

# Synthesis of Graft Copolymers from a Linear Polyolefin Through a Combination of Coordination Polymerization and Atom Transfer Radical Polymerization

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Received 9 June 2009; accepted 13 December 2009

DOI 10.1002/app.31971

Published online 17 March 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This article reports on a facile route for the preparation of methyl acrylate and methyl methacrylate graft copolymers via a combination of catalytic olefin copolymerization and atom transfer radical polymerization (ATRP). The chemistry first involved a transforming process from ethylene/allylbenzene copolymers to a polyolefin multifunctional macroinitiator with pendant sulfonyl chloride groups. The key to the success of the graft copolymerization was ascribed to a fast exchange rate between the dormant species and

active radical species by optimization of the various experimental parameters. Polyolefin-*g*-poly(methyl methacrylate) and polyolefin-*g*-poly(methyl acrylate) graft copolymers with controlled architecture and various graft lengths were, thus, successfully prepared under dilute ATRP conditions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 450–457, 2010

**Key words:** atom transfer radical polymerization (ATRP); graft copolymers; polyolefins

## INTRODUCTION

Although they serve as an important class of polymer materials, the inert nature of polyolefins significantly limit their end uses, particularly with regard to adhesion or compatibility with other polar polymers. The introduction of a polar monomer into polyolefins can efficiently solve this long-lasting challenge. Originally, functionalized polyolefins were mainly prepared by the direct copolymerization of olefins with polar monomers. Commercial copolymers of ethylene and polar vinyl comonomers, such as vinyl acetate, acrylates, and methacrylates, have been successfully synthesized via radical polymerization at a high temperature and a high pressure.<sup>1</sup> The key restriction was to use late transition-metal catalysts, as they have a high tolerance for polar vinyl monomers because of a low Lewis acidity. However, they have to suffer from a significant decrease of both catalyst activity and polymer molecular weight.<sup>2,3</sup>

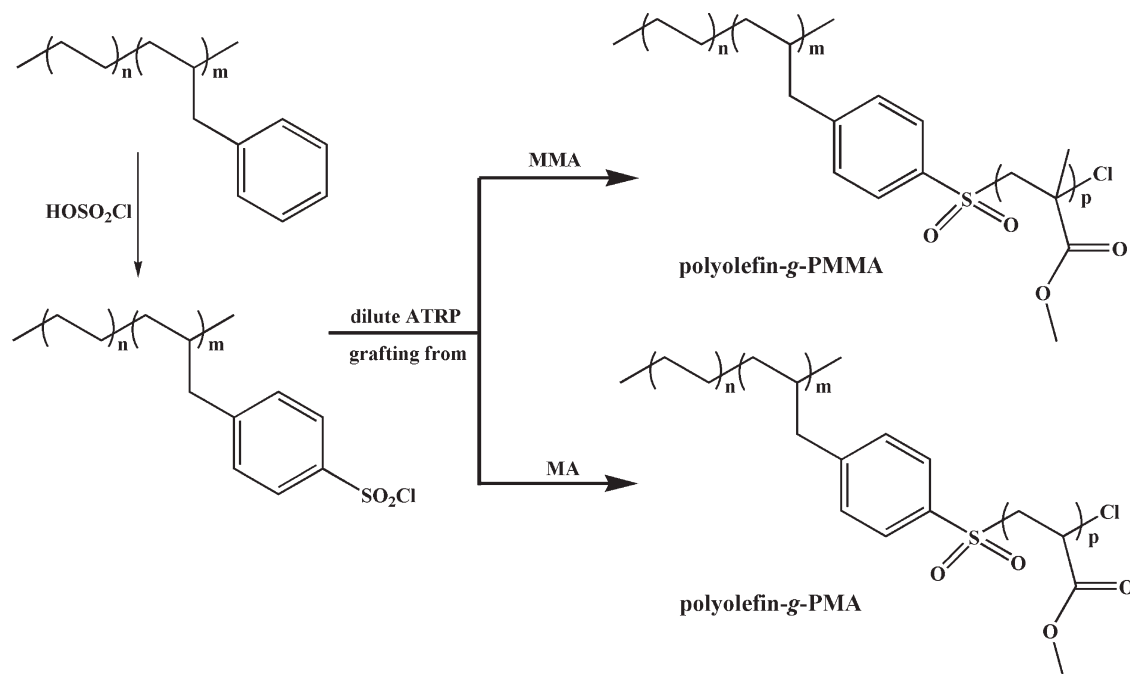
Alternatively, another way to incorporate polar monomer units into olefin polymers is to prepare block and graft copolymers by a combination of coordination polymerization and other living/controlled polymerization techniques. Recently, Boisson et al.<sup>4</sup> published a review on this exact topic. Among relevant studies, controlled/living free-radical polymerization (CRP) is one of the most widely used methods because it is applicable to a wide range of monomers under a variety of reaction conditions and can produce a number of complex polymer architectures.<sup>5–7</sup> The most prominent advantage of CRP is its high tolerance for polar functional groups so that designed polymers based on polar groups can be easily synthesized. The most important CRP methodologies reported here include atom transfer radical polymerization (ATRP),<sup>5</sup> nitroxide-mediated polymerization,<sup>6</sup> and reversible addition–fragmentation chain-transfer polymerization.<sup>7</sup> Basically, the synthesis of polyolefin segments with functional groups that are available for CRP is first required in all cases. There are three methods to produce polyolefin-based block and graft copolymers. The first approach is the preparation of block copolymers via chain-extension polymerization.<sup>5(d,f,i,j),6(c),7</sup> The second is the synthesis of graft copolymers through the grafting-from polymerization of a polyolefin backbone.<sup>5(a–c,e,g),6(a,b)</sup> The third strategy involves the synthesis of graft copolymers with polyolefin side chains via a grafting-through polymerization.<sup>5(f,h)</sup>

In this study, we adopted a two-step process to prepare polyolefin multifunctional macroinitiators,

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50525312 and 20734002.

Contract grant sponsor: Special Funds for Major State Basis Research Projects (Ministry of Science and Technology of China); contract grant number: 2005CB623800.



**Scheme 1** Synthetic route for the preparation of polyolefin-g-poly(meth)acrylates.

including (1) the copolymerization of ethylene and allylbenzene with *rac*-ethylenebis(indenyl)zirconium dichloride [*rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>] as a catalyst and (2) the chlorosulfonation reaction of poly(ethylene-co-allylbenzene) bearing pendant phenyls through a convenient and efficient method with chlorosulfonic acid as a chlorosulfonating agent. As a universal class of ATRP initiators, sulfonyl chloride can efficiently initiate the graft copolymerization of methyl methacrylate (MMA) and methyl acrylate (MA) polyolefin backbone, and the corresponding graft copolymers, polyolefin-g-poly(methyl methacrylate) (polyolefin-g-PMMA) and polyolefin-g-poly(methyl acrylate) (polyolefin-g-PMA), were successfully prepared under dilute ATRP conditions (Scheme 1). The resulting well-defined graft copolymers could potentially serve as compatibilizers for polar/nonpolar polymer blends.

## EXPERIMENTAL

### Materials

1,1,2,2-Tetrachloroethane, MMA, MA, xylene, and petroleum ether with a boiling range of 60–90°C were dried over CaH<sub>2</sub>, filtered, and distilled under reduced pressure before use. Acetone was dried over anhydrous CaSO<sub>4</sub> overnight and distilled. We purified CuCl by grinding and stirring with 1N H<sub>2</sub>SO<sub>4</sub>; we then filtered and washed it successively with glacial acetic acid, ethanol, and ether. The white CuCl powder was dried at 100°C for 30 min and stored in an airtight bottle. 2,2'-Bipyridine was

recrystallized from hexane. All other chemicals were commercially available and were used without further purification.

### Synthesis of the linear polyolefin multifunctional macroinitiator

The copolymerizations of ethylene with allylbenzene were conducted in the presence of *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> as a catalyst and modified methylaluminumoxane as an activator according to a procedure reported previously.<sup>8</sup> The chlorosulfonation reaction was carried out in a 1000-mL, three-necked, round-bottom flask equipped with a condenser, nitrogen inlet, and magnetic stirrer. Poly(ethylene-co-allylbenzene) (1.8 g, 4.27 mmol of  $-\text{CH}_2\text{Ph}$  groups) was dissolved in tetrachloroethane (420 mL) and allowed to stir at 25°C under nitrogen for 1 h. Chlorosulfonic acid (2.27 mL, 34.16 mmol) in tetrachloroethane (120 mL) was added dropwise over 10 min, and a large amount of petroleum ether was added to terminate the reaction after a further 6 h. The precipitates were filtered and thoroughly washed with acetone to remove residual free acid and were then dried overnight *in vacuo* at 70°C.

### Graft copolymerization from the polyolefin multifunctional macroinitiator

A typical graft copolymerization (entry 3, Table I) was performed according to standard Schlenk techniques. The macroinitiator (0.05 g, 0.089 mmol of  $-\text{SO}_2\text{Cl}$  groups) and xylene (3 mL) were added to a

TABLE I  
ATRP with the Polyolefin Multifunctional Macroinitiator

Entry	Monomer	I : C : L : M <sup>a</sup>	Xylene (mL)	Temperature (°C)	Time (min)	Yield (g)	Graft length (N) <sup>b</sup>	M <sub>w</sub> (kg/mol) <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	T <sub>m</sub> (°C) <sup>d</sup>	T <sub>g</sub> (°C) <sup>d</sup>
Macroinitiator	—	—	—	—	—	—	—	16	2.04	90.1	—
1	MMA	1 : 1.5 : 3 : 2000	3	20	20	0.11	9.3	—	—	82.1	—
2	MMA	1 : 1.5 : 3 : 2000	3	80	20	0.28	30.0	—	—	—	97.6
3	MMA	1 : 1.5 : 3 : 2000	3	100	20	0.63	83.8	211	3.11	—	124.5
4	MMA	1 : 1.5 : 3 : 2000	9	100	20	0.43	52.0	132	2.92	—	118.8
5	MMA	1 : 0.5 : 1 : 2000	3	100	20	0.15	19.5	68	2.75	—	93.1
6	MMA	1 : 0.5 : 1 : 2000	12	100	10	0.09	6.4	24	2.43	82.9	—
7	MA	1 : 0.5 : 1 : 2000	12	100	10	0.09	7.6	23	2.05	83.1	—
8	MA	1 : 0.5 : 1 : 2000	12	120	10	0.12	12.9	63	2.82	81.7	—
9	MA	1 : 0.5 : 1 : 2000	12	100	20	0.13	15.1	72	3.15	80.9	—

Reaction conditions: chlorosulfonated ethylene/allylbenzene copolymer as the macroinitiator (0.05 g, 0.089 mmol of SO<sub>2</sub>Cl), CuCl as the catalyst, 2,2'-bipyridine as the ligand, xylene as the solvent, and argon for the atmosphere.

<sup>a</sup> Sulfonyl chloride group/metal catalyst/ligand/monomer molar ratio.

<sup>b</sup> Calculated on the basis of <sup>1</sup>H-NMR.

<sup>c</sup> Determined by GPC.

<sup>d</sup> Determined by DSC.

dry 100-mL Schlenk flask equipped with a magnetic stirrer. After the macroinitiator was dissolved, 2,2'-bipyridine (13.97 mg, 0.089 mmol) and MMA (19.12 mL, 0.178 mol) were added. The solution was stirred for 10 min and degassed by three freeze-pump-thaw cycles, and then, CuCl (4.43 mg, 0.046 mmol) was added. The flask was immersed in a thermostated oil bath at 100°C, and 20 min later, the graft copolymer was precipitated in excess petroleum ether. The graft copolymer was filtered, washed with ethanol, and dried *in vacuo* at 60°C.

### Characterization

<sup>1</sup>H-NMR spectra and two-dimensional <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy (COSY) spectra were recorded on a Varian Unit 400-MHz spectrometer (Palo Alto, CA) at 100°C with standard parameters. 1,1,2,2-Tetrachloroethane-*d*<sub>2</sub> was used as the solvent, and all chemical shifts at 5.94 ppm were referred to the solvent shift. Fourier transform infrared (FTIR) spectroscopy was performed with a Bio-Rad (Richmond, CA) FTS-135 spectrophotometer. The melting temperature (T<sub>m</sub>) values of the copolymers were obtained by differential scanning calorimetry (DSC) with a PerkinElmer (Waltham, MA) Pyris 1 differential scanning calorimeter at a rate of 10°C/min. The T<sub>m</sub> values reported in Table I were obtained from the second heating curve. The molecular weights and molecular weight distributions of the copolymers were determined at 150°C by a PL-GPC 220 type high-temperature chromatograph (Palo Alto, CA) equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene was used as the solvent at a flow rate of 1.0 mL/min. The molec-

ular weights were determined from polystyrene standards. The universal calibration technique was used to determine the molecular weight and molecular weight distribution of the polyolefin multifunctional macroinitiator, and the same calibration technique was applied to the graft copolymers.

## RESULTS AND DISCUSSION

### Synthesis of the polyolefin multifunctional macroinitiator

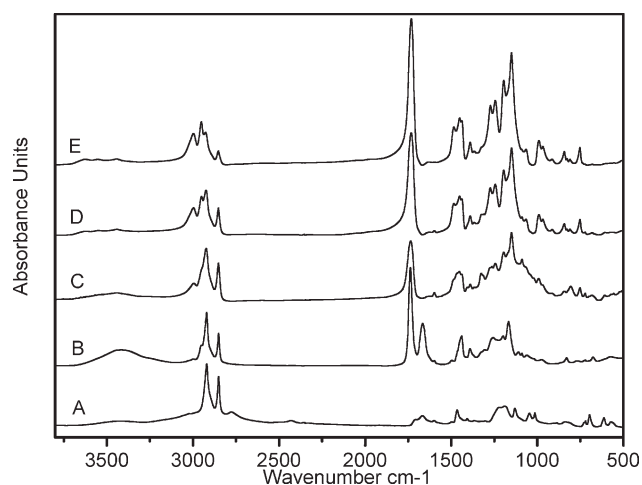
The influences of various reaction conditions on the chlorosulfonation reaction were investigated in detail in our previous study.<sup>9</sup> An ethylene/allylbenzene copolymer with a -CH<sub>2</sub>Ph group content of 2.37 mmol/g was selected to synthesize the polyolefin multifunctional macroinitiator. After the chlorosulfonation reaction, almost all of the phenyls were functionalized with sulfonyl chloride groups. Also, during the chlorosulfonation, a few sulfonyl chloride groups changed into sulfonic acids via the hydrolysis reaction. This side reaction had a great influence on the solubility of the multifunctional macroinitiator and the subsequent ATRP process. Copper(II) halide, via its reaction with sulfonic acids, was then transformed to copper(II) sulfonate, and the number of the deactivators decreased. Thus, some active propagating radicals could not return to the dormant species, and the polymerization grew out of control. To prevent such a disadvantage caused by the hydrolysis side reaction, the whole chlorosulfonation process was conducted under anhydrous conditions. Finally, the resulting chlorosulfonated polyolefin multifunctional macroinitiator possessed a relatively high molecular weight [weight-average

molecular weight ( $M_w$ ) = 16,000] and a low polydispersity index [ $M_w$ /number-average molecular weight ( $M_n$ ) = 2.04].

### Preparation and characterization of the graft copolymers

The ATRP reactions of MMA and MA were carried out in the presence of polyolefin multifunctional macroinitiator under various reaction conditions, and the representative results are listed in Table I. Unlike small molecule initiators, the initiating groups of the polyolefin multifunctional macroinitiator are distributed along the polymer main chain, and thus, it is prone to produce undesirable crosslinking reactions because of radical–radical coupling termination.<sup>10</sup> As an important class of universal functional ATRP initiators, arylsulfonyl chloride initiated polymerizations can considerably lower undesired coupling termination because of its higher rate of initiation versus propagation. Moreover, to further prevent potential crosslinking and improve control of the polymerization, various experimental parameters should also be optimized together. First, a large amount of solvent and monomer must be introduced into the reaction system to reduce the concentration of radicals; that is, the graft copolymerization is conducted under dilute ATRP conditions. In addition, the copolymerization reactions should be terminated at a low level of monomer conversion.

As mentioned previously, the solvent is one of the most important parameters; it significantly influences the occurrence of possible side reactions and the extension degree of polyolefin chains in the medium. The structure change of the catalyst in different solvents should also be considered.<sup>11</sup> On the basis of these rules, various solvents, such as phenyl ether, anisole, xylene, dimethyl sulfoxide, *N,N*-dimethyl formamide, and tetrahydrofuran, with different structures and different physical and chemical properties were estimated. The polymerization results for different molar ratios of initiator to monomer varied significantly with solvent and ligand. Unexpectedly, in certain cases, little or no graft copolymer product was obtained. The tremendous variations possibly reflected the different solubilities and particular polymerization reaction situations. Possessing a high tendency to crystallize, polyolefin only dissolves in hydrocarbons or arenes at a high temperature. Although low-molecular-weight polyethylene can dissolve in these solvents at a lower temperature, the macromolecular chains remain compact coils. Consequently, the catalyst cannot approach and effectively activate the dormant species (P–Cl), which results in a low polymerization rate. Likewise, it does not effectively deactivate the active radicals (P<sup>•</sup>); this increases diradical termination and, thus,

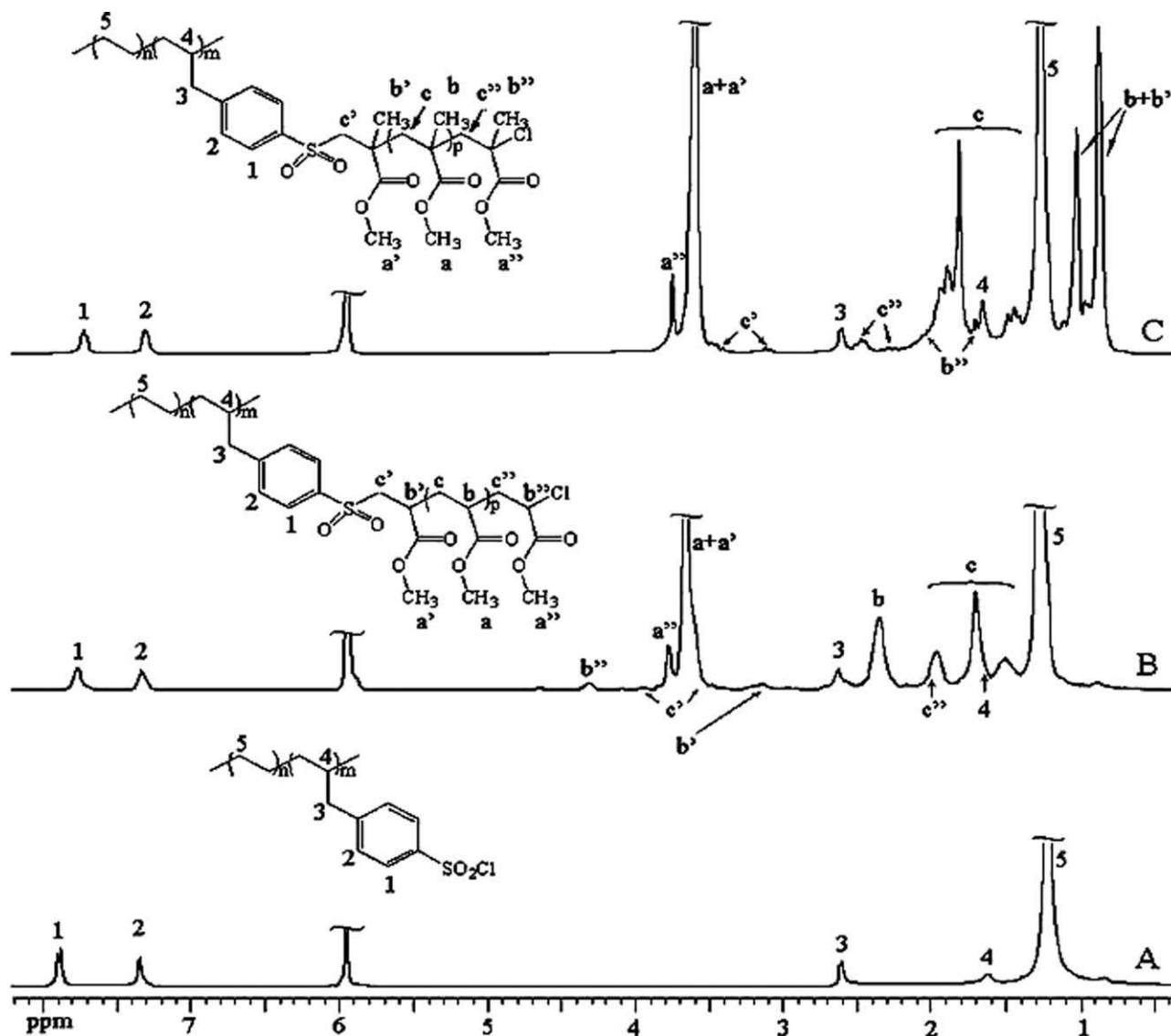


**Figure 1** Comparison of FTIR spectra of (A) the polyolefin multifunctional macroinitiator, (B) polyolefin-g-PMA with a side-chain length of 12.9, (C) polyolefin-g-PMMA with a side-chain length of 6.4, (D) polyolefin-g-PMMA with a side-chain length of 30.0, and (E) polyolefin-g-PMMA with a side-chain length of 83.8.

leads to a low initiator efficiency. Therefore, an excellent good solvent, xylene, was used for the grafting-from copolymerization at an elevated temperature of 100°C. In addition, 2,2'-bipyridine, instead of multiamine, was chosen as the ligand to prevent the amination of the sulfonyl chloride initiator fragment and to obtain a high initiator efficiency.<sup>12</sup>

Furthermore, the reaction temperature significantly affected the graft copolymerization process. As shown in Table I, the average side chain lengths of poly(methyl methacrylate) (PMMA) increased noticeably from 9.3 to 83.8 with the increase in the reaction temperature (entries 1–3). At a low polymerization temperature of 20°C (entry 1), slight crosslinking was still observed for the graft copolymerization. This result was consistent with the reported works; that is, the phenylsulfonyl radicals may have undergone low extents of undesired radical–radical coupling termination or other side reactions.<sup>13</sup> However, at higher reaction temperatures (80 and 100°C, entries 2 and 3 in Table I), the crosslinking reactions did not occur under the same polymerization conditions. This was attributed to the combining effects of two factors. First, an increase in reaction temperature induced a faster exchange rate between the dormant species and active radical species in the ATRP equilibrium system. Second, less compact polyolefin coils were formed in the excellent solvent at a higher temperature. Thus, the catalyst could access the dormant or active chain ends more easily, and the graft copolymerizations proceeded in a more controlled fashion. At this optimized reaction temperature, the average side chain





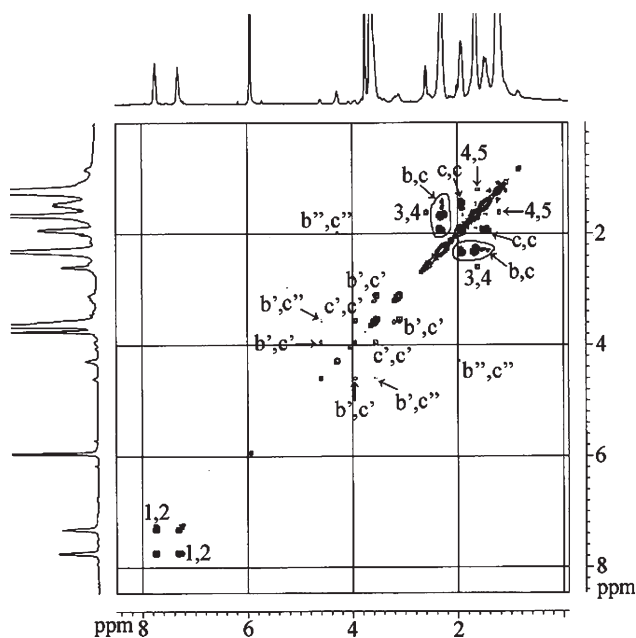
**Figure 2** Comparison of  $^1\text{H}$ -NMR spectra of (A) the polyolefin multifunction macroinitiator, (B) polyolefin-g-PMA (entry 8, Table I), and (C) polyolefin-g-PMMA (entry 5, Table I).

length of PMMA could be adjusted easily from 83.8 to 52.0 by a simple change in the solvent volume (entries 3 and 4).

Finally, the catalyst concentration was also optimized to improve the control of the polymerization. It was obvious that the average side chain lengths decreased significantly from 83.8 to 19.5 when the initiator/catalyst molar ratio was varied from 1 : 1.5 to 1 : 0.5 (entries 3 and 5, Table I). The observed results indicate that the increase of the catalyst concentration brought a faster exchange rate between the dormant species and active radical species and, thus, produced a higher polymerization rate. To further lower the average side chain lengths of PMMA, the reaction conditions of entry 5 were repeated in 12 mL of xylene for 10 min. As expected, the average number of MMA units in the graft polymer

decreased to 6.4. Under similar reaction conditions, the MA graft copolymerizations in the polyolefin backbone were conducted via a dilute ATRP technique. The data in entries 7–9 of Table I show that the average side-chain lengths of poly(methyl acrylate) (PMA) could be controlled over a broad range of 7.6–15.1 by the simple regulation of reaction time and reaction temperature, and the resulting graft copolymers displayed various properties.

Figure 1 reveals the FTIR spectra of the polyolefin multifunction macroinitiator, polyolefin-g-PMA, and polyolefin-g-PMMA. After the grafting-from polymerization, the resulting copolymers showed characteristic bands at  $1732\text{ cm}^{-1}$  (C=O stretching in the MMA and MA units) and  $1149\text{--}1273\text{ cm}^{-1}$  (C—O—C stretching in MMA and MA units). In addition, their corresponding intensities increased with increasing



**Figure 3**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of polyolefin-g-PMA (entry 8, Table I).

number of grafting monomer units. Thus, the FTIR analyses confirmed that the polar polymers were successfully introduced into the polyolefin backbone through the dilute ATRP graft reactions.

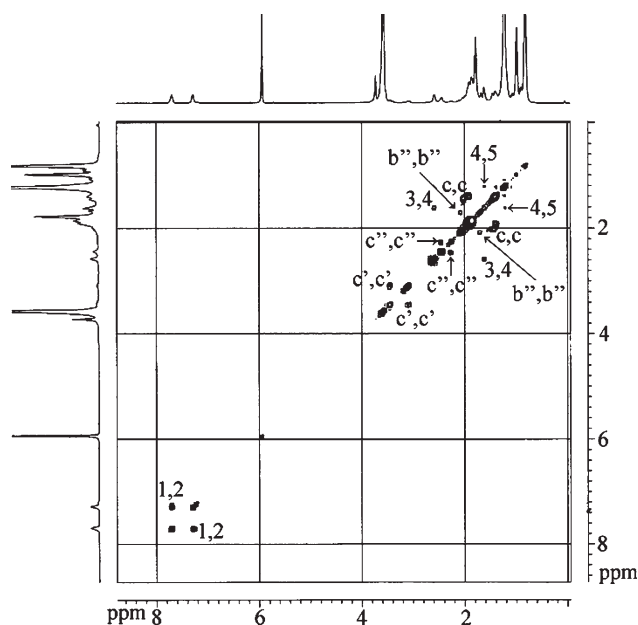
The formation of the graft copolymers was also supported by the  $^1\text{H}$ -NMR spectra, which unambiguously illustrated the microstructure of the graft copolymers (Fig. 2). The aromatic protons (1 and 2) were clearly observed in the spectra of the copolymer. The initiation efficiency of the sulfonyl chloride group in the polyolefin side chains was found to be quantitative via comparison of the integral ratios of the aromatic signals with the protons of the ethylene monomer unit. The  $\omega$ -terminal methylene protons ( $c'$ ) adjacent to the sulfonyl group had chemical shifts similar to those of PMA and PMMA synthesized with small-molecule arenesulfonyl chloride initiators.<sup>14</sup> The  $c''$  and  $b''$  signals in polyolefin-g-PMA and polyolefin-g-PMMA represented the end groups of their branches. By comparing the intensity of  $c''$  (or  $b''$ ) with those of signals 1 and 2, we could estimate the initiation efficiencies of the  $-\text{SO}_2\text{Cl}$  group; they were close to quantitative, which provided more direct evidence for the graft copolymer chain structures. Therefore, these observations demonstrated that the polar polymers were successfully incorporated into the polyolefin backbone and that the polyolefin-g-PMA and polyolefin-g-PMMA graft copolymers were prepared. To further assign various protons ( $a''$ ,  $b''$ , and  $c''$ ) of the  $\alpha$ -chain end connected with the halide group,  $^1\text{H}$ - $^1\text{H}$  COSY measurements of polyolefin-g-PMA [Fig. 2(B)] and polyolefin-g-

PMMA [Fig. 2(C)] were performed and are shown in Figures 3 and 4. All of the peaks of the graft copolymers could be accurately assigned. The details of the chemical shifts for all of the protons are presented in Figure 5.

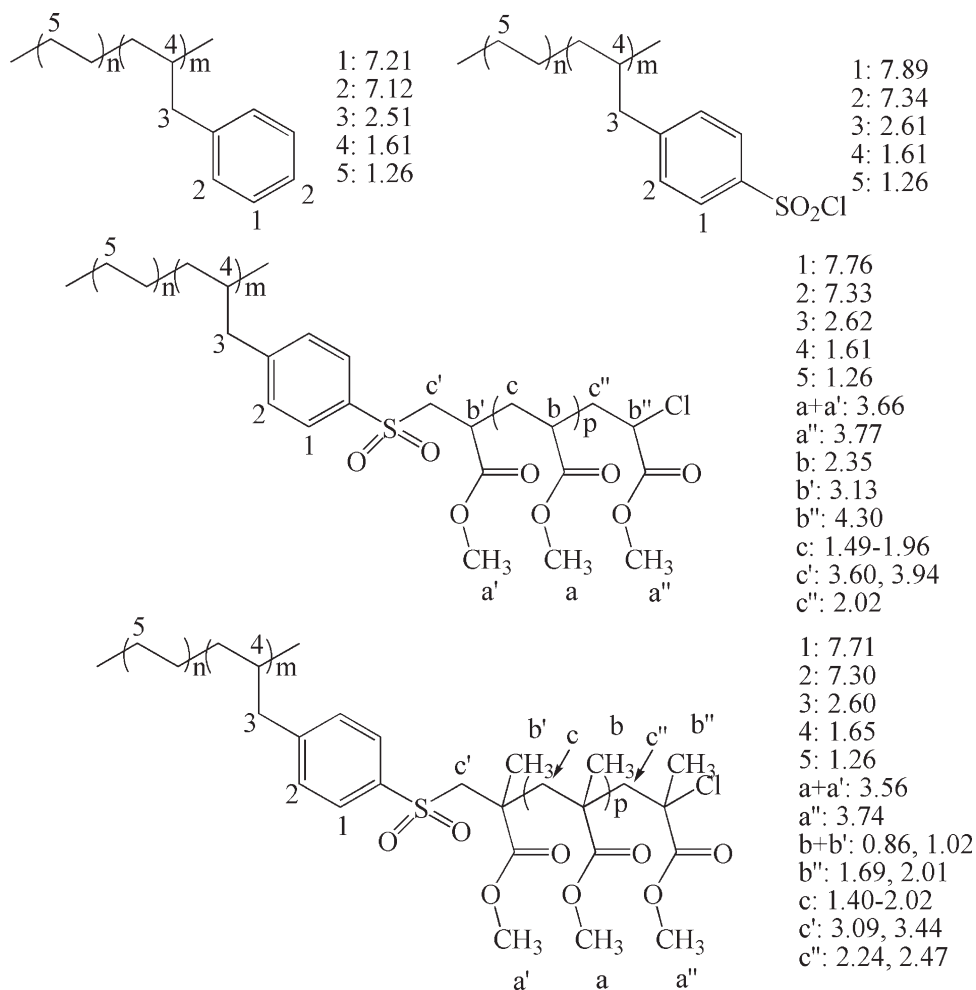
On the basis of the NMR data, the structural parameters, including the graft density and graft length, of the resulting graft copolymer were also determined. For polyolefin-g-PMA and polyolefin-g-PMMA, the initiation efficiency was estimated to be 100% by a complete upfield shift of aromatic protons and the integral ratios. Therefore, the graft density could be governed easily by the alteration of the content of arene sulfonyl chloride groups in the polyolefin multifunctional macroinitiator. Because the aromatic nuclei were quantitatively converted to arene sulfonyl chloride, the graft density was simply reckoned as the pendent aromatic nuclei density in the original ethylene-allylbenzene copolymers, namely, 3.9 given per 100 carbon atoms in the copolymer backbone. Furthermore, the average graft length was estimated by the ratio of the integrated area of the aromatic and methoxy protons according to the following equation:

$$\text{Graft length} = [(I_a + I_{a'} + I_{a''})/3]/[(I_1 + I_2)/4]$$

where  $I$  represents the resonance integrals and the subscripted letters and numbers refer to the peaks shown in Figure 2. As exhibited in Table I, the average graft length of the incorporated polar monomer varied significantly with the reaction conditions. Because the obtained graft copolymers possessed



**Figure 4**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of polyolefin-g-PMMA (entry 5, Table I).

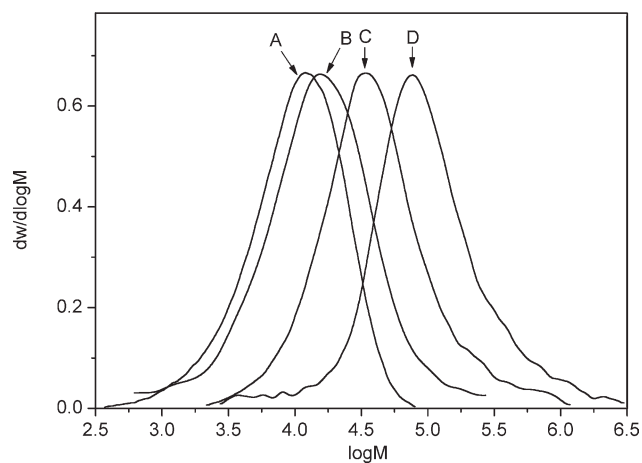


**Figure 5**  $^1\text{H-NMR}$  data for poly(ethylene-co-allylbenzene), the polyolefin multifunction macroinitiator, polyolefin-g-PMA, and polyolefin-g-PMMA.

controlled graft densities and average graft length, they could be used to explore the relationship between the chain architectures and the aggregate morphologies of the amphiphilic copolymers, including the polar and nonpolar polymers.

The gel permeation chromatography (GPC) traces of the polyolefin multifunction macroinitiator and polyolefin-g-PMMA graft copolymers were measured and are shown in Figure 6. The corresponding molecular weights and molecular weight distributions of the graft copolymers are listed in Table I. Obviously, the graft copolymers showed clear and complete shifts to higher molecular weights with the increase of graft lengths. We also noticed that the subsequent grafting-from copolymerization did not give any peaks in the low-molecular-weight region. These results demonstrate the exclusive formation of the targeted graft copolymer via the ATRP process. Moreover, the  $M_w/M_n$  value of polyolefin-g-PMA was higher than that of the polyolefin-g-PMMA synthesized at the same molar ratio of initiator to catalyst to ligand to monomer. This broadening trend-

ency was possibly caused by a higher propagation rate constant of MA than of MMA, which led to a



**Figure 6** Molecular weight distributions of (A) the polyolefin multifunction macroinitiator and (B–D) polyolefin-g-PMMA with side-chain lengths of 6.4, 19.5, and 83.8, respectively.  $M$ , molecular weight.

slower deactivation rate of the growing chains and, thus, to the loss of polymerization control.<sup>11,15</sup>

The DSC measurements provided additional evidence for the efficient incorporation of MMA and MA polar monomer units into the polyolefin chain. Noticeably, the  $T_m$  values derived from the nonpolar polyolefin segments of the graft copolymers decreased with increasing graft chain lengths (<15); this suggested that the increased graft side chains destroyed the crystallizability of polyolefin backbone and induced a decrease in  $T_m$ . As the graft lengths increased above 20, the  $T_m$  peak of the graft copolymers disappeared, and a glass-transition temperature ( $T_g$ ) originating from the polar polymers was observed. The  $T_g$  values also increased proportionally with the graft chain length. All these results clearly indicate that the dilute ATRP process indeed produced the graft copolymer products instead of a blend of polyolefin and MMA and MA homopolymers.

### CONCLUSIONS

Polyolefin-g-PMA and polyolefin-g-PMMA graft copolymers were successfully synthesized via the combination of metallocene-catalyzed coordination polymerization and dilute ATRP techniques. The influence of various experimental parameters, such as solvent, reaction temperature, catalyst, and molar ratios of various reagents, on the grafting copolymerizations and the average graft lengths was investigated in detail. It was found that crosslinking could be prevented, and the initiation efficiency was nearly quantitative when the graft copolymerization conditions were optimized. Furthermore, the average graft lengths in the polyolefin backbone were regulated easily. We believe that this simple strategy of combining coordination polymerization and the dilute ATRP technique can be extended to other systems to, thus, provide various amphiphilic copolymers containing polar polymers and nonpolar polyolefins.

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