Synthesis of Triphenyl Phosphine Oxide-Containing Polymers via Atom Transfer Radical Polymerization

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ABSTRACT: Bis[(4 -β-(2-bromopropanoate)ethoxy)phenyl]phenylphosphine oxide was used for the first time as the initiator of atom transfer radical polymerization of styrene and methyl methacrylate in the presence of CuBr/N, N,N′, N′′, N′′-pentamethyldiethylene-triamine as catalyst/ligand and dimethyl sulfoxide as solvent. The presence of phosphine oxide linkages in the backbone gives the polymers special properties; low T_g, high char yield, and decreases the oxygen induction time value. A linear increase of number average molecular weight (M_n) versus monomer conversion was observed, and the molecular weight distribution was relatively narrow ($M_w/M_n = 1.1$–1.3). FTIR, ^{1}HNMR, gel permeation chromatography, ultraviolet spectroscopies were used for the characterization of the related polymers. The thermal properties of these polymers were investigated by differential scanning calorimetry and thermogravimetric analysis. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Phosphorus-containing polymers have been known for many years to exhibit the primary advantage of flame retardancy, and they are increasingly gaining popularity over their halogen counterparts because they generally generate less toxic combustion products.[1]

The combustion of the outer layers of the polymeric material leads to an intumescent carbonaceous char. This acts as a physical and thermal barrier to further combustion by impeding heat transfer to the underlying layers of polymer and, therefore, impeding the release of further flammable volatiles.[2]

When phosphorus chemically bonded to the polymer structure, it brings a better solution for migration problems that were frequently observed for additive types of fire retardants.[3] The polymers containing triphenylphosphine oxide (TPO) groups have been known to be thermally stable and flame retardant.[4]

High-performance TPO-containing polymers have shown thermal stability, flame retardancy, high glass transition temperatures, and excellent resistance to atomic oxygen.[4,5]

The TPO group has been incorporated into a variety of polymeric systems including poly(arylene ether)s, poly(imide)s, poly (quinoxaline)s, poly(phenylene)s, fluorinated cyclobutanes, poly (amide)s, poly(arylenevinylene)s, poly(etherimide)s, poly(benzimidazole)s, and phenolic novalac resins.[6,7]

Atom transfer radical polymerization (ATRP) is one of the most effective methods to control radical polymerization. The end groups of the polymers are defined by the structure of the initiator used. The alkyl group of the alkyl halide initiator remains at one end of the produced polymer chain, a halogen atom is quantitatively transferred to the other end of the chain.[8–12] Bifunctional initiators have been used to control the combination of polymers, and functional initiators have been used to control the functionality of polymers.[13]

This study focused on the preparation of a bifunctional phosphine oxide containing initiator and ATRP of different monomers in the presence of this bifunctional initiator. The bifunctional initiator [Bis[(4 -β-(2-bromopropanoate)ethoxy)phenyl] phenylphosphine oxide (BBEPPO)] was prepared by esterification of bis[(4 -β-hydroxyethoxy)phenyl]phenylphosphine oxide (BHEPPO) compound with 2-bromopropionyl bromide. The ATRP of styrene (St) and methyl methacrylate (MMA) using CuBr as catalyst, pentamethyldiethylenetriamine(PMDETA) as ligand, dimethyl sulfoxide (DMSO) as solvent, and BBEPPO as
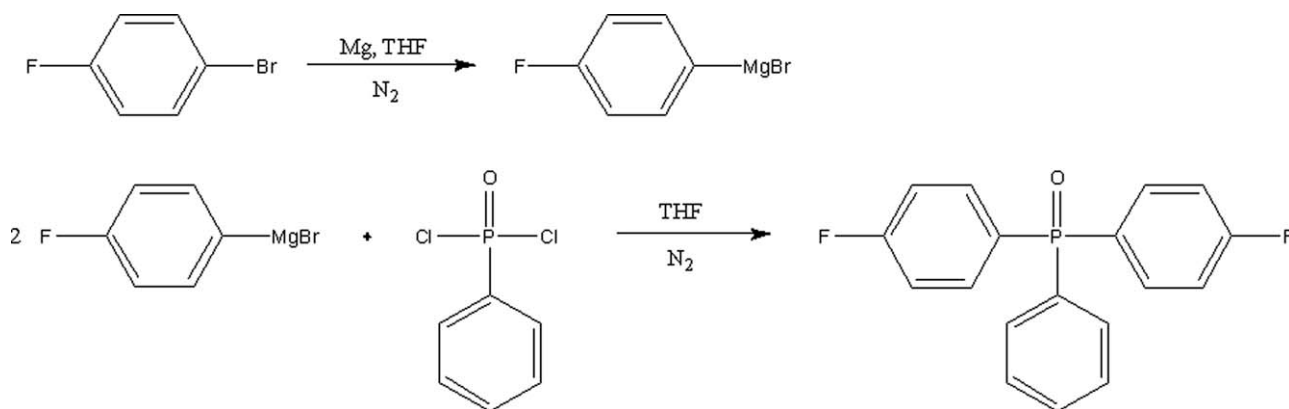
Scheme 1. Synthesis of the BFPPO.

bifunctional initiator were described. Polystyrene (PSt) and polymethyl methacrylate (PMMA) possessing two reactive bromine end groups in the main chain were obtained.

EXPERIMENTAL

Materials

Styrene and MMA from Fluka, Steinheim, Germany was stirred over CaH_2 overnight and distilled under reduced pressure. Chloroform from Lab Scan, Gliwice, Poland was shaken with several portions of concentrated H_2SO_4, washed thoroughly with water, and dried with $CaCl_2$ before filtering and distilling. DMSO obtained from Lab Scan, Gliwice, Poland was dried and distilled over CaH_2, mixed over sodium/benzophenon ketyl, and distilled before use. Methanol (Lab Scan, Gliwice, Poland), p-bromofluorobenzene (Acros, Geel, Belgium), triethylamine (Acros, Geel, Belgium), dichlorophenylphosphine oxide (Merck, Darmstadt, Germany), sodium carbonate (Merck, Darmstadt, Germany), potassium hydroxide (Merck, Darmstadt, Germany), sodium bicarbonate (Merck, Darmstadt, Germany), 2-bromo-propionyl bromide (Aldrich, Steinheim, Germany), copper (I) bromide (Aldrich, Steinheim, Germany), PMDETA (Aldrich, Steinheim, Germany), magnesium turnings according to Grignard synthesis (Merck, Darmstadt, Germany), and ethylene carbonate (Merck, Darmstadt, Germany) were used without further purification.

Characterization

^{1}HNMR spectra was obtained at ambient temperature on a Bruker 250 MHz Spectrometer using deuterated chloroform (CDCl$_3$-d_1) and deuterated DMSO (DMSO-d$_6$). A Shimadzu FTIR spectrometer was used for infrared analysis. Ultraviolet (UV) spectra of the materials were recorded on a Pharmaspec

UV-1700 Shimadzu spectrophotometer. Molecular weights were analyzed using gel permeation chromatography (GPC). GPC analysis were carried out with a set up consisting of the Agilent pump and refractive index detector and three Agilent Zorbax Columns (1000S, 300S, and 60S). THF was used as the eluent at a flow rate of 0.5 mL/min at 30°C. The molecular weights of the polymers were calculated with the aid of PSt standards. The glass transition temperatures (T_g) were obtained by differential scanning calorimetry (DSC) on a TA DSC Q10; 2–3 mg of polymer was initially heated under nitrogen from 30 to 350°C at a rate of 10°C min^{-1} and the T_g values quoted later in Table III were obtained, following rapid cooling, from a second heating at the same heating rate. Thermogravimetric analysis (TGA) was carried out on a TA TGA Q50 from 20 to 550°C at a heating rate of 20°C min^{-1} in nitrogen.
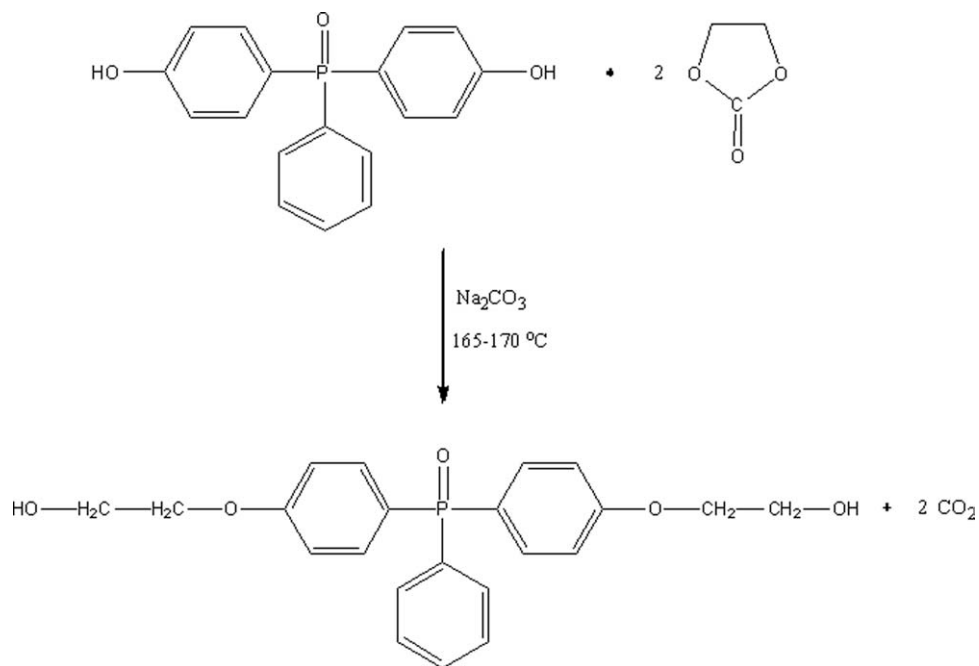
Preparation of Bifunctional Initiator

Preparation of Bis(4-fluorophenyl)phenylphosphine Oxide. Bis(4-fluorophenyl)phenylphosphine oxide (BFPPO) was prepared as previously reported.[14] The crystals typically giving overall yields around 65% of monomer grade material with melting point of 126–127°C is obtained. The reaction occurred according to Scheme 1.

Preparation of Bis(4-hydroxyphenyl)phenylphosphine Oxide. Bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO) was prepared according to literature.[15] The resulting material was considered to be monomer grade with a melting point of 236–237°C. The yield of the reaction was 65% after the purification. The reaction took place according to Scheme 2.

Preparation of Bis[(4 -β-hydroxyethoxy)phenyl]phenylphosphine Oxide. BHEPPO was prepared according to the
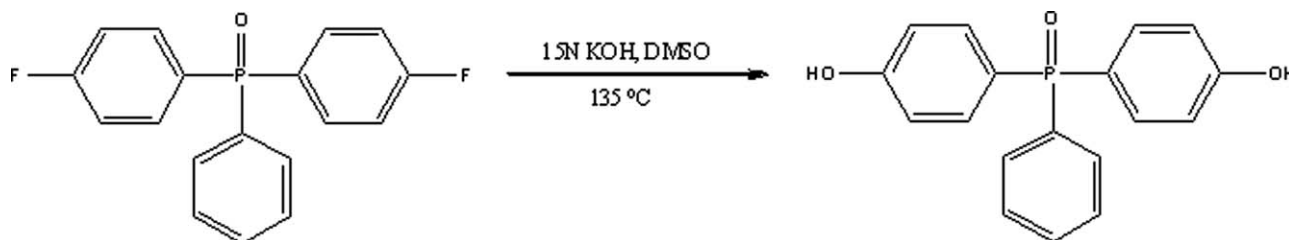
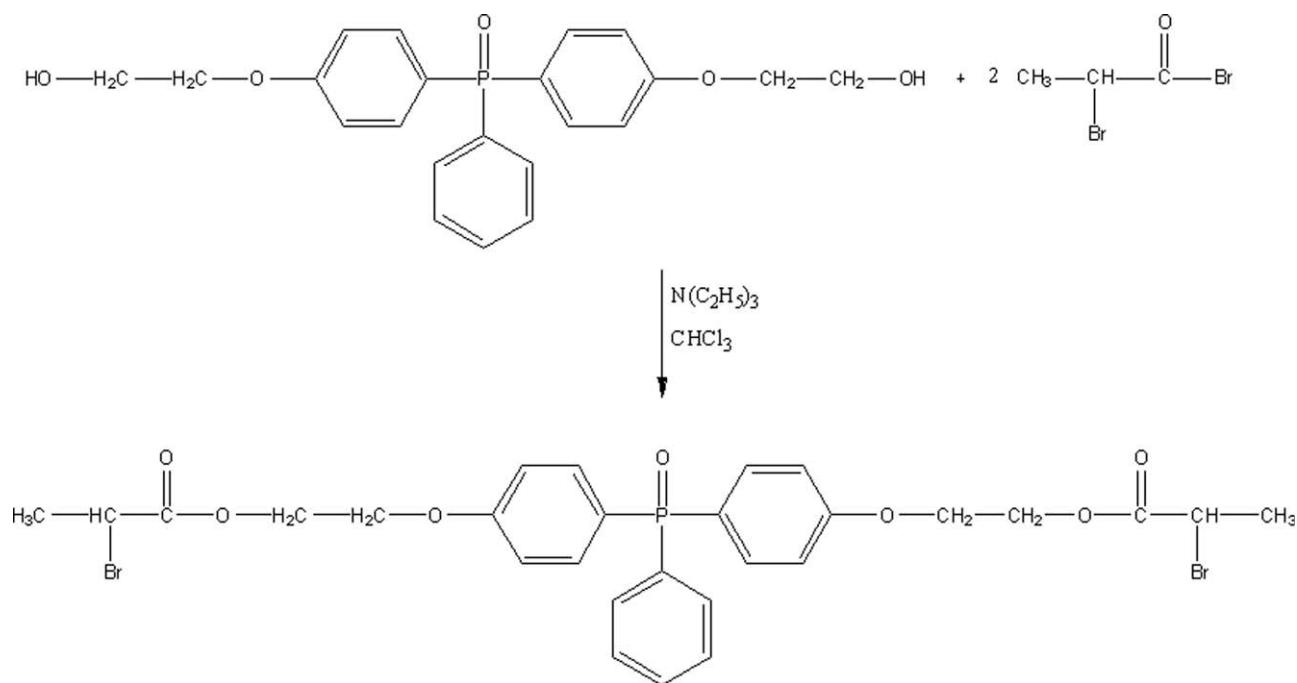**Scheme 2.** Synthesis of the BHPPO.

Scheme 3. Synthesis of the bifunctional organic material BHEPPO for the bifunctional initiator.

procedure.[16] A light brown viscose liquid was obtained. The yield of the reaction was 90% after purification. The reaction takes place according to Scheme 3.

Preparation of BBEPPO. BBEPPO was synthesized according to procedure.[13,17] Under nitrogen, 1.7 mL (0.0162 mol) of 2-bromopropionyl bromide was added dropwise to a stirring mixture of 2 g BHEPPO (0.0054 mol) and 2.3 mL triethylamine

(0.00162 mol) in 20 mL of $CHCl_3$ in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 1 h. The reaction mixture was washed with water (3 × 20 mL) and then dried overnight with $MgSO_4$. After filtration and evaporation of $CHCl_3$ a sticky light brown, very viscose product was obtained. It was dried under oven and recrystallized from methanol twice (yield 58%). The reaction occurred according to Scheme 4.

Scheme 4. Synthesis of the bifunctional initiator BBEPPO for ATRP.

Table I. ATRP of St by Using BBEPPO[a]

Run No	[BBEPPO][a] (mol/L)	[M]$_0$ (mol/L)	[I$_0$]$_0$[b]/[Cu$^+$]/[PMDETA]/[M]$_0$[c]	Time (h)	Conv. (%)	M_n[d]	$M_{n(theo)}$[e]	M_w/M_n
PSt1	0.06	6	1/1/2/100	4	7	3400	774	1.20
PSt2	0.06	6	1/1/2/100	8	10	4100	1004	1.20
PSt3	0.06	6	1/1/2/100	18	20	9600	2041	1.10

[a]Temperature: 57°C, [b]Initial initiator concentration, [c]Initial monomer concentration, [d]Determined by means of GPC calibrated with PSt standards, [e]Calculated by [M]$_0$/[I]$_0$ × conv. × M_w (monomer), Solvent: DMSO.

Polymerization of Styrene and MMA

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three times, then 1.7 mL styrene, 0.021 g copper(I)bromide, 62 μL ligand (PMDETA), and initiator 0.1 g BBEPPO were added under nitrogen. DMSO (1.5 mL) was used as solvent.[18] The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostat at 57°C. The polymerization was performed for 4, 8, 18 h and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The filtrate was dried under vacuum. The conversion was determined gravimetrically. ATRP conditions and results are given in Tables I and II. The synthesis of MMA was done in the same conditions with styrene. The amount which was taken from MMA is 1.6 mL.

RESULTS AND DISCUSSION

Preparation of BFPPO

BFPPO was synthesized via Grignard chemistry involving p-bromofluorobenzene and dichlorophenylphosphine oxide. The structure was confirmed using FTIR. The FTIR spectrum of BFPPO contains the characteristic broad band (P=O) v = 1394 cm$^{-1}$, (P—Ph) v = 1434 cm^{-1}, (C—F) v = 1220 cm^{-1}, (aromatic C—H) v = 3057 cm^{-1}, and (C=C) v = 1434–1589 cm^{-1}.

Preparation of BHPPO

BHPPO was synthesized by hydrolyzing BFPPO with potassium hydroxide in DMSO. The molecular structure of this material was confirmed using FTIR. The characteristic absorption peak of the functional group (Ph—OH) 3138 cm^{-1} was detected for BHPPO. Peaks at 1278 cm^{-1} (P=O), 1436 (P—Ph), 1122 cm^{-1} (C—O), and 1583–1600 cm^{-1} (C=C) proved the existence of phenylphosphine oxide and hydroxyl structure.

Preparation of BHEPPO

The organic material (BHEPPO) incorporating phosphine oxide groups were synthesized by reacting BHPPO with ethylene carbonate in the presence of sodium carbonate as the catalyst. The formation of BHEPPO was confirmed by UV, FTIR, and ^{1}HNMR. The UV spectra showed absorption at 244 and 282 nm for the BHEPPO which originates from π-π* transition of the aromatic C=C. UV spectra of BHEPPO were taken in methanol. The FTIR of BHEPPO absorptions due to hydroxyl groups was observed at 3302 (CH$_2$—OH), 1162–1045 (C—O), 2931–2872 (C—H), 1594–1500 (C=C), and an absorption based on triphenylphosphine (P—Ph) 1436 cm^{-1}. The BHEPPO was further characterized by ^{1}HNMR as shown in Figure 1 measured with CDCl$_3$ as an external reference. Absorptions of characteristic aromatic protons were found at δ = 6.9–7.7 ppm, δ = 3.9–
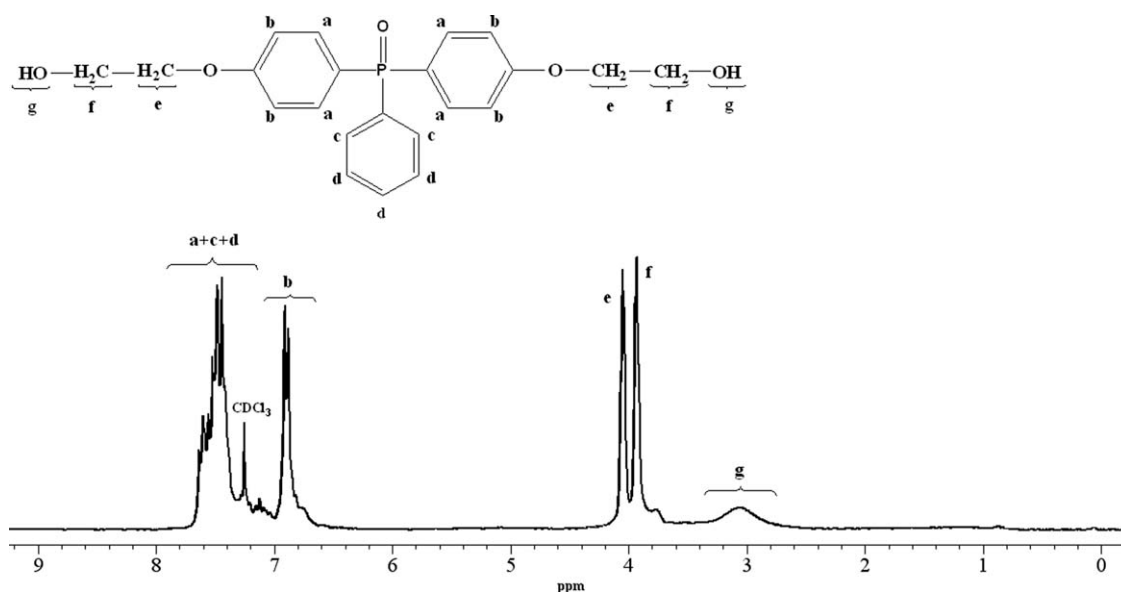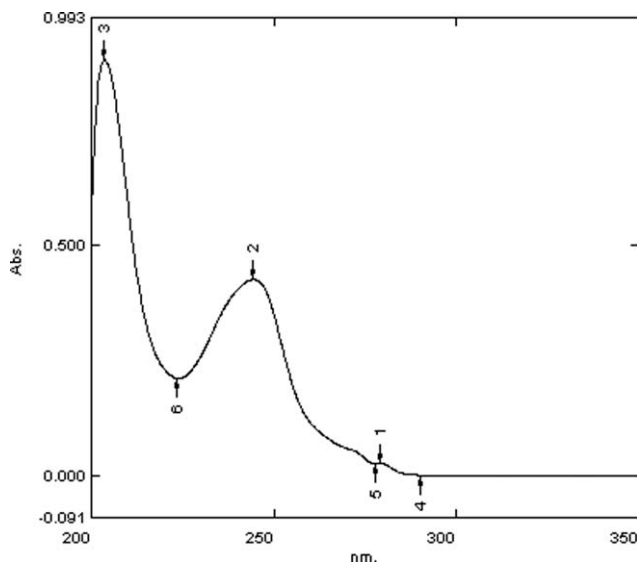

Figure 1. ^{1}HNMR of BHEPPO.

Figure 2. UV spectrum of BBEPPO.

4.1 ppm ($-$OCH$_2$), and $\delta = 2.0$–2.4 ($-$OH). The FTIR and ^{1}HNMR confirmed the formation of the desired product.

Preparation of BBEPPO

The bifunctional macroinitiator was synthesized by reacting 2-bromopropionyl bromide with BHEPPO in the presence of triethylamine as the catalyst and chloroform as the solvent. The structure of BBEPPO was confirmed by UV, FTIR, and ^{1}HNMR spectroscopy. The spectrum of BBEPPO was recorded at UV spectrophotometer over the wavelength range 200–350 nm, as seen in Figure 2. The first and the second absorption bands, which originates the π-$\pi^\star$ transition, were observed at $\lambda = 282$ and 244 nm in methanol, respectively. The FTIR spectrum of BBEPPO exhibited characteristic absorption bands for the ester at 1736 (C$=$O). Moreover, other peaks arising from 1252 (P$=$O), 2928 (C$-$H), 1150–1067 (C$-$O), 1595–1501 (C$=$C),

and 1428 (P$-$Ph) as shown in Figure 3 are observed to confirm the structure. ^{1}HNMR spectrum of BBEPPO was taken in DMSO-d$_6$ as shown in Figure 4. The spectrum proves the expected structure of the initiator BBEPPO. According to the spectrum, the signals originating from esterificated Br end group of BBEPPO were discerned at 1.6–1.7 ppm ($-$CH(Br)CH$_3$), 4.2–4.7 ppm [($-$CH(Br)CH$_3$) and ($-$OCH$_2$)], and 7–7.6 ppm phenyl protons. The ^{1}HNMR analysis of BHEPPO and BBEPPO was checked and compared with calculation of the peak integral areas. BHEPPO [Phenyl protons, 13 H, peak area: 39.3, OCH$_2$ (etheric protons), 8 H, peak area: 23] and BBEPPO [Phenyl protons, 13 H, peak area: 12.7, OCH$_2$ (etheric protons) and CH (protons near to bromine), 10 H, peak area: 9.6, CH$_3$ protons (protons of methyl near to bromine), 6 H, peak area: 6]. The ratios of the protons were in accordance so that it can prove that the bromination process was successful.

After the crystallization of BBEPPO, the product was dried under vacuum. The initiator was soluble in DMSO and methanol but not common solvents used for ATRP such as toluene, anisole, benzene, THF, etc. Due to the poor solubility of the initiator in more conventional solvents commonly used for transition metal-mediated living radical reactions, polymerization was carried out in DMSO as solvent which resulted in homogeneous reaction solutions in all cases.[18]

ATRP of St and MMA with Bifunctional Initiator

Styrene and MMA were polymerized by ATRP in the presence of copper bromide complexed with PMDETA ligand in DMSO solution. BBEPPO was used as the bifunctional initiator (Scheme 5). Polymerization of St and MMA was carried out in DMSO solution at 57°C using 1 : 1 : 2 : 100 ratio of [I]$_0$/[Cu$^+$]/[PMDETA]/[M]$_0$. The results are summarized in Tables I and II. Table I shows that M_n of PSts increases linearly with conversion up to over 20% while the M_w/M_n remains consistently low throughout the course of the reaction. The polydispersity indexes (PDIs) values remain about 1.20–1.10 throughout the polymerization process. The results are consistent with
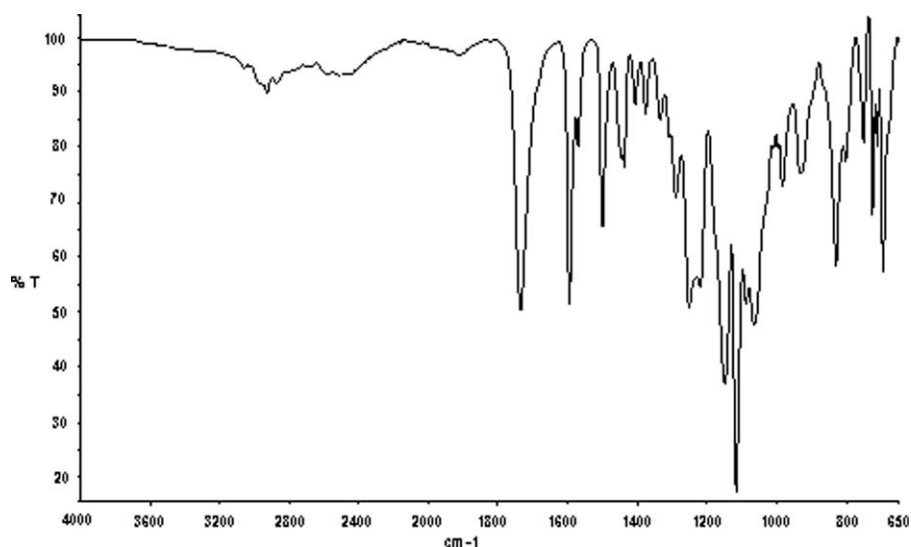

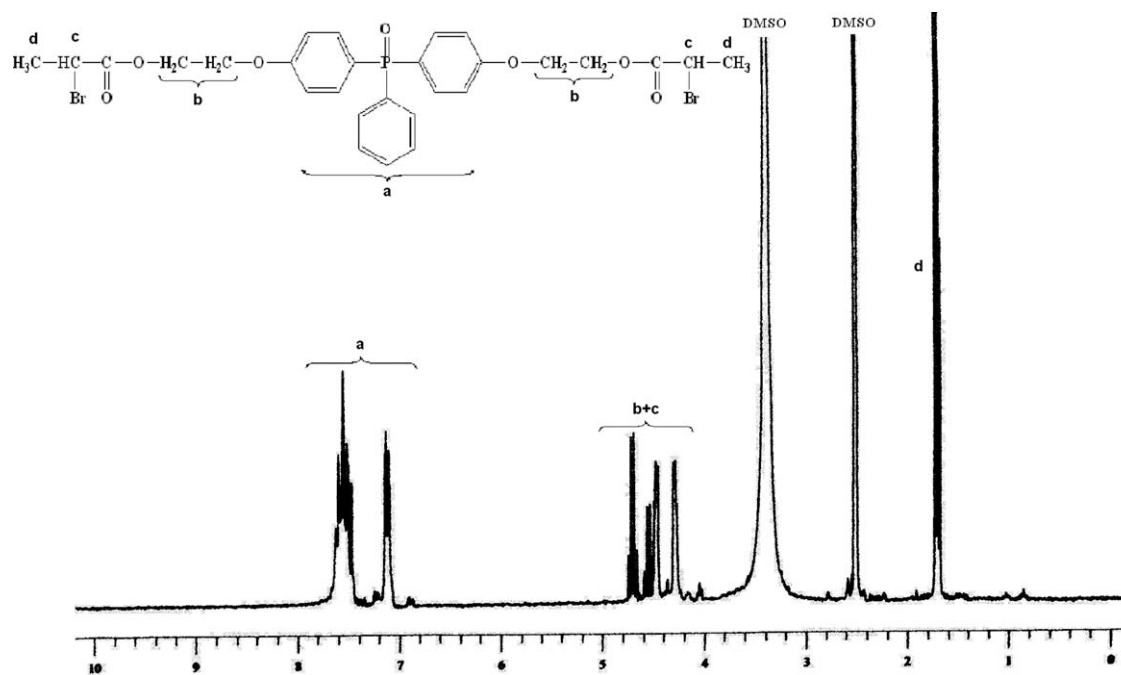**Figure 3.** FTIR spectra of BBEPPO.

Figure 4. ^{1}HNMR of BBEPPO.

a "living" ATRP. Even the M_w/M_n decreases by the time, the conversions are not so high. The results of the ATRP of MMA in DMSO are presented in Table II. During the polymerization, the solutions became very viscous as the reaction time increased. The data indicate that the polymerization of MMA in DMSO has uncontrolled character resulting in rather broad molecular weight distribution (MWD) and higher experimental M_n values (GPC) than the calculated ones. The PDI values remain about 1.60–1.3. On the other hand, by increasing the time, the conversions of PMMA increase from 45 to 90%.
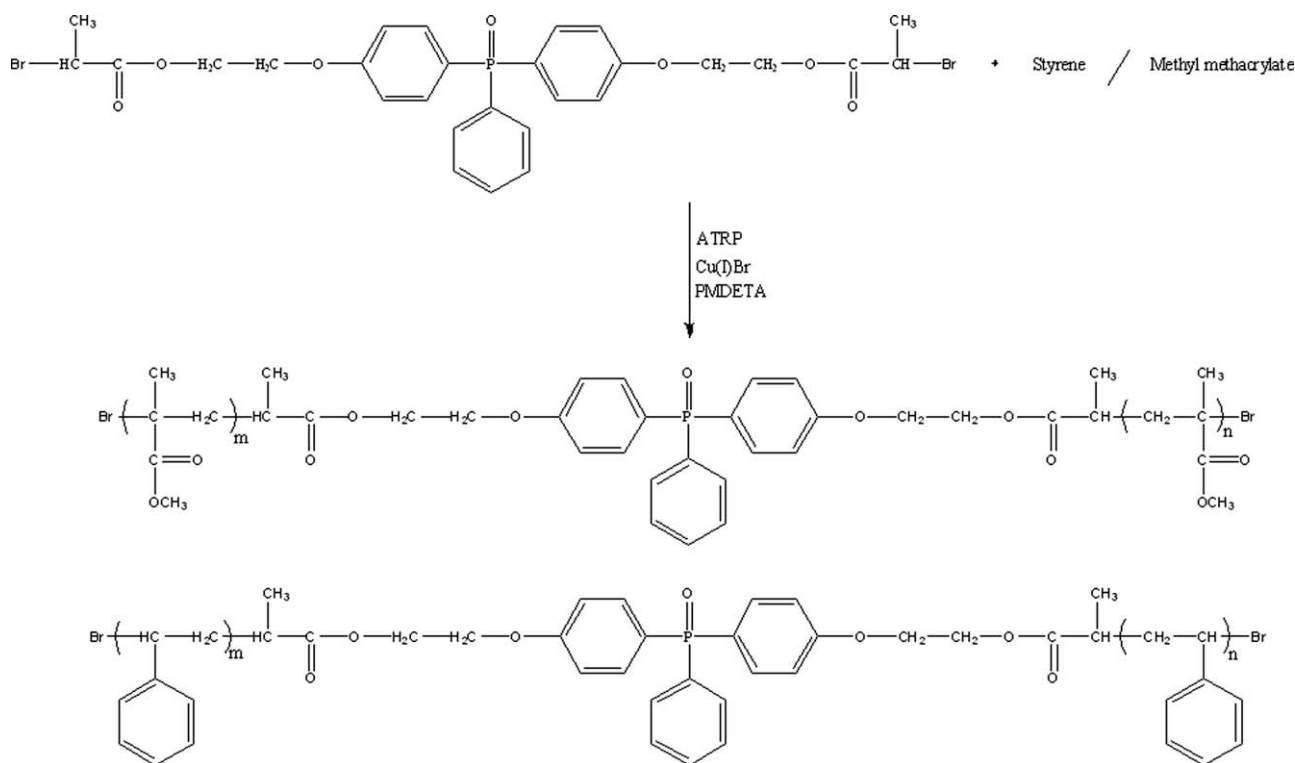
Scheme 5. Synthesis of PSt and PMMA.

Table II. ATRP of MMA by Using BBEPPO[a]

Run No	[BEHPPO][a] (mol/L)	[M]$_0$ (mol/L)	[I$_0$]$_0$[b]/[Cu$^+$]/[PMDETA]/[M]$_0$[c]	Time (h)	Conv. (%)	M_n[d]	$M_{n(theo)}$[e]	M_w/M_n
PMMA1	0.06	6	1/1/2/100	4	45	12,000	4500	1.60
PMMA2	0.06	6	1/1/2/100	8	57	16,000	5700	1.40
PMMA3	0.06	6	1/1/2/100	18	90	24,000	9000	1.30

[a]Temperature: 57°C, [b]Initial initiator concentration, [c]Initial monomer concentration, [d]Determined by means of GPC calibrated with PSt standards, [e]Calculated by [M]$_0$/[I]$_0$ × conv. × $M_{w\ (monomer)}$, Solvent: DMSO.

From the very beginning of the reaction, $M_{n,\exp}$ values are higher than M_nth values. The solvent type, its structure and solubility could be one reason for this difference. Because usually nonpolar solvents such as p-xylene, p-dimethoxybenzene, diphenyl ether, and anisole and occasionally polar solvents such as ethylene carbonate and propylene carbonate were used for solution-based ATRP systems. Nonpolar solvents are recommended for styrene.[19] DMSO is an important aprotic polar solvent which can dissolve both polar and nonpolar compounds. Due to the structure of the catalyst and rate enhancement in polar media, the rate of polymerization has an influence in ATRP.[20] The bifunctional initiator can dissolve in rare solvents, such as DMSO and methanol, because of that reason, in this study, DMSO was used to dissolve the bifunctional phenyl phosphine oxide-based initiator. Even DMSO could dissolve both polar and nonpolar compounds, also the catalyst at ambient temperature and the monomer, during the activation and deactivation process the increase in the polarity can change the influence of the polymerization intermediates.[20] The initiator synthesized have solubility problem that it also could effect on the selectivity of the monomer. Also, it was observed that when the rate constant for radical propagation and atom transfer constant increases related with the temperature increase, the rate of polymerization increases. Termination by radical combination and disproportionation is remarkably less than the energy of activation for radical propagation. Ultimately, at higher temperatures the control of the polymerization will be better, and k_p/k_t ratio will be higher.[19] Due to this assumption, the temperature that we choose was 57°C for polymerization and this temperature level affected on the control of the polymerization resulted with high $M_{n,\exp}$ values.

The uncontrolled behavior could be explained due to the steric hindrance of BBEPPO, it could be difficult to react with the monomers in the first step of the reaction, so the PDI values will be high. This can cause chain termination that, it could get difficult to add a new monomer to the chain growed with a phenyl containing BBEPPO group at the end, so the chains preferred termination by combining two growing chains resulting in high M_n and PDI (probably for MMA). Also, the termination process can be slow for styrene when bromine-mediated ATRP is used rather than chlorine-mediated ATRP. This could explain the low molecular weight and low PDI value of styrene-based polymers. Usually, the radical propagation rate for MMA is higher than styrene, so that the propagation step should be controlled. Steric hindrance, propagation, and termination of the polymerization are also other reasons for the uncontrolled behavior which resulted with high $M_{n,\exp}$ values than M_{nth}.

Also, the termination reaction of PMMA is disproportionation and it is faster than the termination reaction of PSt, so the molecular weight values are high with PMMA. This uncontrolled behavior can be explained by the researches related with slow initiation, termination, slow exchange, transfer and the effects on kinetics, molecular weight, MWDs of "living" chain growth polymerization.[21]

The structure of the monomer and initiator is important in ATRP mechanism. The structure of alkyl group (initiator) should be similar to the structure of the dormant polymer species (monomers). The bifunctional initiator structure and monomer structure are similar with styrene because of the phenyl groups, but it is different for MMA. Depending on this theory, the PDI values of PSt are better than PMMA values related with the groups in styrene, MMA, and BBEPPO.[19,22]

It was assumed that the choice and efficiency of catalyst and ligand could affect on the control of the polymerization and this can cause $M_{n,\exp}$ of the product to be much higher than M_{nth} and the MWD to be relatively narrow. The main role of copper (I) complex is the generation of radicals. Catalyst should be highly soluble in polymerization medium, on the other hand with the heterogeneous copper-mediated ATRP, high polydispersities are observed.[19] ATRP system is depended on the equilibrium of the metal catalyst and ligand. More electron-donating ligands generally better stabilize the higher oxidation state of the metal and accelerate the polymerization The equilibrium constant rate should be between 10^{-6} and 10^{-10} to have good polymerization of acrylates, acrylonitrile, and styrene. The dynamics of the exchange between dormant and active species also plays an important role like equilibrium constant values. The control of the polymerization such as molecular weight and polydispersity could be poor if the deactivation step of the polymerization is low ($k_d = 10^{7\pm1}$/M/s).[20,22]

Because of the competitive coordination of the oxygen atoms at DMSO, the rate of polymerization should be related with the change of Cu(I) catalyst. Additionally because of its affinity with Cu(II), DMSO can influence the polymerization as mentioned in literature. The complexation and non complexation of ligand and catalyst are totally related with DMSO.[20] For this reason, the equilibrium of the catalyst and ligand which is used in the polymerization of St and MMA could be less appropriate to control the reaction.

Finally with the addition of the monomers, the bromine end function is away from the origin of the polymer chain, and chain ends can move easily. In this case, the PDI values
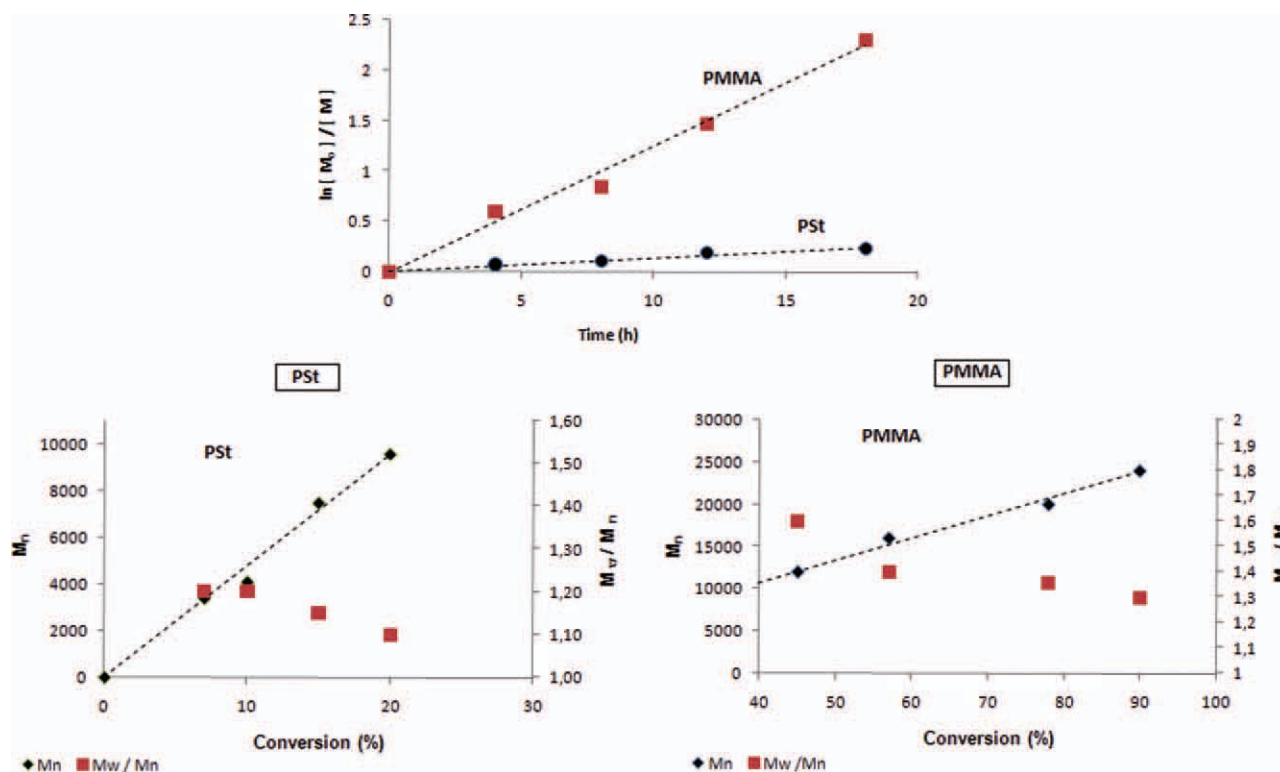
Figure 5. First-order kinetic plots for the polymerization of MMA and St using CuBr catalyst in DMSO at 57°C. ■: $[M]/[I]/[Cu]/[PMDETA] = 100/1/1/2$, $[M_{MMA}]_0 = 6$ M, ●: $[M]/[I]/[Cu]/[PMDETA] = 100/1/1/2$, $[M_{St}]_0 = 6$ M. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased by the addition of monomers and the bromine end functional groups have option to react easily with the monomers.

Due to the explanations mentioned below as a summary, the catalyst/ligand effect, solvent type, solvent efficiency, steric hindrance of the bifunctional initiator, the chemical similarity of
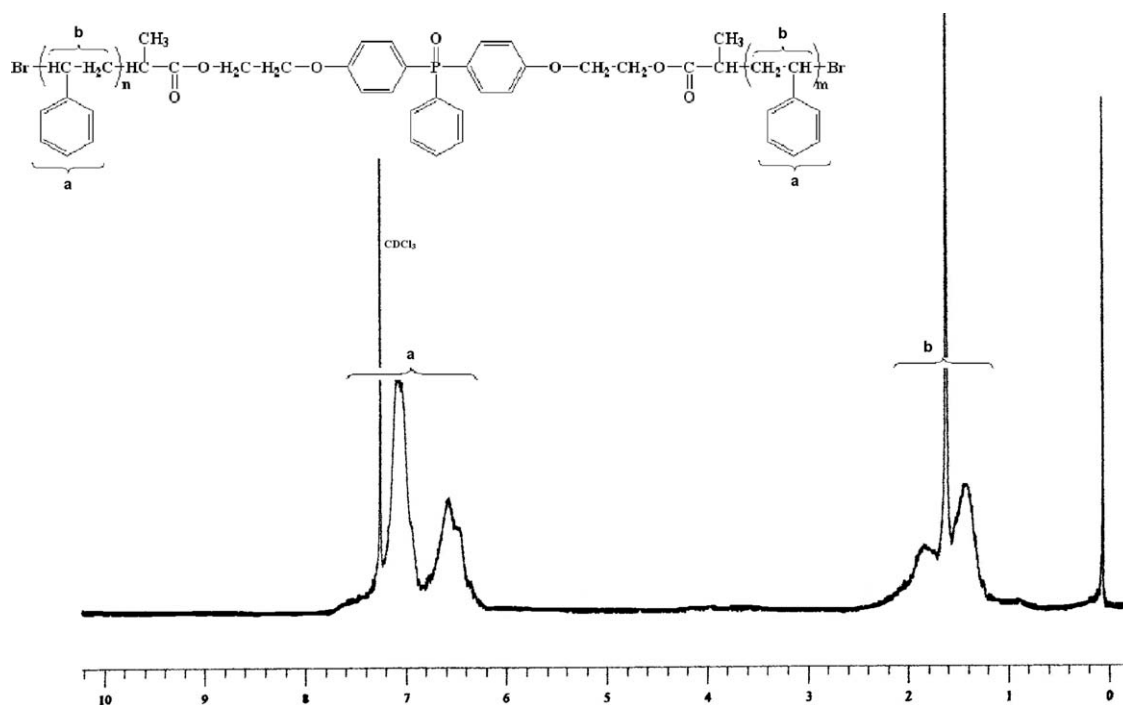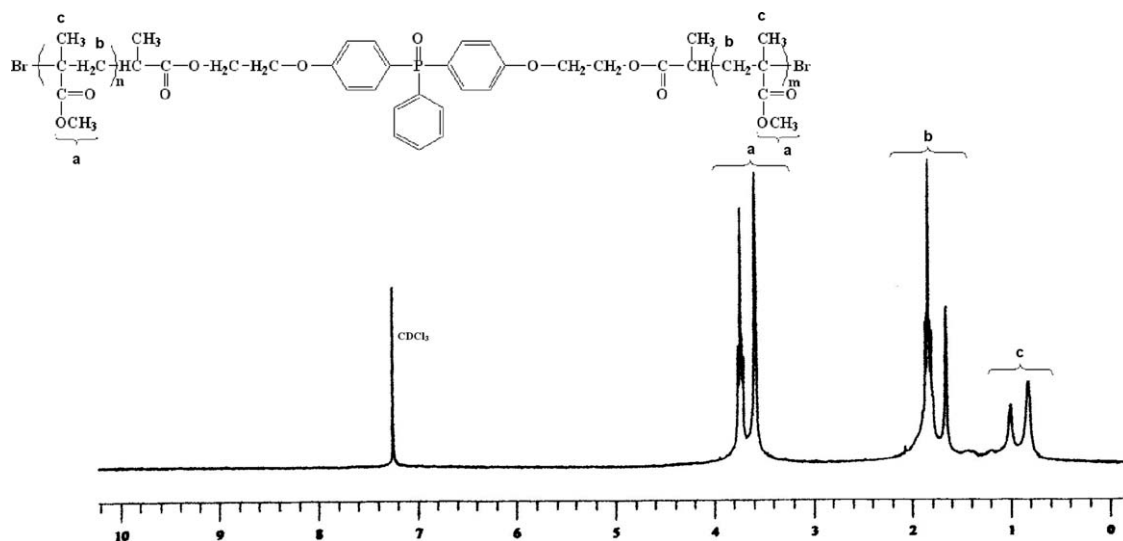

Figure 6. ^{1}HNMR of PSt.

Figure 7. ^{1}HNMR of PMMA.

the initiator and the monomer, the initiation, propagation, termination, and chain transfer affected on the control of the polymerization. The theoretical M_n values and the experimental M_n values are different because of this uncontrolled behavior of the polymerization.

For a typical polymerization of St and MMA with BBEPPO, the GPC traces at various time intervals, showing the increment of molar masses with narrow distribution. Figure 5 shows, semilogarithmic kinetic plot of ln ($[M]_0/[M]_t$) versus time, t, where $[M]_0$ is initial concentration of the monomer, and $[M]_t$ is the monomer concentration at any time and also plots of M_n and PDIs (M_w/M_n) as a function for the St indicate that the concentration of growing radicals is constant.

To characterize the polymers formed in greater detail, the polymer was confirmed by ^{1}HNMR. The prepared PSt initiated by BBEPPO was characterized by ^{1}HNMR as shown in Figure 6. There are signals at 6.5–7.3 ppm attributed to aromatic phenyl protons and at 1.4–1.8 ppm attributed to CH_2 and CH protons.

^{1}HNMR, in addition to the large absorption of the repeat units of PMMA, the characteristic signals were clearly visible (Figure 7). The ^{1}HNMR was taken in $CDCl_3$. CH_3 protons can be seen at $\delta = 0.8$–1.4 ppm, OCH_3 $\delta = 3.5$–3.9 ppm, and CH_2 $\delta = 1.8$–2.1 ppm.

Thermal Analysis

The thermal properties of the PSt and PMMA were evaluated by DSC and TGA. DSC measurements were conducted with a heating rate of 10°C/min. In all cases, the T_g's could be easily measured in the second heating traces of DSC. The thermal stability measurements were evaluated by TGA under nitrogen at a heating rate of 20°C/min. The thermal behavior data for all polymers are listed in Table III. The T_g values of the PSts were in the range of 85–95°C, depending on the molecular weight increase. The T_g diagrams of PSt can be seen in Figure 8. While being heated under nitrogen, PSts showed a one-stage weight loss behavior. From TGA analysis, all three PSts appear to possess enough thermal stability approximately at 290°C. Figure 9
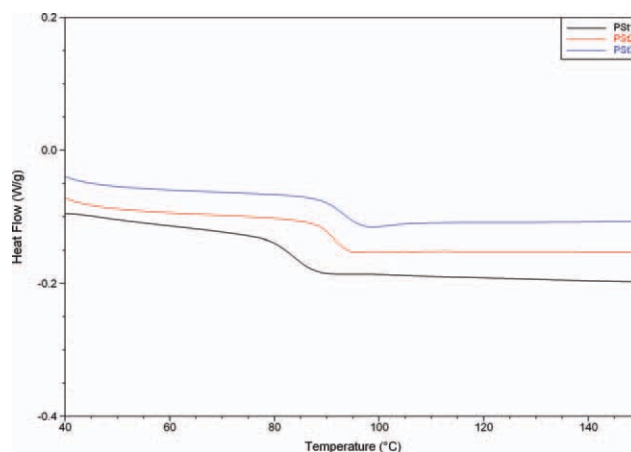
Table III. Thermal Properties of PSt and PMMA

	^aT_g (°C)	Weight Loss (%)
PSt1	85	93
PSt2	89	93
PSt3	95	94
^{c}STD PSt	100	97
PMMA1	112	95
PMMA2	120	96
PMMA3	122	96
^{d}STD PMMA	120	100

^{a}From the second heating traces of DSC measurements conducted with a heating rate of 10°C/min under nitrogen, ^{b}Weight loss was recorded by TGA at heating rate of 20°C/min under nitrogen atmosphere at 500°C, ^{c}Polystyrene standard, $M_n = 19,000$ g/mol, ^{d}Polymethyl methacrylate standard, $M_n = 30,530$ g/mol.

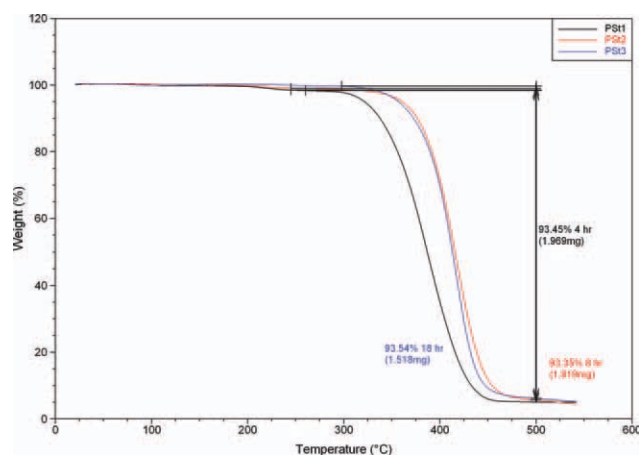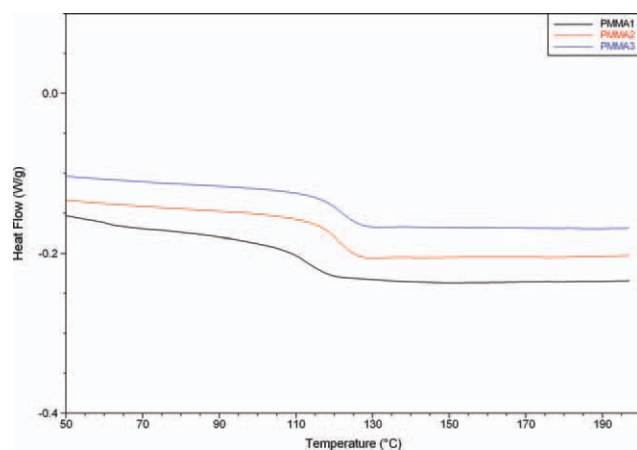**Figure 8.** DSC thermogram of PSt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. TGA of PSt under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

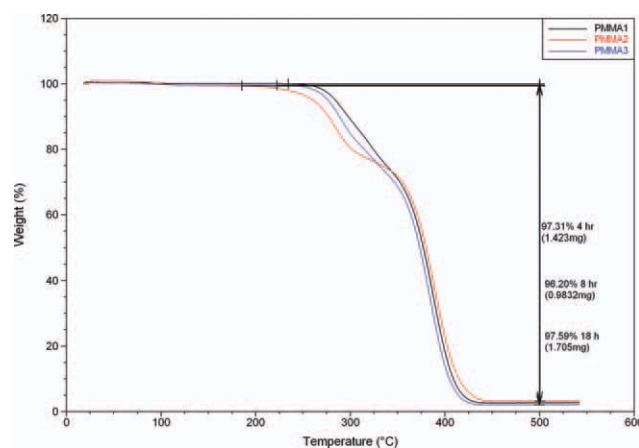**Figure 11.** TGA of PMMA under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows the thermal stability and the weight changes of the PSts. Glass transition temperatures within the 112–122°C range were recorded, the values increase by the increase of the molecular weight of PMMA. The T_g diagrams of PMMA can be seen in Figure 10. As observed from TGA, weight loss begins at around 190°C and then gives another weight loss at about 320°C, to result in a two-stage weight loss as shown in Figure 11.

The phosphine oxide group has often been incorporated into polymers to enhance the thermal and thermal/oxidative stability and ignition resistance of polymer matrices.[23] Thermal effect of phosphine oxide group on the polymers was examined. To make a comparison, the T_g and TGA of standard PSt which has a number average molecular weight (M_n) of 19,000 g/mol, and PMMA which has a number average molecular weight of 30,530 g/mol were measured. The T_g of the standard PSt is 100°C and the weight loss is 97%. The T_g of the standard PMMA is 120°C and the weight loss is 100%. So the results show us that phosphorus-containing PSts have lower T_g and the char yield is higher than the standard PSt. That is because of the narrow polydispersity of PSts due to the one phosphine oxide group

within each chain of the polymer. The low molecular weight, the free volume of phosphine oxide groups, bromine end functionalized groups, and also the etheric groups which give flexibility to chains probably effected to decrease the T_g value of PSt.

However, the phosphorus containing PMMAs have nearly the same T_g and the char yield value with standard PMMA. That would be because of the polydispersity of PMMA which are between 1.60–1.3. The selectivity of the initiator for MMA monomer, the molecular weights are high and the effect of phosphine structure and etheric groups will be low. For PMMA, the chains preferred termination by combining two growing chains resulting in high M_n and this cause high molecular weight. Even all the chains have the bromine end function and etheric groups, because of the long chains, the bromine and etheric units could not affect to the flexibility of PMMA and the T_g does not changed much.

CONCLUSIONS

A new bifunctional bromine functionalized TPO-containing initiator has been successfully prepared. The PSt and PMMA were synthesized by using the new initiator in combination with PMDETA and CuBr as the catalyst system and DMSO as a solvent. The structures of the bifunctional initiator and polymers were thoroughly characterized and confirmed using FTIR and ^{1}HNMR spectroscopy. Even though the uncontrolled polymerization system, the PDI values are lower than expected. The PSt designated more decisive behavior than PMMA, related with the selectivity of monomer and initiator structure.

The T_g values of both PSt and PMMA increase accompanying the molecular weight increase. The presence of BHEPPO and etheric group in the polymer chain affected on the T_g results of the polymers. However, the phosphine oxide group does not affect much on PMMA that could be because of the molecular weight and reaction steps of PMMA (propagation, termination). The T_g and the char yield are nearly the same with standard PMMA.

Figure 10. DSC thermogram of PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

1. Liou, G. S.; Hsiao, S. H. *J. Polym. Sci. Part A: Polym. Chem.* **2002,** *40,* 459.

2. Alcon, M. J.; Ribera, G.; Galia, M.; Cadiz, V. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43,* 3510.

3. Inan, T. Y.; Ozarslan, O.; Kuyulu, A.; Ekinci, E.; Gungor, A. *J. Appl. Polym. Sci.* **1999,** *73,* 2575.

4. Delaviz, Y.; Gungor, A.; McGrath, J. E.; Gibson, H. W. *Polymer* **1992,** *33,* 24.

5. Dang, T.; Dalton, M. J.; Venkatasubramanian, N.; Johnson, J. A.; Cerbus, C. A.; Feld, W. A. *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42,* 6134.

6. Kaiti, S.; Fossum, E. *J. Polym. Sci. Part A Polym. Chem.* **2006,** *44,* 2099.

7. Jin, J.; Topping, C. M.; Suresh, S.; Foulger, S. H.; Rice, N.; Mojazza, B. H.; Smith, D. W. *Polymer* **2005,** *46,* 6923.

8. Coessens, V.; Matyjaszewski, K. J. M. S. *Pure Appl. Chem.* **1999,** *A36,* 667.

9. Zhao, Y.; Wang, L.; Xiao, A.; Yu, H. *Prog. Polym. Sci.* **2010,** *35,* 1195.

10. He, G.; Zhang, G.; Hu, J.; Sun, J.; Hu, S.; Li, Y.; Liu, F.; Xiao, D.; Zou, H.; Liu, G. *J. Fluorine Chem.* **2011,** *132,* 562.

11. Palaskar, D. V.; Sane, P. S.; Wadgaonkar, P. P. *React. Funct. Polym.* **2010,** *70,* 931.

12. Park, J. T.; Seo, J. A.; Ahn, S. H.; Kim, J. H.; Kang, S. W. J. *Ind. Eng. Chem.* **2010,** *16,* 517.

13. Paik, H. J.; Teodorescu, M.; Xia, J.; Matyjaszewski, K. *Macromolecules* **1999,** *32,* 7023.

14. Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, A.; Whigtman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991,** *3,* 211.

15. Riley, D. J.; Gungor, A.; Srinivasan, S. A.; Sankarapandian, M.; Tchatchoua, C.; Muggli, M. W.; Ward, T. C.; McGrath, J. E. *Polym. Eng. Sci.* **1997,** *37,* 1501.

16. Liaw, D. J.; Chen, P. S. *J. Polym. Sci. Part A: Polym. Chem.* **1996,** *34,* 885.

17. Çakır, T.; Serhatli, I. E.; Önen, A. *J. Appl. Polym. Sci.* **2006,** *99,* 1993.

18. Monge, S.; Haddleton, D. M. *Eur. Polym. J.* **2004,** *40,* 37.

19. Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998,** *10,* 901.

20. Monge, S.; Darcos, V.; Haddleton, D. M. *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42,* 6299.

21. Matyjaszewski, K. *J. Phys. Org. Chem.* **1995,** *8,* 197.

22. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001,** *101,* 2921.

23. Babb, D. A.; Bone, H. W.; Smith, J. R.; D. W.; Rudolf, P. W. *J. Appl. Polym. Sci.* **1998,** *69,* 2005.