Graft Copolymers of Polyethylene by Atom Transfer Radical Polymerization

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ABSTRACT: Poly(ethylene-*g*-styrene) and poly(ethylene-*g*-methyl methacrylate) graft copolymers were prepared by atom transfer radical polymerization (ATRP). Commercially available poly(ethylene-*co*-glycidyl methacrylate) was converted into ATRP macroinitiators by reaction with chloroacetic acid and 2-bromoisobutyric acid, respectively, and the pendant-functionalized polyolefins were used to initiate the ATRP of styrene and methyl methacrylate. In both cases, incorporation of the vinyl monomer into the graft copolymer increased with extent of the reaction. The controlled growth of the side chains was proved in the case of poly(ethylene-*g*-styrene) by the linear increase of molecular weight with conversion and low polydispersity ($M_w/M_n < 1.4$) of the cleaved polystyrene grafts. Both macroinitiators and graft copolymers were characterized by ^{1}H NMR and differential scanning calorimetry. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2440–2448, 2000

Keywords: atom transfer radical polymerization; graft copolymers; polyethylene; poly(ethylene-*co*-glycidyl methacrylate); styrene; methyl methacrylate

INTRODUCTION

Polyolefins form the largest class of thermoplastic polymers. Because of their low chemical reactivity and polarity, high ductility, and good processability, polyethylene (PE) and polypropylene (PP) are often used in blends with other plastics in order to improve their performance. However, as polyolefins are incompatible with almost all other polymers due to their low surface energy, compatibilizing agents are necessary in order to avoid macrophase separation.[1] The compatibilizers are usually block or graft copolymers, which contain a polyolefin segment. Free radical graft polymerization is the most used technique to prepare compatibilizing agents starting from PE, PP, or ethylene–propylene rubber (EPDM). Grafting "from" method via initiation from the backbone has been usually employed, using either ionizing radiation, both gamma and electron beam, UV with accelerators, or peroxide-initiated chemistry.[2] However, the approach leads to ill-defined products due to crosslinking and chain cleavage reactions and/or formation of large amounts of homopolymer. An interesting method for the preparation of polyolefin–poly(methyl methacrylate) graft copolymers has been developed recently by Chung et al.,[3–5] involving the use of borane-containing polyolefins as polymeric initiators for MMA polymerization, in the presence of small amounts of oxygen.

Better control of the graft copolymer structure was achieved when ionic polymerization tech-

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niques were employed.[6–8] However, they require stringent conditions, like complete absence of moisture and other acidic impurities. From this point of view, a better approach may be the controlled/living" free radical techniques, which enable the control of both molecular weights and polydispersities under less restrictive application conditions and can be applied to a larger number of monomers. The most important types of controlled/"living" radical polymerizations[9] are: (1) stable free-radical polymerization (SFRP), which employs nitroxyl radicals, and (2) atom transfer radical polymerization (ATRP), which uses complexes of transition metals in conjunction with alkyl halides. Both SFRP[10–13] and ATRP[14,15] have been used to prepare polyolefin graft copolymers. In the former case, polymeric initiators were synthesized by the copolymerization of ethylene,[12] propylene[10,11] or 4-methylpentene[10] with an alkene-substituted alkoxyamine using transition metal complexes as catalysts, followed by the controlled radical polymerization of styrene initiated by the alkoxyamine groups covalently linked to the polyolefin backbone. Alternatively, PP was oxidized by γ-irradiation in air to produce peroxide groups along the backbone, and the modified polymer was used to initiate styrene-controlled polymerization in the presence of TEMPO.[13] Both graft copolymer and styrene homopolymer resulted from the reaction. In the case of ATRP, the polymeric initiators were prepared by the chemical modification of some commercially available polyolefin copolymers. For example, bromination of EPDM rubber to yield the 5-ethylidene-2-norbornene units, followed by controlled polymerization of methyl methacrylate initiated by the allylic bromine and catalyzed by a CuBr/2,2′-bipyridine complex, led to a polyolefin–poly(methyl methacrylate) graft copolymer.[14]

In our continuing effort to develop new materials by ATRP, we addressed the field of graft copolymers, using both the grafting "from"[15–20] and grafting "through"[21] techniques. This article describes the preparation of polyethylene-*graft*-polystyrene [P(E-*g*-St)] and polyethylene-*graft*-poly(methyl methacrylate) [P(E-*g*-MMA)] by ATRP, starting from commercially available poly(ethylene-*co*-glycidyl methacrylate). The resulting graft copolymer could potentially serve as a compatibilizer for polyethylene, though it could be efficient only for LDPE, since its branch structure may be incompatible with linear HDPE.

EXPERIMENTAL

Materials

Poly(ethylene-*co*-glycidyl methacrylate) [P(E-*co*-GMA)] containing 11 wt % (2.3 mol %) GMA units, as determined by elemental analysis, tetrabutylammonium hydroxide (TBAH), 1 M solution in methanol, chloroacetic acid (ClAA), and 2-bromoisobutyric (BrIBA) acid were used as received from Aldrich. Styrene (St, Aldrich) and methyl methacrylate (MMA, Aldrich) were distilled from CaH_2 prior to use. CuCl (97%, Aldrich) was purified according to the published procedure.[22] 4,4′-Di-nonyl-2,2′-bipyridine (dNbpy) was synthesized by a previously reported procedure.[23] All of the solvents were used without further purification. In many cases, monomers and solvents were bubbled with nitrogen for at least 15 min immediately before polymerization.

Measurements

Monomer conversion was determined by GC using chlorobenzene or xylene as internal standards. A Shimadzu GC-14A gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column was used. The compositions of the purified samples were measured by ^{1}H NMR on a 300 MHz General Electric GN 300 spectrometer with variable temperature capability using Tecmag data acquisition software. The NMR spectra were recorded in deuterated benzene at 75 °C [P(E-*co*-GMA), macroinitiators, P(E-*g*-MMA)] or in CCl_4/deuterated DMSO mixture at 70 °C [P(E-*g*-St)]. Size exclusion chromatography (SEC) measurements in THF were carried out using a Waters 510 liquid chromatograph pump equipped with four PSS columns (100 Å, 1000 Å, 10^5 Å and guard) in series with a Waters 410 differential refractometer. Polystyrene standards were used for calibration. Differential scanning calorimetry (DSC) data were obtained from a Rheometrics DSC Plus instrument. The DSC traces were recorded during the second heating [P(E-*g*-MMA)] or second cooling [P(E-*g*-St)] cycle, with a heating rate of 20 °C. Elemental analyses were measured by Midwest Microlabs, Indianapolis, Indiana.

Synthesis of the Macroinitiators

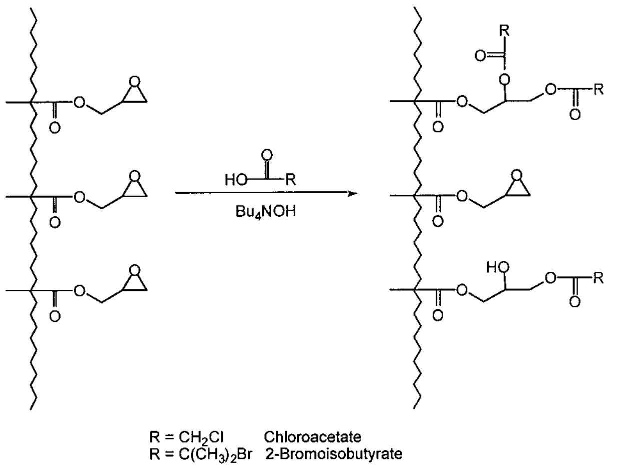
Chloroacetate Functional Macroinitiator (PECl)

P(E-*co*-GMA) (5.0 g, 3.8 mmol GMA), ClAA (0.30 g, 3.2 mmol), and 100 mL xylene were heated to

115 °C under nitrogen and stirred until the polymer completely dissolved. TBAH solution (0.28 mL, 0.28 mmol) was added and the reaction was stirred at 115 °C for 43 h. The hot solution was precipitated into excess methanol and the polymer was collected by filtration. One more precipitation from hot xylene into methanol afforded a white material, which was dried under vacuum.

2-Bromoisobutyrate Functional Macroinitiator (PEBr)

P(E-*co*-GMA) (10.0 g, 7.8 mmol GMA), BrIBA (2.60 g, 15.5 mmol), and 150 mL xylene were heated to 115 °C under nitrogen, with stirring. After the polymer dissolved, the TBAH solution (0.8 mL, 0.8 mmol) was added and the reaction was stirred at 115 °C for 38 h. The reaction mixture was then worked up as in the case of PECl, yielding a yellowish material.



Scheme 1

Polymerizations

Synthesis of P(E-g-St)

PECl (0.2 g, 7.4×10^{-2} mmol Cl), CuCl (7.3 mg, 7.4×10^{-2} mmol) and dNbpy (60 mg, 14.8×10^{-2} mmol) were placed into three glass ampoules and degassed by three vacuum/nitrogen cycles. To each tube, a degassed styrene/chlorobenzene mixture 1/0.05 vol/vol (1.05 mL, 8.7 mmol styrene) was added. The tubes were sealed under nitrogen and placed into a 130 °C oil bath. The tubes were removed periodically and the reaction mixtures were placed in tightly closed vials with benzene. All samples swelled in benzene and after at least 24 h equilibration time, conversions were measured by GC. The products from each tube were purified by two precipitations from solutions of hot toluene into methanol. The white materials were dried at room temperature under vacuum.

Synthesis of P(E-g-MMA)

PEBr (0.1 g, 4.9×10^{-2} mmol Br) was placed in four glass ampoules, which were three times evacuated and filled back with nitrogen. Separately, a mother solution of methyl methacrylate, o-xylene, CuCl, and dNbpy was prepared in a Schlenk flask under nitrogen. This solution (3.2 mL), containing 1.04 mL (9.8 mmol) MMA, 2.08 mL o-xylene, 4.8 mg (4.9×10^{-2} mmol) CuCl, and 39.8 mg (9.8×10^{-2} mmol) dNbpy, were added to each ampoule. The tubes were sealed under nitrogen and placed in an oil bath kept at 90 °C. At time intervals, tubes were removed from the oil bath, cooled down and the contents were transferred to tightly closed vials by using THF as dispersant. All samples were heated up to complete dissolution, left to cool down (precipitation occurred), and then conversions were determined by GC using xylene as internal standard. The polymer samples were isolated by precipitation from hot THF into methanol, and purified by one more dissolution—precipitation cycle. The white products were dried at room temperature under vacuum.

Cleavage of Polystyrene Grafts

P(E-*g*-St) samples (0.1 g) were placed in a 25 mL round bottom flask with 10 mL THF. The mixture was refluxed under nitrogen until the graft copolymer dissolved and then a solution TBAH 1M in methanol (TBAH/Cl end groups = 20/1 mole ratio) was added. The mixture was refluxed for 15 more hours. Upon cooling to room temperature, the polyethylene precipitated from solution. The liquid phase was removed, neutralized with HCl, and injected onto the SEC chromatograph for molecular weight determination of the polystyrene.

RESULTS AND DISCUSSION

Synthesis of the Macroinitiators

The PECl and PEBr macroinitiators were synthesized through the addition reaction of ClAA and BrIBA, respectively, to the epoxy ring of the GMA units in the P(E-*co*-GMA) copolymer, catalyzed by TBAH (Scheme 1). The incorporation of the ha-

Table I. The Degree of Functionalization (f) of the Macroinitiators Synthesized

Macroinitiator	Haloacid/GMA Units mole/mole	Halogen Content[a] wt %	f mole Haloester/mole GMA
PECl	0.84	1.31	0.5
PEBr	2	3.90	1.4

[a] Determined by elemental analysis.

loester units was confirmed by both elemental analysis, which indicated the presence of the halogen in the reaction products (Table I), and ^{1}H NMR (Fig. 1).Figure 1 shows that the peak characteristics to the glycidyl ester group in the P(E-*co*-GMA) copolymer (a, b, c in Fig. 1) are completely absent in the ^{1}H NMR spectra of both PECl and PEBr, and new peak formed. Among them, the peaks at $\delta = 4.0$ and $\delta = 4.2$ ppm, corresponding to ester α methylene (d, Fig. 1) and alcohol α methine (2, Fig. 1) protons, respectively, prove the haloacid addition to the oxirane ring.

The degree of functionalization, defined as number of haloester groups/GMA moiety and calculated based on the halogen content of the macroinitiators (Table I), showed that not only single, but also double additions of BrIBA to the epoxy ring occurred in the case of PEBr, under the conditions employed. The addition of two BrIBA molecules to the same oxirane ring is additionally supported by the presence of the peak at $\delta = 4.9$ ppm in the ^{1}H NMR spectrum of PEBr (f, Fig. 1). A similar peak may be observed in the ^{1}H NMR spectrum of PECl, which seems to indicate that the double addition occurred even at a much lower acid/GMA unit ratio (Table I).

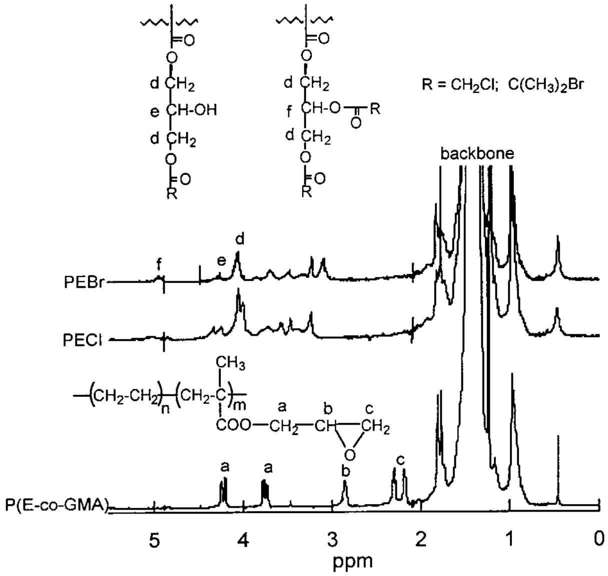
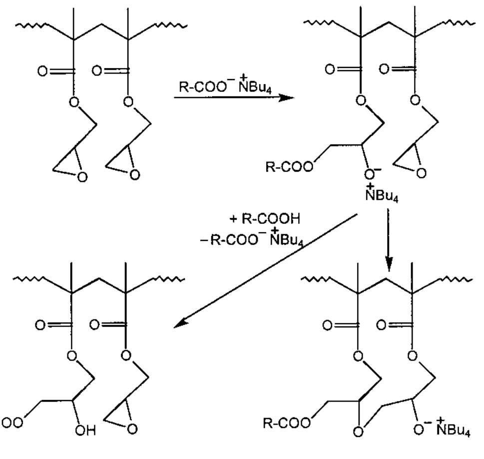
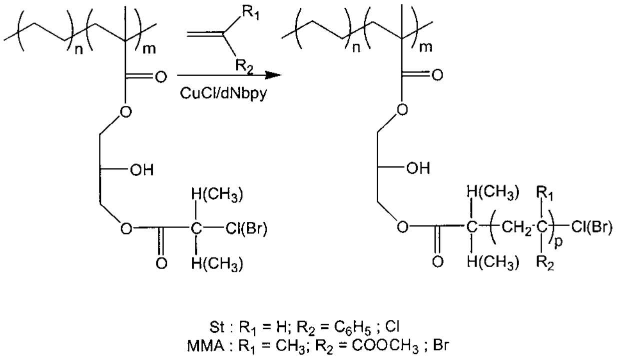


Figure 1. ^{1}H NMR spectra of the starting material and macroinitiators. Solvent: deuterated benzene; temperature: 75 °C.

The preparation of PECl was carried out at a ratio ClAA/GMA units < 1 in order to completely consume the acid, which would have allowed performance of a one-pot synthesis of the graft copolymer, without the isolation of the macroinitiator. However, the results showed that not all acid was consumed (0.5 mol haloester/mole GMA in PECl versus 0.84 mol haloacid/mole GMA employed, Table I), despite the fact that all epoxy rings are depleted, as can be seen from the complete absence of the peaks at $\delta = 2.2$, 2.3, and 2.9 ppm in the ^{1}H NMR spectrum of PECl (Fig. 1). The excessive consumption of the epoxy groups may be ascribed to the nucleophilic attack at the oxirane rings, initiated by the tetrabutylammonium carboxylate formed through the reaction between the acid and TBAH, which leads to the formation of some cyclic structures (Scheme 2). Despite the low concentration of GMA units (2.3 mol %) in the P(E-*co*-GMA) copolymer, they very likely form



Scheme 2



Scheme 3

longer sequences because of the large difference between the reactivity ratios of the ethylene and methacrylic acid esters in the radical copolymerization.[24,25] Because of the proximity of the GMA units, the nucleophilic attack of the alkoxy anion to the next oxirane ring is favored by comparison with its protonation by reaction with the excess acid. The formation of the cyclic structures is supported by the presence of the peaks at $\delta = 3-4$ ppm in the ^1H NMR spectrum of PECl (Fig. 1), which may be ascribed to ether and alcohol α methylene and α methine protons. The existence of similar peaks in the ^1H NMR spectrum of PEBr (Fig. 1) shows that the epoxy group oligomerization could not be avoided even at higher acid concentration. It is also possible to consider the corresponding intermolecular reactions as well as hydrolysis of glycidyl groups to diols and perhaps acid-catalyzed ring-opening to a different regioisomer.

Synthesis and Characterization of P(E-*g*-St) Copolymer

PECl macroinitiator was used to initiate bulk ATRP of styrene with CuCl/dNbpy as the catalytic system, at 130 °C. Formally, the grafting process occurred as depicted in Scheme 3. Based on the chlorine content determined from elemental analysis, the monomer/chloroacetate groups/CuCl/dNbpy molar ratio employed was 118/1/1/2. Upon completion, benzene was added to each sample in order to extract the monomer and GC standard. All polymer samples swelled, the degree of swelling increasing with progress of the reaction. After 24 h equilibration time, conversions were determined by GC, and checked again after 24 more hours. The values obtained were almost identical, indicating that the equilibrium state had been reached.

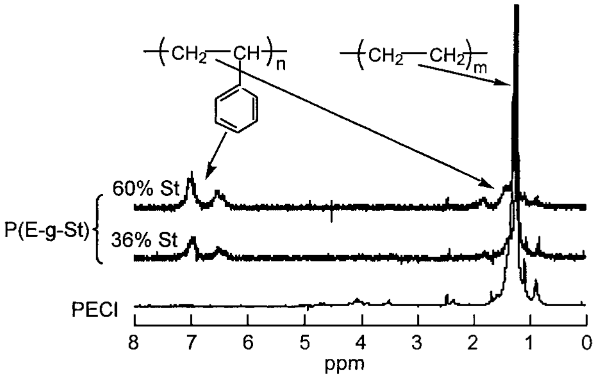


Figure 2. ^1H NMR spectra of PECl and P(E-*g*-St) samples with different compositions. Solvent: CCl_4/deuterated DMSO; temperature: 70 °C.

The increase of styrene conversion with time (Table II), together with the presence in the ^1H NMR spectra of the purified products (Fig. 2) of both aromatic ($\delta = 6.5–7$ ppm) and aliphatic proton peaks ($\delta = 1–2$) characteristic to polystyrene, along with the peak due to the polyethylene backbone ($\delta = 1.3$) proved the formation of the graft copolymer. As expected, styrene proportion in the graft copolymer, determined by ^1H NMR using the aromatic/aliphatic peak ratio, increased with conversion. The conversions determined by ^1H

Table II. Conversion and Composition Data for the ATRP of Styrene from PECl

Sample	Time (min)	Conversion (%)	Styrene Content[a] (wt %)	Styrene Content[b] (wt %)
1	65	10	36	31
2	180	34	60	61
3	302	64	69	74

Bulk; styrene:chloroacetate groups:CuCl:dNbpy = 118:1:1:2; 130°C.

[a] Determined by ^1H NMR.

[b] Calculated from styrene conversion.

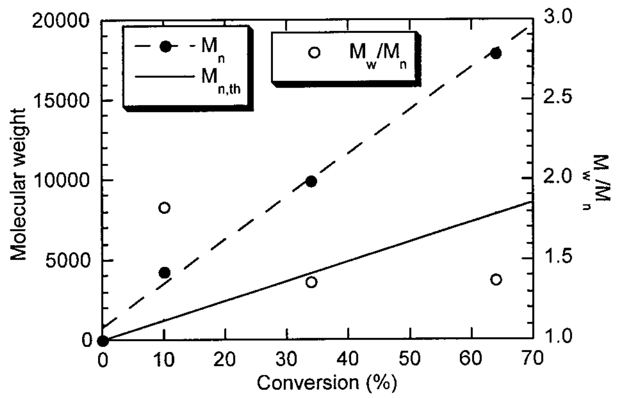


Figure 3. Dependence of number-average molecular weight, M_n, and polydispersity, M_w/M_n, of polystyrene grafts on conversion. Bulk polymerization; styrene: chloroacetate groups:CuCl:dNbpy = 118:1:1:2; 130 °C.

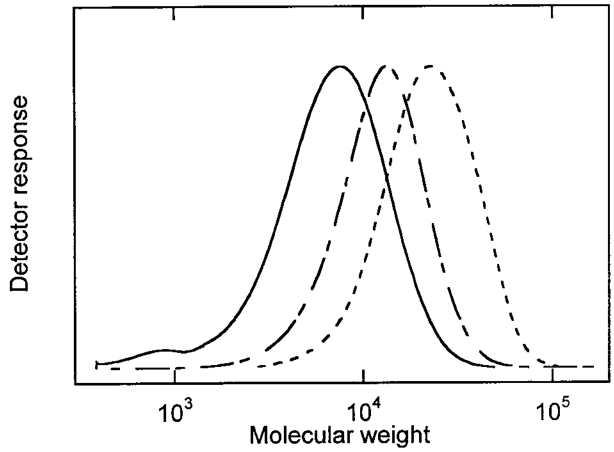


Figure 4. SEC traces of the polystyrene arms after cleavage from the polyethylene backbone.

NMR agreed well with those calculated from monomer conversion (eq 1).

$$\text{wt. \% St} = m_{\mathrm{St}}/(m_{\mathrm{St}} + m_{\mathrm{PECl}}) \qquad (1)$$

where wt % St = amount of styrene in copolymer; m_{st} = amount of styrene converted to polymer, calculated from the initial amount of styrene and styrene conversion, as determined by GC; m_{PECl} = amount of macroinitiator introduced (0.2 g).

To verify the controlled character of the grafting process, the polystyrene grafts were detached from the polyolefin backbone by refluxing the copolymer solution in THF with TBAH. This way, the ester groups of both functionalized glycidyl methacrylate and acetate moieties were cleaved. Indeed, the molecular weight of the polystyrene chains increased linearly with conversion and the polydispersities were low, $M_w/M_n < 1.4$ (Fig. 3). The controlled growth of the polystyrene chains is additionally supported by the SEC chromatograms in Figure 4, which shows that the entire peak shifted to higher molecular weight with increasing extent of the reaction. However, the experimental molecular weights were much higher than the theoretical values, indicative for a low initiation efficiency (approximately 42% according to Fig. 3). Indeed, chloroacetate groups are not very efficient initiators for the ATRP process.[26] The efficiency may be further reduced due to the attachment of the initiator to the polymer backbone.

The P(E-*g*-PSt) samples were analyzed by DSC to check for the presence of phase separation (Fig. 5). The melt transitions for the crystalline regions of the polyethylene coincided with the polystyrene glass transition during the heating cycle. However, in the cooling runs the crystallization occurred at a lower temperature, which allowed the T_g for the polystyrene segment (about 100 °C) to be visualized, especially in samples with higher styrene content. This value is higher than that predicted by the Fox–Flory equation,[27] but in good agreement with the glass-transition temperatures reported by Lu and Chung for polystyrene chains of similar molecular weight, grafted on PP.[8] The glass-transition temperature of the polyethylene backbone (about −20 °C) could also be clearly seen in samples with high polystyrene content, which indicated that phase separation had occurred.

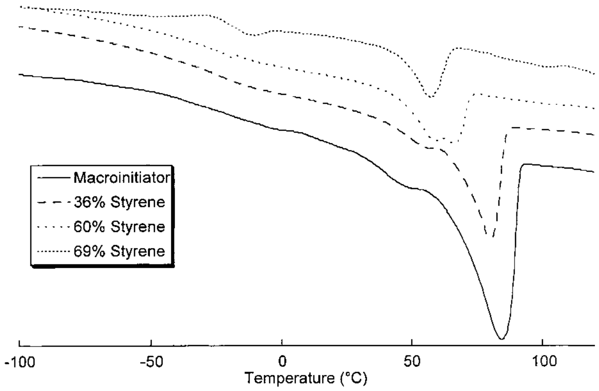


Figure 5. DSC traces of PECl macroinitiator and P(E-*g*-St) copolymers with different styrene content. Second cooling cycle.

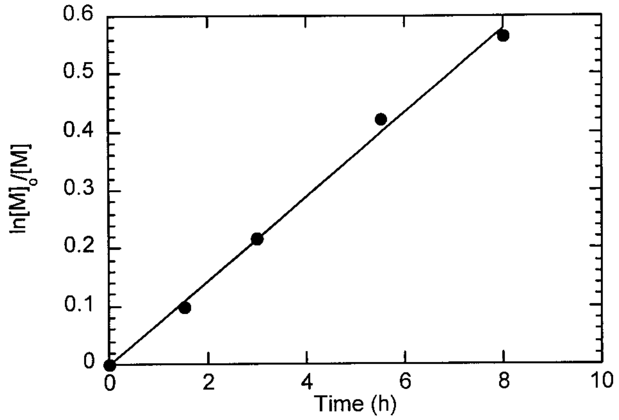


Figure 6. Kinetic plot for the polymerization of MMA initiated by PEBr. $[\mathrm{MMA}]_o$ = 3.12 M; [2- bromoisobutyrate]$_o$ = $[\mathrm{CuCl}]_o$ = $[\mathrm{dNbpy}]_o/2$ = 15.6 mM; solvent o-xylene, 90 °C.

Synthesis and Characterization of P(E-*g*-MMA) Copolymer

The synthesis of the P(E-*g*-MMA) copolymer (Scheme 3) was carried out in xylene solution in order to improve the solubility of the PEBr polyethylene macroinitiator. 2-Bromoisobutyrate moieties in conjunction with CuCl/dNbpy were used as initiating system in order to improve the reaction control through halide exchange.[26,28] This technique, which is especially suitable for the ATRP of MMA and consists in the replacement of the bromine atom at the chain ends by chlorine shortly after the polymerization is started, allows for the decrease of the termination reactions by decreasing the concentration of the radicals, while initiation is maintained fast by comparison with propagation. Indeed, a linear first-order kinetic plot was obtained for the grafting process, indicating that the proportion of the termination reactions was low (Fig. 6).

The ^{1}H NMR spectra of the purified polymerization products displayed peaks for both polyMMA [δ = 3.4 ppm $\text{—OC}\underline{\underline{\text{H3}}}$; 2.1 ppm $\text{—C}\underline{\underline{\text{H2}}}\text{—C(CH}_3\text{)—}$; 1.3 ppm $\text{—CH}_2\text{—C(C}\underline{\underline{\text{H3}}}\text{)—}$] and polyethylene ($\delta$ = 1.4 ppm) segments (Fig. 7), demonstrating the formation of the graft copolymer.

As conversion increased, the amount of MMA in the graft copolymer increased as well (Table III). The MMA content of P(E-*g*-MMA) was determined by ^{1}H NMR, using the area of the triplet at δ = 3.4 ppm versus the area of the peaks at δ = 1.2–1.5 ppm, and also calculated from monomer conversion (eq 1). The two sets of copolymer compositions agreed very well.

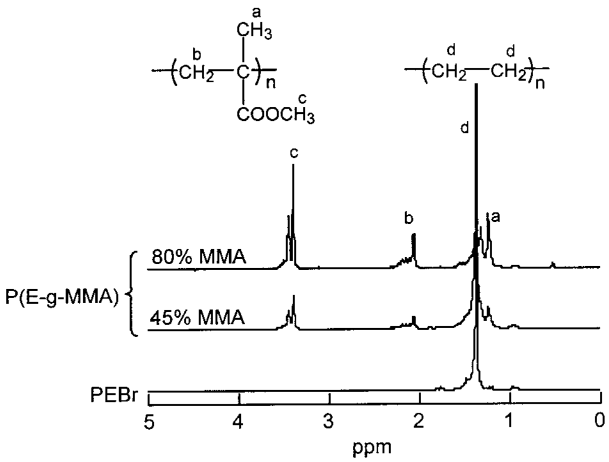


Figure 7. ^{1}H NMR spectra of PEBr and P(E-*g*-MMA) samples with different compositions. Solvent: deuterated benzene; temperature: 75 °C.

Unfortunately, it was not possible to selectively cleaved polyMMA side chains due to similar reactivities of ester groups in the linking moiety and polyMMA chains.

DSC analysis of the P(E-*g*-MMA) samples showed the presence of the glass transition of polyMMA grafts (about 125 °C), indicative for the phase separation (Fig. 8). The T_g found is higher than the usually accepted glass-transition temperature for PMMA synthesized by free radical polymerization (T_g = 105 °C[29]); however there are recent reports in literature indicating a T_g over 120 °C for PMMA.[30,31] The glass-transition temperature of polyMMA was more visible in samples with MMA content above 67 wt %.

CONCLUSIONS

Graft copolymers of polyethylene with methyl methacrylate and styrene were successfully pre-

Table III. Conversion and Composition Data for the ATRP of MMA from PEBr

Sample	Time (min)	Conversion (%)	MMA Content[b] (wt %)	MMA Content[c] (wt %)
1	90	9	45	47
2	180	20	67	66
3	330	34	77	77
4	480	43	80	81

$[\mathrm{MMA}]_o$ = 3.12 M; [2-bromoisobutyrate]$_o$ = $[\mathrm{CuCl}]_o$ = $[\mathrm{dNbpy}]_o/2$ = 15.6 mM; solvent o-xylene, 90°C.

[a] Determined by ^{1}H NMR.

[b] Calculated from MMA conversion.

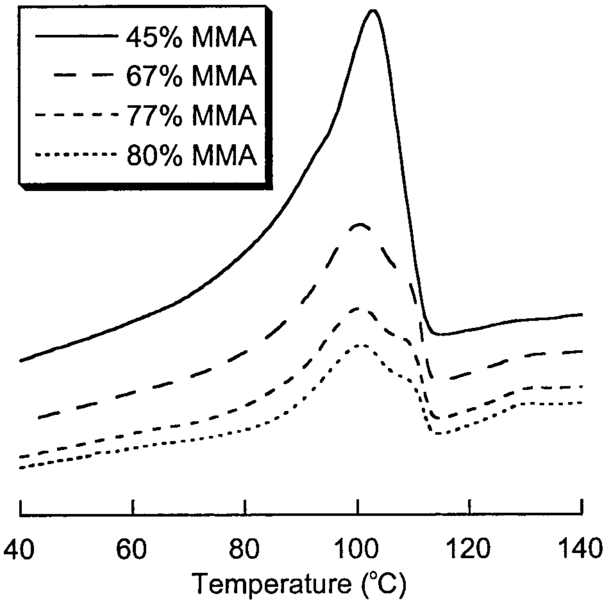


Figure 8. DSC traces of P(E-*g*-MMA) copolymers with different MMA content. Second heating cycle.

pared by ATRP starting from commercially available P(E-*co*-GMA). In the first step, P(E-*co*-GMA) was converted into ATRP macroinitiators by the addition reaction of ClAA and BrIBA to the epoxy ring of the GMA units, catalyzed by TBAH. ^{1}H NMR analysis of the macroinitiators showed that anionic polymerization of the oxirane rings and double additions to the epoxy ring occurred as side reactions. The pendant-functionalized polyolefins were used to initiate the ATRP of styrene and methyl methacrylate to produce graft copolymers. The ^{1}H NMR spectra of products displayed the characteristic peaks for both polyethylene backbone and polyMMA or polySt grafts, and allowed for the determination of the composition of the graft copolymers. In both cases, incorporation of the vinyl monomer into the copolymer increased with extent of reaction. The controlled character of the polymerizations was proved in the case of P(E-*g*-St) by the linear increase of molecular weight with conversion and low polydispersity of the cleaved polystyrene grafts. DSC measurements revealed that each graft copolymer had two glass-transition temperatures, characteristic to the segments forming the graft copolymer, which proved the presence of phase separation.

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