Grafting of Poly(methyl methacrylate) or Polyacrylonitrile onto Polystyrene Using ATRP Technique

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ABSTRACT: One of the most useful methods for synthesizing the graft and well-defined copolymers is the atom transfer radical polymerization (ATRP) method. The polymerization was initiated by polystyrene (PS) carrying chloroacetyl groups as macroinitiator, in the presence of copper chloride (CuCl) and bipyridine (bpy). The macroinitiator (chloroacetylated PS) was prepared by successive chloroacetylation of PS under mild conditions and these reaction conditions overcome the problem of gelation and crosslinking in polymers. Successful graft copolymerizations were performed with methyl methacrylate (MMA) in toluene at 80°C and with acrylonitrile (AN) in tetrahydrofuran/ethylenecarbonate (62.5/37.5 v/v %) mixed solvent at 55°C. The characterization of the copolymers was investigated by ^{1}H-NMR and FT-IR spectroscopices. Gel permeation chromatography measurement indicated an increase of the molecular weight of the graft copolymers, as compared to that of the macroinitiator. This measurement also indicated the monomodal molecular weight distribution. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2619–2627, 2006

Key words: living radical polymerization; polystyrene; methyl methacrylate; acrylonitrile; ATRP

INTRODUCTION

Well-defined linear polymers are usually prepared via living polymerization techniques. These techniques can also be applied to the synthesis of block copolymers and graft copolymers. The importance of graft copolymers is that they combine the properties of two immiscible polymers and act as compatibilizers for polymer blends, and also can be used as amphiphilic copolymer. After living anionic and cationic polymerization was achieved, living radical polymerization has been one of the most targeted goals for synthetic polymer chemists. In the past few years, two new methods to realize living radical polymerization techniques were reported. These are stable free radical polymerization (SFRP),[1–4] using stable nitroxide radicals such as TEMPO, and atom transfer radical polymerization (ATRP), using transition metal complexes such as copper,[5–7] ruthenium,[8] nickel,[9] etc. In either of these processes, the key to the control of chain length is the equilibrium between active free radicals and dormant species where the steady state concentration of radicals remains low, thereby limiting termination reaction to high monomer conversions.

ATRP catalyzed by copper halide complexes with 2,2′-bipyridine (bpy) derivatives for the polymerization of various monomers, such as styrene,[10–13] methacrylates,[6,14,15] acrylates,[5,16] dienes, and acrylonitrile (AN),[17] has been developed in our laboratory and other laboratories.

ATRP employs an equilibrium between dormant alkyl halides and active propagating radicals, to maintain a low concentration of active species. The activated radical species can either propagate or be deactivated to reform the dormant species (Scheme 1). ATRP also has an advantage in utilizing a wide range of initiators. Alkyl halides with radical stabilizing substituents such as carbonyl, cyano, or aryl groups adjacent to the C—*X* can be used as initiators. In addition to compounds containing activated carbon–halogen bonds, those compounds with weak halogen bonds, like RSO_2—*X*,[12] are good initiators. Any compound, including macromolecular species, can potentially be used to initiate ATRP as long as they contain activated halogen atoms.

In this work, we present the preparation of grafted polystyrene (PS) with methyl methacrylate (MMA) and AN via ATRP, using the chloroacetylated PS as a macroinitiator. The obtained copolymers were characterized with ^{1}H-NMR, FT-IR spectroscopy, and differential scanning calorimetry (DSC) methods.

METHODS

Reagents and solvent

PS (M_w = 211,000, PDI = 3.3) was obtained from Tabriz Petrochemical Co. Chloroacetyl chloride (99%,

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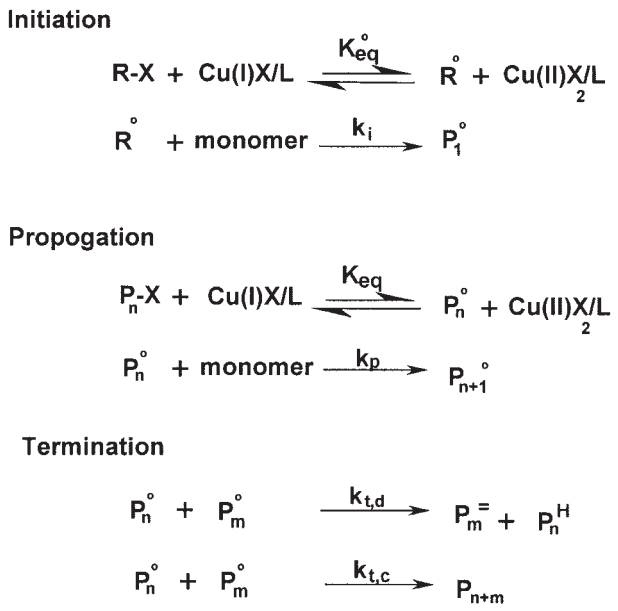


Scheme 1 Mechanism of ATRP.

ρ = 1.418 g/mL) was obtained from Merck. Toluene, tetrahydrofuran (THF), and chloroform were purchased from Merck and dried by refluxing over sodium and distilled under argon, prior to use.

MMA and AN (Merck) were vacuum distilled just before polymerization. 2,2′-bipyridine (bpy) (Merck) was used without purification. Cuprous chloride (Merck) was purified and dried by conventional methods before using.[18] All other chemicals were purchased from Merck and used without further purification. Aluminum trichloride was purchased from Aldrich Co.

Characterization

^{1}H-NMR spectra were recorded on FT-NMR (500 MHz) Brucker in $CDCl_3$. FT-IR spectra were recorded using Shimadzu FT-IR-8101M. The molecular weight of the resulting polymers was obtained with a maxima 820 GPC analysis instrument using PS (10^6, 10^5, and 10^4Å) calibration standards with a THF mobile phase.

DSC analyses were performed on a Mettler 4000 TA thermal analytical system.

Synthesis of chloroacetylated PS with degree of substitution = 3%

A chloroform solution (38 mL) of PS (3 g, 28.8 mmol) was added under argon to a stirred solution of chloroacetyl chloride (0.58 mL, 7.2 mmol), $AlCl_3$ in nitrobenzene (14.4 mL, 0.0144 mol of $AlCl_3$), and chloroform (30 mL). The mixture was stirred for 5 h at room temperature and then precipitated into acidified 80% methanol (v/v 1000 mL; 15 mL of HCl). The resulting yellowish product was reprecipitated from THF into 80% methanol and dried at 40°C under vacuum.

Yield: 2.85 g (white powder). Degree of substitution (D. S.), determined from ^{1}H-NMR, was 0.25. FT-IR (KBr, cm^{-1}): 1686 (υ C═O), 1258 (υ CH_2—Cl). ^{1}H-NMR ($CDCl_3$, ppm): δ = 4.66 (CO—CH_2Cl), δ = 7.6 (aromatic protons).

Synthesis of chloroacetylated PS with D. S. = 10%

A chloroform solution (40 mL) of PS (3 g, 28.8 mmol) was added under argon to a stirred solution of chloroacetyl chloride (1 mL, 12.4 mmol), $AlCl_3$ in nitrobenzene (12.5 mL, 12.5 mmol), and chloroform (25 mL). The mixture was stirred for 5 h at room temperature and then precipitated as described earlier.

Yield: 2.6 g (white powder). D. S., determined from ^{1}H-NMR, was 0.43. FT-IR (KBr, cm^{-1}): 1686 (υ C═O), 1258 (υ CH_2—Cl); ^{1}H-NMR ($CDCl_3$, ppm): δ = 4.66 (CO—CH_2Cl), δ = 7.6 (aromatic protons).

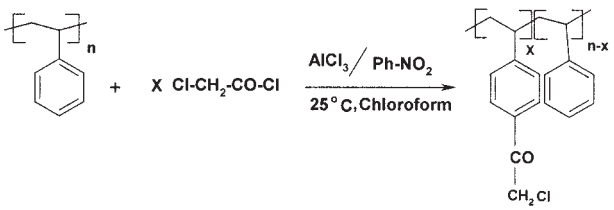
Graft copolymerization of MMA onto PS by ATRP

The ATRP copolymerization was carried out under nitrogen in a dried Schlenk flask equipped with a magnetic stirring bar. The flask was charged with chloroacetylated PS (0.3 g, 0.944 mmol, D. S. = 0.43) and 25 mL of dried toluene. After complete dissolution under stirring, copper chloride (CuCl; 0.0468 g, 0.473 mmol) and bpy (0.22 g, 1.4 mmol) were added. The system was degassed to remove oxygen by stirring the solution under nitrogen for 1 h. Then, MMA (5 mL, 46.6 mmol) was added and the flask was immersed in an oil bath and stirred at 80°C for 4 h. The mixture was precipitated into methanol and the obtained powder was dried at room temperature under vacuum. Then, the obtained powder was extracted with cyclohexane at 30°C for three times, to remove PS homopolymer.

Yield: 0.6 g; FT-IR (KBr, cm^{-1}): 1730 (υ C═O of MMA); ^{1}H-NMR ($CDCl_3$, ppm): 3.61(O—CH_3, PMMA), 6.5–8(aromatic protons).

Graft copolymerization of AN onto PS by ATRP

Chloroacetylated PS (0.4 g, 1.259 mmol) with D. S. = 0.43 was dissolved in a mixture of 12 mL ethyl carbonate and 20 mL THF in a three-necked flask. After complete stirring under nitrogen, CuCl (0.063 g, 0.629 mmol) and bpy (0.295 g, 1.88 mmol) were added to system. The system was degassed to remove oxygen by stirring the solution under nitrogen for 1 h. Then, AN (4 mL, 60.37 mmol) was added and the reaction mixture was immersed in an oil bath and stirred at 55°C, by which time the color changed from red to black red.



Scheme 2 Chloroacetylation of PS.

The mixture was precipitated into methanol and the obtained powder was dried at 40°C. Then, the crude product was extracted with cyclohexane at 30°C for three times, to remove PS homopolymer.

Yield: 0.41 g; FT-IR (KBr, cm^{-1}): 2240 (υ C≡N).

RESULTS AND DISCUSSION

Acylation

Friedel–Crafts acylation of PS has been used as an initial step in a number of methods for the preparation of functionalized PS resins.[19,20] However, the Lewis acid catalyst used in this reaction may lead to chain scission, and thus, changes the molecular mass of the PS, under certain conditions. In many instances, especially in the functionalization of crosslinked PS, chain cleavage is of little significance.

However, even a relatively small extent of chain scission leads to a significant broadening of the molecular-mass distribution of monodisperse polymer. Thus, reaction conditions must be mild enough to avoid any chain scission in the preparation of monodisperse carboxylated PS.

It is well established that, in the Friedel–Crafts acylation reactions, the ratio of catalyst to acyl component and the sequence in which the reactants are mixed can be of great importance, especially when the substrate is susceptible to disproportionate by free catalyst.[21,22] For example, when aluminum trichloride and acetyl chloride are allowed to react together prior to the addition to the substrate, as in the Perrier procedure, the ratio of catalyst to acyl component remains constant throughout the re-

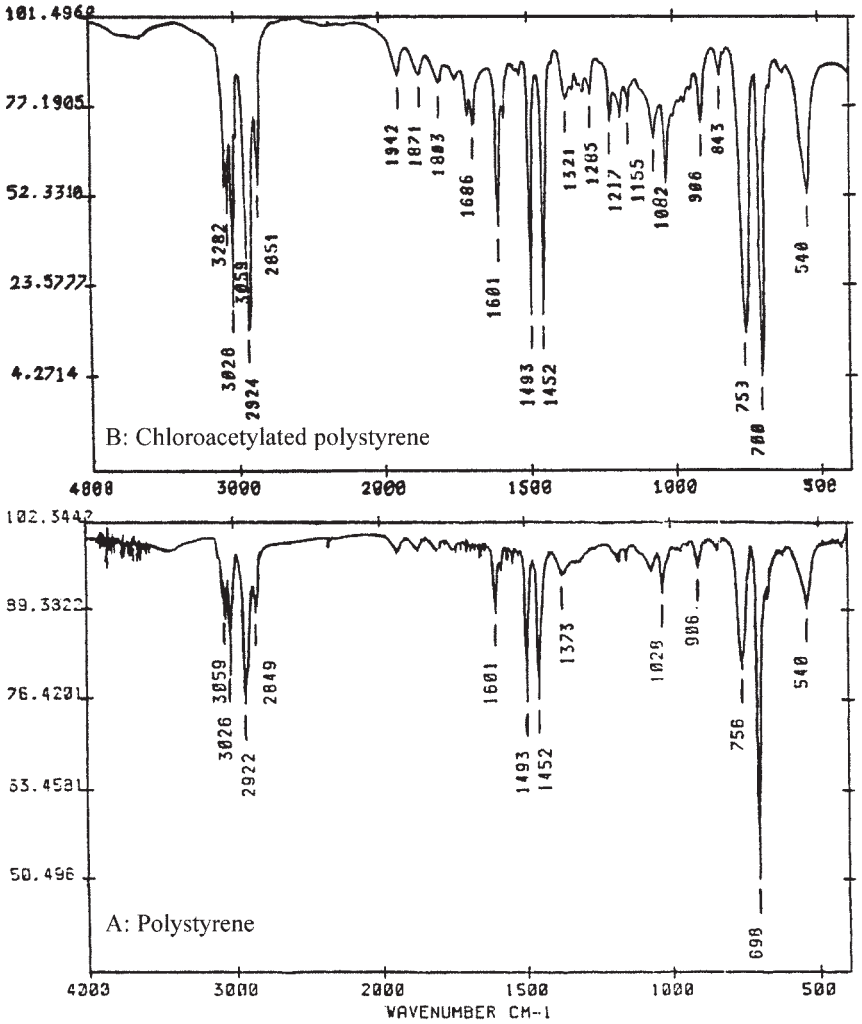


Figure 1 FT-IR spectra of PS (A) and chloroacetylated PS with D. S. = 3% (B).

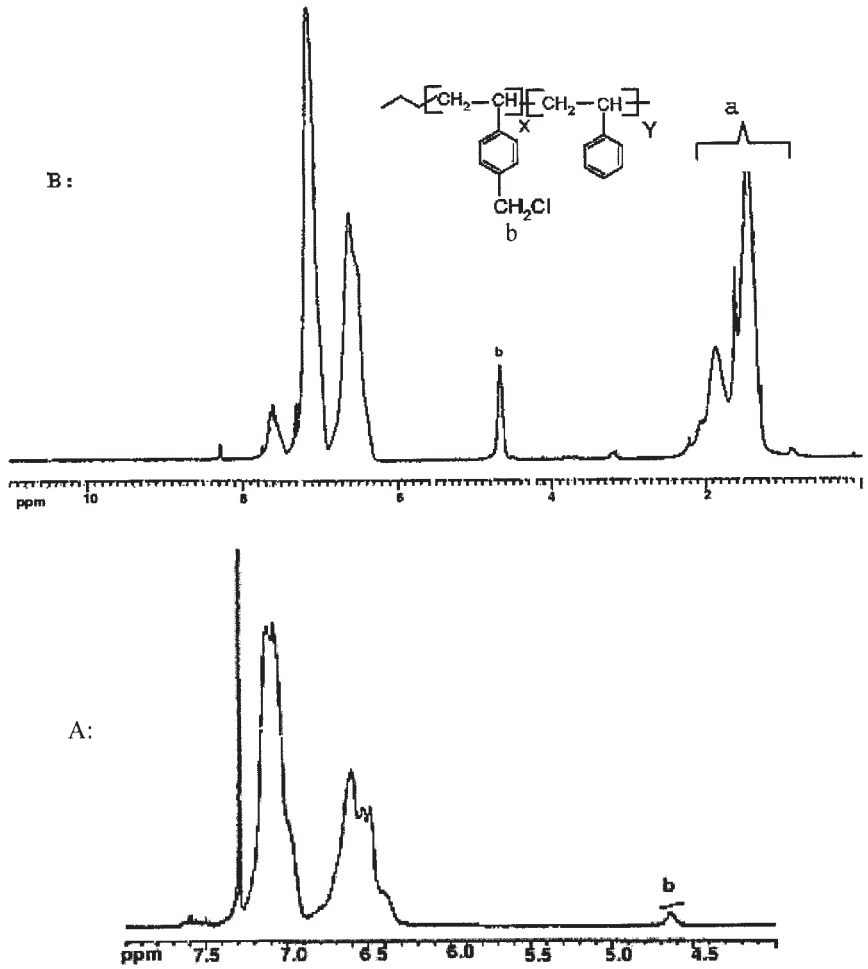


Figure 2 ^{1}H-NMR spectra of chloroacetylated PS with D. S. = 3% (A) and D.S. = 10% (B).

action, and the results are reproducible. However, in the Bouvealt procedure in which the acyl chloride is added as the final reactant or the most widely used Elbs procedure in which the catalyst is added as the last component, there is a continuous variation in the ratio of catalyst to acyl chloride, which depends on the rate of addition of the final component and the acylation rate. This fact is responsible for the nonreproducibility of many such reactions.[22,23]

Another method using a mild catalyst and reaction conditions was developed to overcome this problem.[24,25] In this method, we used chloroacetyl chloride as the acylating agent, $AlCl_3$ complexed with nitrobenzene as the catalyst, and chloroform as the diluent (Scheme 2). The catalyst and the chloroacylation agent were allowed to react prior to the addition of the substrate (PS), according to the Perrier procedure. Because of the bulky chloroacetylating complex, we assumed that chloroacylation occurred only in the most accessible positions of the aromatic ring, i.e., in the para position. The poly chloroacetylation of an aromatic ring is improbable, as the mono chloroacetylated product deactivates the ring in further substitution.

We characterized the resulting ring-chloroacetylated PS (D. S. = 3%) by DSC, gel permeation chromatography (GPC), FT-IR, and ^{1}H-NMR spectroscopy. FT-IR spectra for the starting PS and the chloroacetylated PS product are shown in Figures 1(A) and 1(B).

The FT-IR spectra of chloroacetylated PS exhibits a sharp absorption band at 1686 cm^{-1} attributed to carbonyl stretching bond and absorption bond at 1285 cm^{-1} attributed to CH_2—Cl bending bond.

Figures 2(A) and 2 (B) show the ^{1}H-NMR spectra of chloroacetylated PS obtained from Friedel–Crafts acylation of PS. It is obvious that the signal peak at $\delta = 4.66$ ppm could be attributed to chloroacetyl protons, and the peak at $\delta = 7.6$ ppm could be attributed to the α aromatic protons of chloroacetyl group, respectively.[25]

The D. S. content of chloroacetylated PS was determined by ^{1}H-NMR, using the intensity of aliphatic protons versus methylene protons of chloroacetylated PS. D. S. can be calculated by eq. (1).

$$\begin{aligned} 3x + 3y &= a \\ 2x &= b \end{aligned} \tag{1}$$

TABLE I
Effect Amounts of Compound Catalyst in Chloroacetylation of Polystyrene

Run	Polystyrene (mmol)	Chloroacetyle chloride (mmol)	1*M* of $AlCl_3$ in nitrobenzene (mL)	D. S. (%)
1	28.8	7.2	7.2	3
2	28.8	12.5	12.5	10

where *a* is the intensity of aliphatic protons and *b* is the intensity of protons of chloroacetylated PS [Fig. 2(B)].

The D. S. increased with increasing amounts of chloroacetyl chloride and aluminum trichloride. This fact was proved by FT-IR and ^{1}H-NMR spectra of PS with D. S. = 3% and D. S. = 10% [Figs. 2(A) and 2(B)]. The effect amounts of these compounds are summarized in Table I.

Friedel–Crafts acylation of PS was also confirmed by DSC analysis of chloroacetylated PS.

Substitution of PS with chloroacetyl groups exhibited a slightly higher glass-transition temperature (T_g) than that of the original PS (100 versus 111°C). The increased T_g was probably due to the introduction of steric interaction and polarity factors by having the chloroacetyl group in the para position as well as some intermolecular interaction between adjacent polymer chains. A similar phenomenon has been observed for para halo substituted and trifluoroacetylated PS[26] (Fig. 3).

The GPC trace of the chloroacetylated polymer [Figs. 4(A) and 4(B)] was unimodal and showed no tailing or broadening of molecular-weight distribution, thus confirming that no crosslinking or chain scission occurred during the functionalization procedures.[25]

Graft copolymers

The synthesis of graft copolymers can be accomplished through one of the three following routes: (i) "Grafting from" reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), (ii) "Grafting through" processes (operating by homo or copolymerization of a macromonomer), and (iii) "Grafting onto" processes (occurring when the growing chain is attached to a polymer backbone). The first two methods have been used in conjunction with ATRP in the design of graft copolymers and underscore the versatility of this controlled radical polymerization technique to synthesize a variety of (co)polymers.

Synthesis and characterization of PS-*g*-PMMA

The graft copolymerization of MMA initiated by the chloroacetylated PS as macroinitiator in the presence of CuCl/bpy catalyst system was first studied in toluene solvent to solubilize the catalyst and also the chloroacetylated PS (Scheme 3). The graft copolymer was analyzed by FT-IR (Fig. 5) and ^{1}H-NMR spectroscopy (Fig. 6). The spectrum of the graft copolymer displays a typical carbonyl stretch (1730 cm^{-1}), which is related to the carbonyl groups of the PMMA segments.

It is obvious that the peak at 560 cm^{-1} could be attributed to —CCl in the end of PMMA and it indicates that the polymerization is living.[25]

The ^{1}H-NMR spectrum of PS-*g*-PMMA is illustrated in Figure 6. The spectrum of PS-*g*-PMMA displays a characteristic peak at δ = 3.61 ppm (peak e), which is related to the —OCH_3 groups of the PMMA segments, and a peak at δ = 0.8–1.1 ppm, which is related to the —CH_3 groups of the PMMA (peaks c and d). The related intensity of the chloroacetyl groups of the chloroacetylated PS macroinitiator showed the formation of grafted copolymer (PS-*g*-PMMA).

The grafting efficiency can be determined from the values of Mn of the PMMA segments obtained by SEC, using eq. (2).[27]

$$G_{\text{eff}} = N_{\text{PMMA}} / N_{\text{Cl}} \times 100 = g_{\text{PMMA}} / M_n \times N_{\text{Cl}} \quad (2)$$

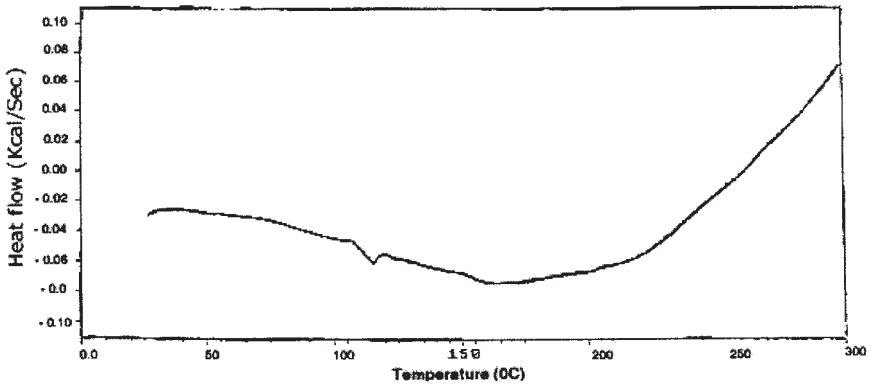


Figure 3 DSC thermogram of chloroacetylated PS.

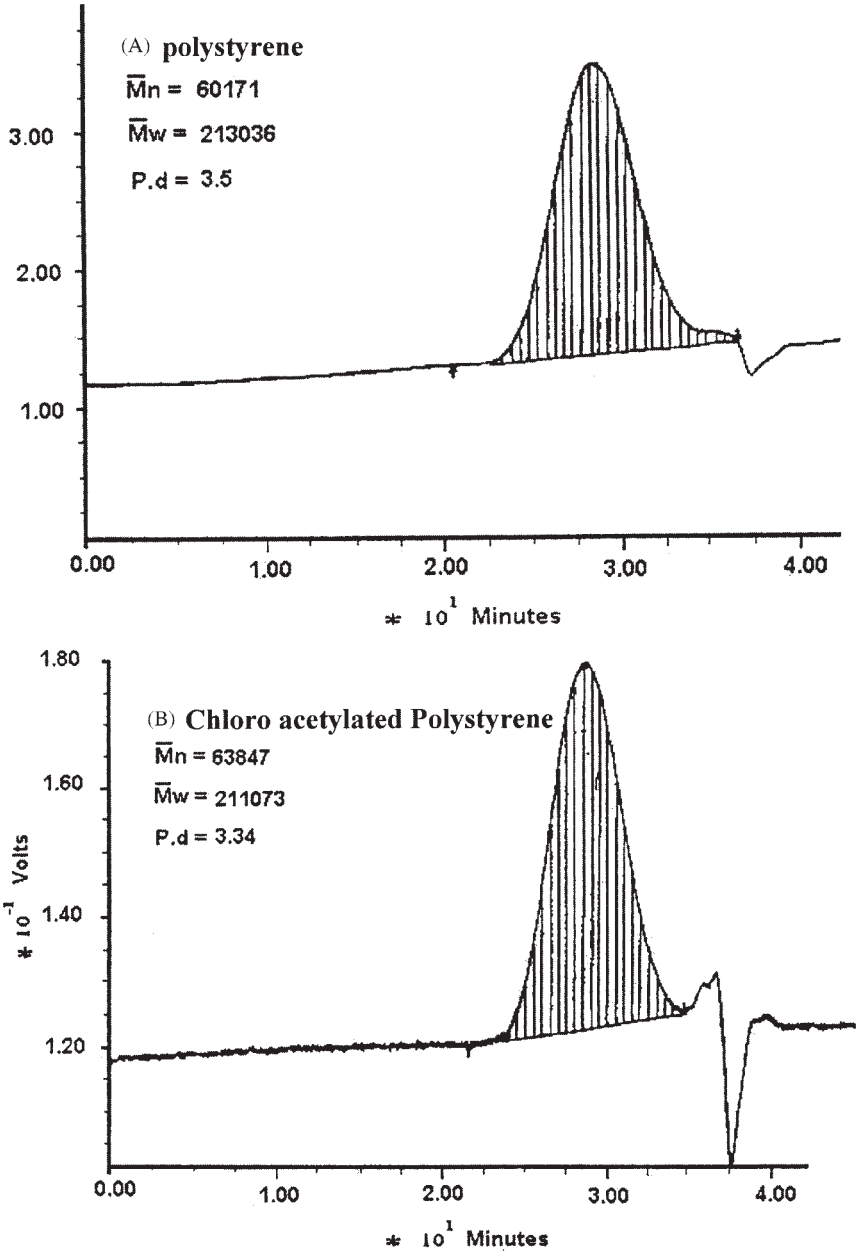
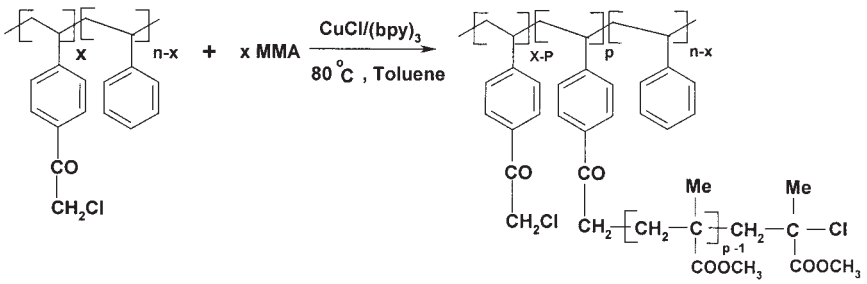


Figure 4 GPC trace of PS (A) and chloroacetylated PS (B).



Scheme 3 Graft copolymerization of MMA onto polystyrene.

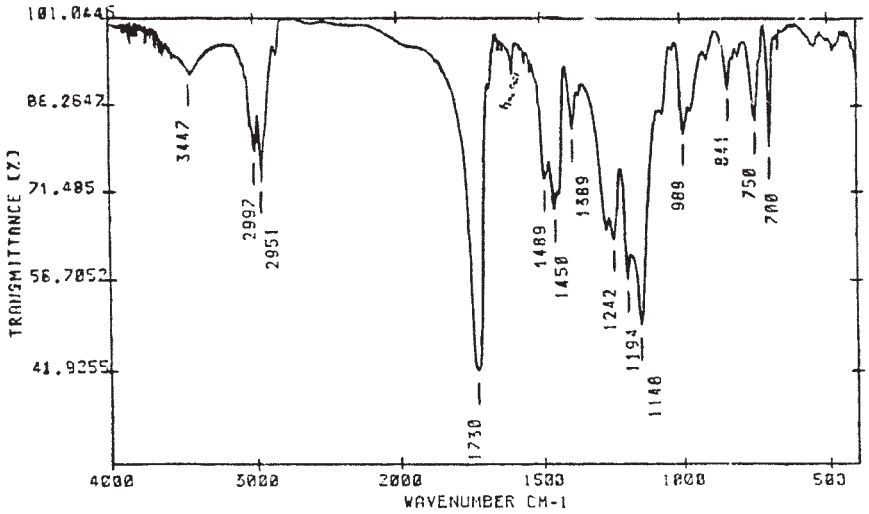


Figure 5 FT-IR spectra of PS-*g*-PMMA.

where NCl is the number of chloride groups in chloroacetylated PS (in mol) and NPMMA is the number of PMMA chains (in mol), which was determined from eq. (3):

$$N_{\mathrm{PMMA}} = \text{amount of PMMA in the graft copolymer} / M_n \text{ of the graft segment} \quad (3)$$

But when the number of PMMA chains is not defined, the grafting efficiency (Geff) can be determined from 1H-NMR spectra, using eq. (4).

$$G_{\mathrm{eff}} = (b / a+b)\times 100 = (0.3752 / 0.3753+0.0342)\times 100 = 91.65\% \quad (4)$$

The percentage of polymer chain (PMMA) was calculated according to eq. (5).

$$G_{\mathrm{per}} = \text{D. S.} \times G_{\mathrm{eff}} = 0.43 \times 91.65 = 39.4 \quad (5)$$

where D. S. = degree of substitution and G_{per} = percentage of polymer chain.

Additional evidence on the effectiveness of the graft copolymerization was also obtained from the DSC data. The graft copolymer studied in this work consists of PS backbone carrying amorphous PMMA. The presence of the graft segments should affect the melting behavior of the PS backbone.

PS-*g*-PMMA showed higher melting temperature (180°C) than that of chloroacetylated PS (115°C) (Fig. 7).

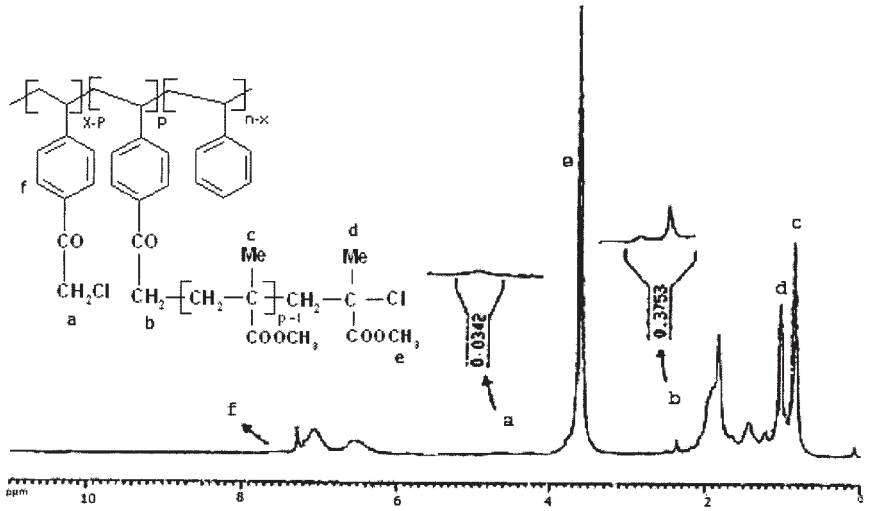


Figure 6 ^{1}H-NMR spectra of PS-*g*-PMMA.

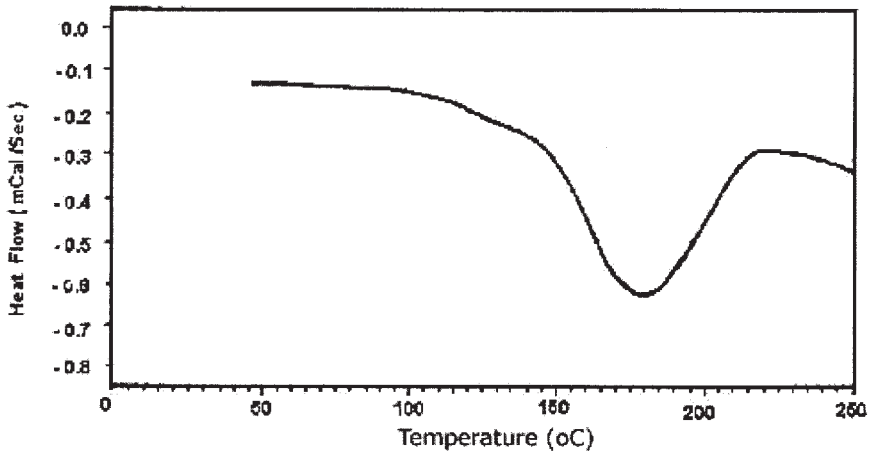


Figure 7 DSC thermogram of PS-*g*-PMMA.

These results showed the absence of microphase separation in these copolymers. This was an expected result because it is well known that PS is miscible with PMMA.

$M_{n,\ \text{total (NMR)}}$ was estimated using eq. (6):

$$M_{n,\text{total(NMR)}} = M_{n,\text{PS}}[1 + X \times M_{w,\text{MMA}} / M_{w,\text{St}}] \quad (6)$$

where $X = n_{\text{MMA}}/n_{\text{St}}$ (n_{MMA} = Integral (OCH_3)/3 = 5.177/3 = 1.72566 and n_{St} = Integral ($a + b$)/0.43/2 = 0.3753 + 0.0342/0.43/2 = 0.4761) and $M_{n,\ \text{PS}}$ = 63,847. Therefore, $M_{n,\ \text{total (NMR)}}$ = 63,847 × [1 + 1.72,566/0.4751 × 100/104] = 286,318.

An increase in molecular weight supports the formation of graft copolymer.

Synthesis and characterization of PS-*g*-PAN

The graft copolymerization of AN initiated by the chloroacetylated PS macroinitiator in the presence of CuCl/bpy catalyst system was studied in ethylene carbonate (EC; 37.5%) and THF (67.5%) mixed solvent at 55°C. The mixed solvents were used as the solvent, to provide solubility for the catalyst and the resulting polymer.

The mechanism of polymerization of AN by ATRP is presumably similar to that proposed for the ATRP with other vinyl monomers such as styrene and (meth)acrylates[5,11] (Scheme 4).

The obtained graft copolymer was analyzed by FT-IR spectroscopy (Fig. 8). A typical FT-IR spectrum of the graft copolymer clearly shows a bond at 2240 cm^{-1}, assigned to the stretching absorption of the —C≡N and illustrates the occurrence of the graft copolymerization.

CONCLUSIONS

The graft copolymers composed of PS as a backbone and PMMA and polyacrylonitrile as branches were obtained for the first time by ATRP technique. The increase in M_n and the monomodal shape of the GPC traces of the copolymers suggest the formation of graft

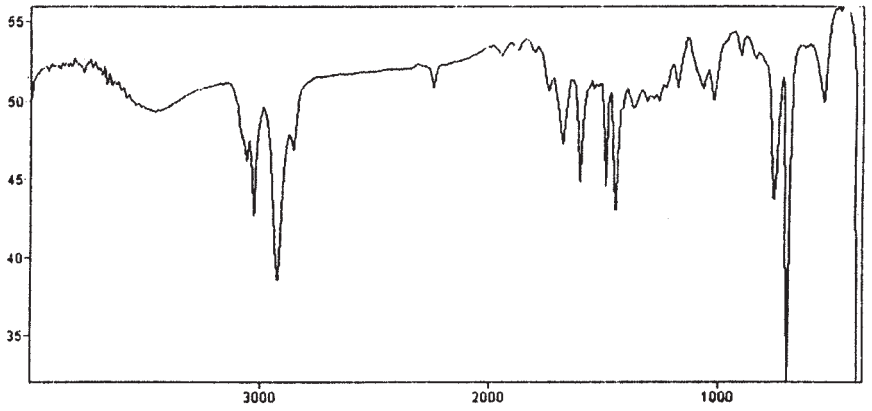
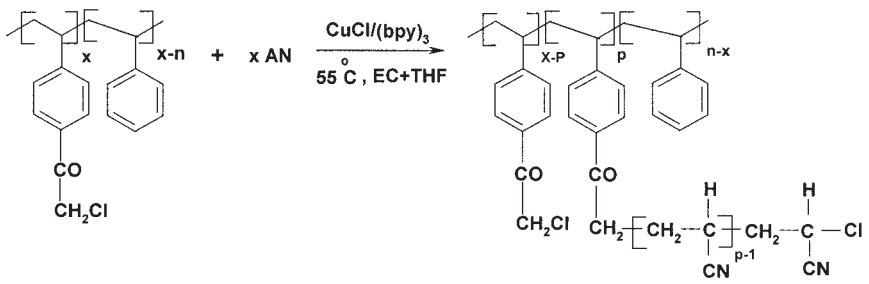


Figure 8 FT-IR spectrum of AN-*g*-PMMA.



Scheme 4 Graft copolymerization of AN onto PS.

copolymers without homopolymerization. New reaction condition using mild state to synthesize controlled graft copolymers overcomes the problem of gelation and crosslinking in the syntheses of similar graft copolymers reported in the literature. The formation of the graft copolymer was supported by analysis using GPC, ^{1}H-NMR, and FT-IR.

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