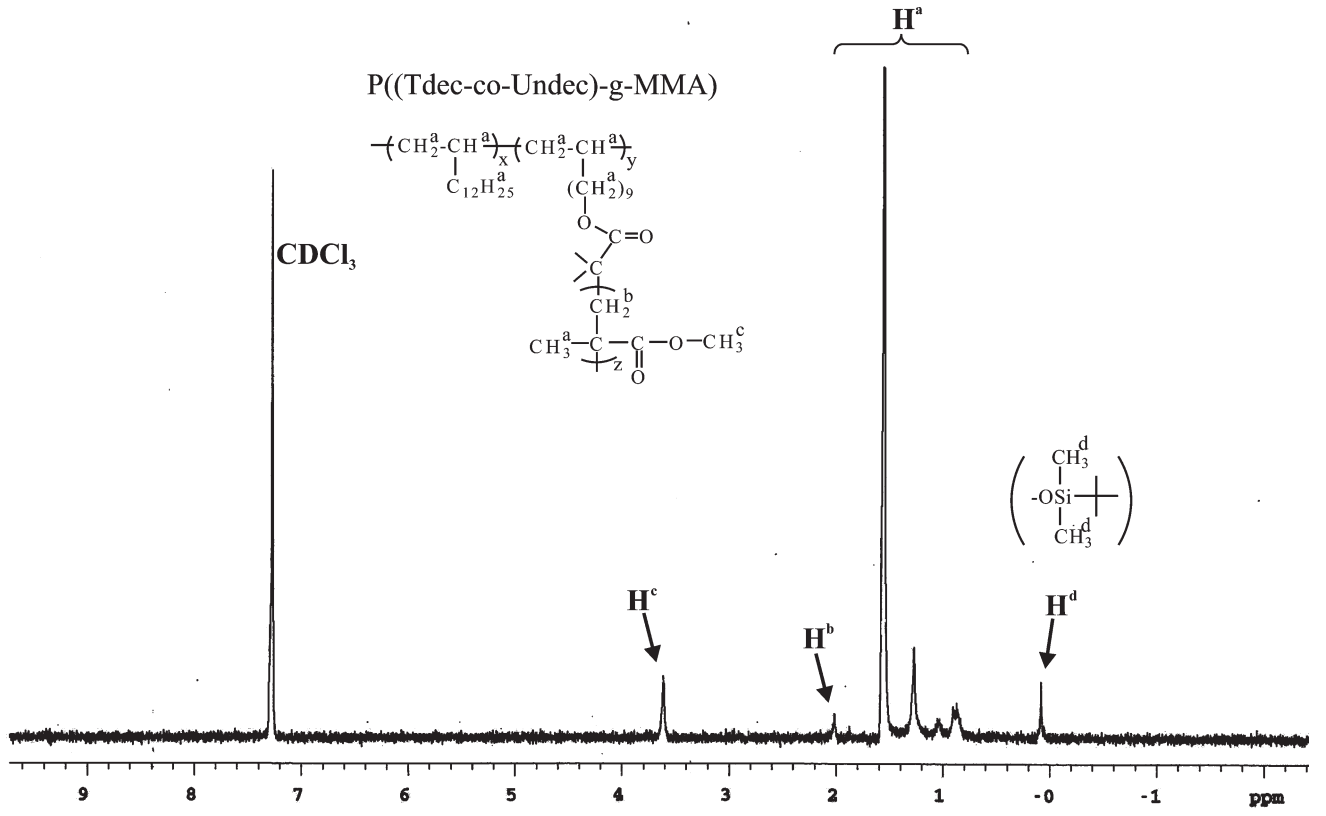


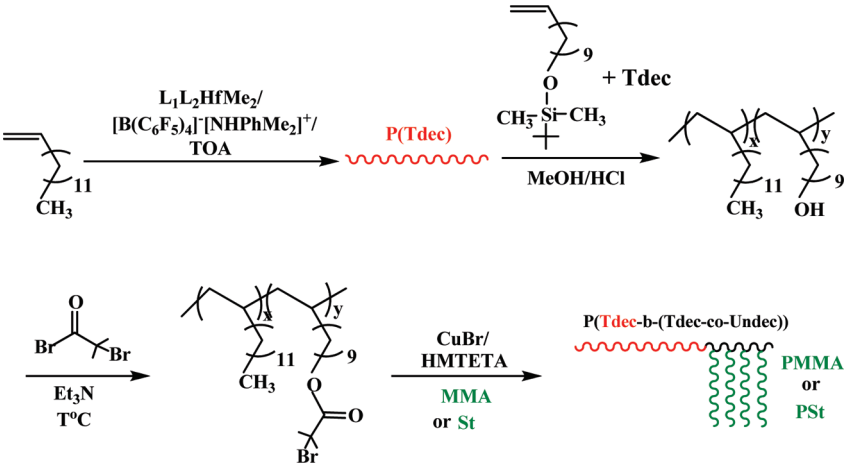
Figure 10. 300 MHz ^{1}H NMR spectrum of P[(Tdec-*co*-Undec)-*g*-MMA] graft copolymer, (sample 2, Table 5) in $CDCl_3$ at 25 °C.

Table 6. DSC Results of the Graft Copolymers[a]

copolymers	M_n (kg/mol)	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_m (J/g)
P((Tdec-*co*-Undec)-*g*-MMA)	830	1.22	119.5	−19.3	3.71
P((Tdec-*co*-Undec)-*g*-St)	690	1.35	97.4	−17.6	18.37
P((Oct-*co*-Undec)-*g*-MMA)	1050	1.35	125.4	−51.8	-
P((Oct-*co*-Undec)-*g*-St)	890	1.30	98.3	−49.5	-

[a] Characteristic thermograms are given in the Supporting Information.

Scheme 5



clear shift to higher molecular weights was observed from the first block to the final copolymer macroinitiator. This small change in the SEC trace has to do with the low molecular weight of the random copolymer, which is the second block of the backbone.

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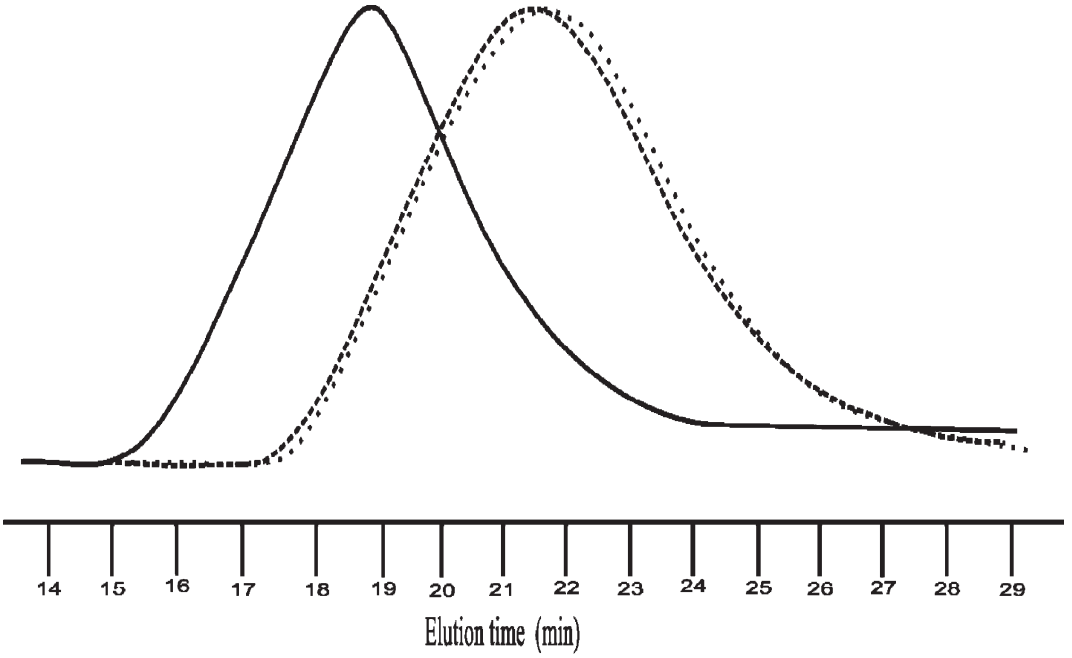

Figure 11. Monitoring the synthesis of P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-MMA)] block−graft copolymer by SEC: (···) PTdec block, (---) P(Tdec-*b*-(Tdec-*co*-Undec)) copolymer, and (—) P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-MMA)] block−graft copolymer.

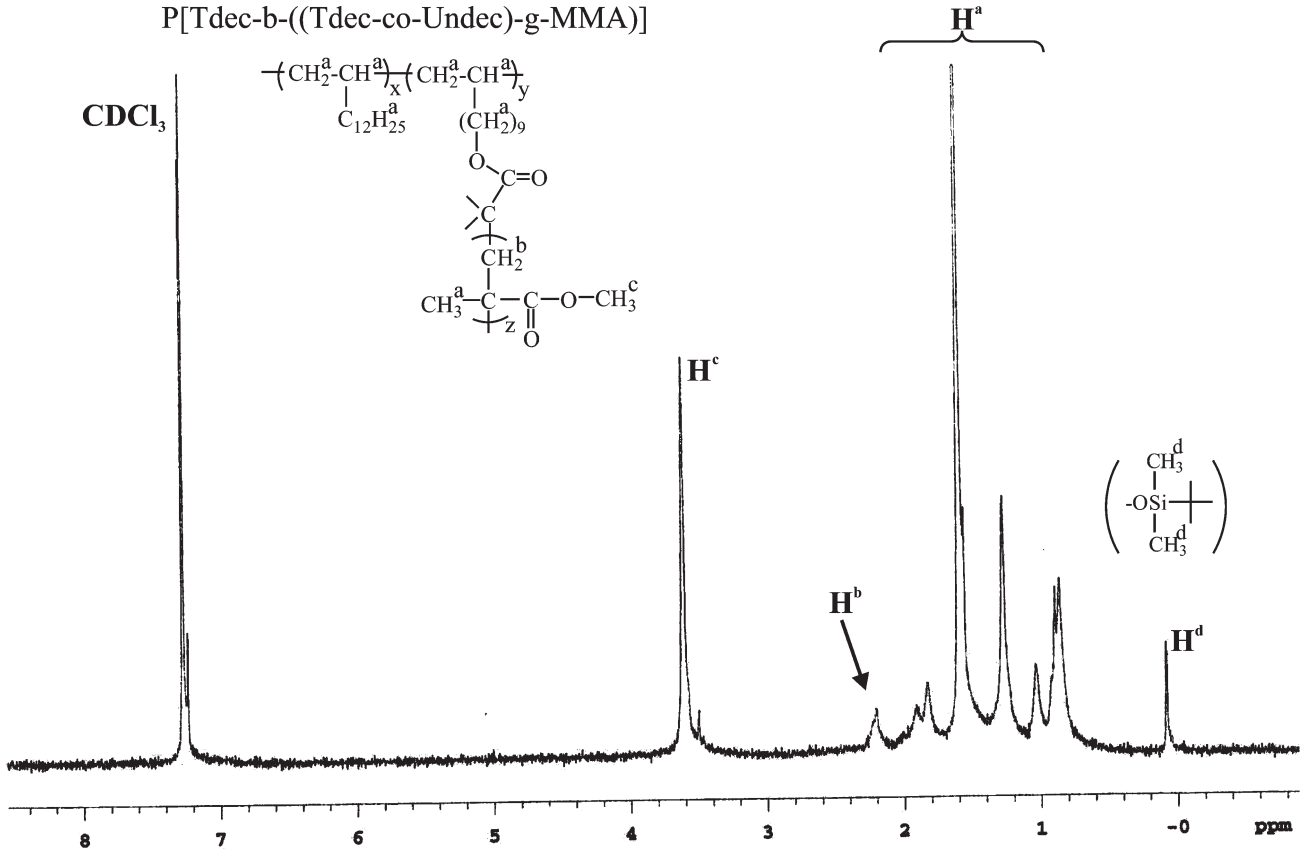

Figure 12. 300 MHz ^{1}H NMR spectrum of P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-MMA)] block−graft copolymer in $CDCl_3$ at 25 °C.

However, the chromatogram of the block−graft copolymer was shifted to much higher molecular weights, showing that the macroinitiator was quantitatively consumed during the grafting reaction. The synthesis of the desired products was also

Table 7. Molecular Characteristics of the Block−Graft Copolymers from Tetradecene-1 with MMA and St

copolymers[a]	time (h)	$(M_n)_{P(Tdec)}$ (kg/mol)[b]	$(M_n)_{Macroin.}$ (kg/mol)[b]	$(M_n)_{Graft}$ (kg/mol)[c]	$M_w/M_{nP(Tdec)}$[d]	$M_w/M_{nMacroin.}$[d]	M_w/M_{nGraft}[d]	% w/w[e] MMA or St	M_n[f] (kg/mol)	N[g]
P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-MMA)]	4	160	180	420	1.77	1.61	1.66	57	5.7	42
P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-St)]	20	160	180	1020	1.77	1.61	1.68	82	20	42

[a] T_p for MMA 80 °C and 110 °C for St. [b] By LALLS in THF and the M_w/M_n values by SEC. [c] By the M_n of macroinitiator and the composition by ^{1}H NMR in $CDCl_3$. [d] By SEC in THF. [e] By ^{1}H NMR in $CDCl_3$. [f] By the number of branches and the molecular characteristics. [g] N: number of branches measured by ^{1}H NMR in $CDCl_3$ of the P[Tdec-*b*-(Tdec-*co*-Undec)] macroinitiator .

Table 8. DSC Results of the Block−Graft Copolymers[a]

copolymers	M_n (kg/mol)	M_w/M_n	T_g (°C)	T_m(°C)	ΔH_m (J/g)
P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-MMA)]	420	1.66	117.7	1.4	0.941
P[Tdec-*b*-((Tdec-*co*-Undec)-*g*-St)]	1020	1.68	96.1	0.9	0.294

[a] Characteristic thermograms are given in the Supporting Information.

confirmed by the ^{1}H NMR spectra. An example of the PTdec-*b*-[(PTdec-*co*-Undec)-*g*-PMMA] block−graft copolymer, is shown in Figure 12. The molecular characteristics of the samples are given in Table 7.

The thermal properties, measured by DSC, are given in Table 8. The melting point of the PTdec backbone was lower than the one reported for the homopolymer, as in the case of the graft copolymers. The glass transition temperature of the PMMA and PS side chains were higher than the corresponding values reported for the corresponding homopolymers with the same molecular weight for reasons similar to those reported for the graft copolymers.

CONCLUSIONS

Coordination polymerization chemistry based on the catalytic system, which consisted of the C_s-symmetry hafnium metallocene catalyst $[(p\text{-}Et_3Si)Ph]_2C(2,7\text{-di-}tert\text{-BuFlu})(Cp)Hf(CH_3)_2$, and the tetrakis(pentafluorophenyl) borate dimethylanilinium salt, $([B(C_6F_5)_4]^-[Me_2NHPh]^+)$, cocatalyst in the presence of trioctylaluminum (TOA) has been employed for the synthesis of diblock copolymers and triblock terpolymers of different α-olefins and methyl methacrylate, MMA. Poly[(hexene-1)-*b*-(tetradecene-1)], P(Hex-*b*-Tdec), poly[(octene-1)-*b*-(tetradecene-1)], P(Oct-*b*-Tdec), poly[(hexene-1)-*b*-(methyl methacrylate)], P(Hex-*b*-MMA), and poly[(octene-1)-*b*-(methyl methacrylate)], P(Oct-*b*-MMA) block copolymers were prepared by sequential addition of monomers. The low boiling point olefin was polymerized first. In the case of the copolymers bearing PMMA chains the polymerization of the α-olefin was conducted first. Using the same methodology P(Hex-*b*-Oct-*b*-Tdec), P(Hex-*b*-Oct-*b*-Dec), and P(Hex-*b*-Oct-*b*-MMA) triblock terpolymers were prepared. More complex macromolecular architectures were obtained from the combination of metallocene-catalyzed polymerization and atom transfer radical polymerization, ATRP. Statistical copolymers of α-olefins with 1-*tert*-butyldimethylsilyloxy-10-undecene were synthesized using the same catalytic system. The 1-*tert*-butyldimethylsilyl group was removed and the resulted hydroxyl groups were transformed to initiation sites for ATRP. From these sites either MMA or styrene was polymerized leading to the synthesis of graft and block−graft copolymers. The samples were thoroughly characterized by size exclusion chromatography, SEC, ^{1}H and ^{13}C NMR spectroscopy, and differential scanning calorimetry, DSC.

ASSOCIATED CONTENT

Supporting Information. Selected SEC, NMR, and DSC figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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