Preparation of SBS/Poly(styrene–methyl methacrylate) Thermoplastic Interpenetrating Polymer Network

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ABSTRACT: SBS as polymer I, poly(styrene–methyl methacrylate) polymerized by atom transfer radical polymerization as polymer II, and a thermoplastic interpenetrating polymer network of SBS/poly(styrene–methyl methacrylate) were prepared by the sequential method. The effects of the polymerization temperature, the composition of the catalyst, the ratio of the monomers studied, and the kinetics at 90°C were also investigated. It was shown that when polymerization was initiated by a BPO/CuCl/bpy (BPO: CuCl:bpy = 1:1:3) system at 90°C, the mass averaged molecular weight of the poly(styrene–methyl methacrylate) in-creased with monomer conversion, and the polydispersities were kept very low. Fourier transform infrared spectroscopy and gel permeation chromatogram showed that poly(styrene–methyl methacrylate) with low polydispersities had been synthesized. Thus, a thermoplastic interpenetrating polymer network comprised of both narrow molecular-weight-distribution components was successfully prepared. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2007–2011, 2003

Key words: atom transfer radical polymerization (ATRP); interpenetrating polymer network (IPN); monomers

INTRODUCTION

As a new type of polymer with excellent properties, a thermoplastic interpenetrating polymer network (TIPN) is widely used in the automobile, electric, electron, medical materials, coatings, and adhesive fields, especially in damping materials because of its unique mechanism. In recent years TIPN has attracted much attention in polymer chemistry circles.

TIPN has been prepared mostly by traditional radical polymerization, in which neither polymer structures nor molecular weight and its distribution can be effectively controlled. So it was hard to design and prepare tailor-made TIPN. This article reports on the preparation of the TIPN of SBS/poly(styrene–methyl methacrylate) using the sequential method, with SBS as polymer I, poly(styrene–methyl methacrylate) polymerized by atom transfer radical polymerization (ATRP) as polymer II. ATRP is a new type of living radical polymerization.[1] Compared with other living polymerization systems, it works well with a broader class of monomers under less critical conditions, which offers a more general and efficient way to make various tailor-made polymers. Therefore, the chemical composition, polymer structure, morphology, molecular weight, and molecular weight distribution of the TIPN component (i.e., polymer II) can be well controlled, which has never been reported.

In addition to a typical ATRP initiating system (using a simple alkyl halide, RX, as an initiator and a transition-metal species complexed by a suitable ligand, Mt^n/L, as catalyst),[1,2] a "living"/controlled process can also be achieved using a conventional radical initiator (e.g., AIBN) and a transition-metal compound at a higher oxidation state (e.g., $Cu^{II}Cl$) complexed with suitable ligands (e.g., 2,2'-bipyridine,bpy) as a catalyst.[3] The latter is called reverse ATRP.

In this work we found that "living"/controlled radical polymerization of styrene (St) and methyl methacrylate (MMA) is also accessible using BPO/Cu^ICl/bpy as the initiator. So, SBS as polymer I, poly(St-MMA) polymerized by ATRP as polymer II, and thermoplastic IPN with both narrow molecular-weight-distribution components were successfully prepared by the sequential method.

EXPERIMENTAL

Reagents

The monomers, styrene and MMA (analytical reagent), were dried by $CaCl_2$ to remove water and vacuum-distilled just before polymerization.

The initiator, BPO (chemically pure), was recrystallized in methanol. The catalysts, CuCl and $CuCl_2$ (analytical reagents), were used as received without further purification. The ligand, 2,2'-bipyridine (analytical reagent), was used as received without further purification.

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TABLE I
Effect of Temperature on Copolymerization of St and MMA

Polymerization temperature (°C)	Polymerization time (h)	Conversion[a] (%)	M_n II[b]	M_w II/M_n II
70	2	4.66	10900	1.478
	4	7.12	11300	1.634
	6	10.21	15000	1.708
	8	12.34	17900	1.648
90	2	4.32	16500	1.397
	4	7.88	18900	1.386
	6	13.68	21100	1.346
	8	15.42	24100	1.412

[a] BPO:CuCl:bpy = 1:1:3 (mol); BPO:St:MMA = 1:500:50 (mol).
[b] Subscript II: polymer II.

SBS, YH-1401 (M_wI/M_nI < 1.2), was vacuum-dried before use.

Polymerization

The general procedure for polymerization was as follows. To a previously dried three-necked flask with stirring, a certain amount of SBS, styrene, and MMA were introduced and degassed by nitrogen. Once the SBS was dissolved, the desired amount of catalysts was added while stirring and then degassed for a certain time. Finally, the flask was immersed in an oil bath and heated at the predetermined temperature. The polymerization was carried out under a little positive pressure maintained by nitrogen and kept being stirred. After a certain time the polymerization was stopped, and a little amount of sample was taken out from the flask and vacuum-dried until the weight did not change.

Measurements and characterizations

The conversion of monomers was determined gravimetrically after elimination of the residual monomers and subtraction of the weight of SBS.

The molecular weight and molecular weight distribution were obtained using a Waters 150 GPC/ALC in tetrahydrofuran (THF) at 25°C. Calibration was performed with polystyrene standards.

A Fourier transform infrared (FTIR) spectrum was performed using a Nicolet 20 NB FTIR.

RESULTS AND DISCUSSION

Choice of polymerization temperature

It is known that cuprous salts act as very efficient accelerators in the decomposition of peroxides, and the advantages of a reaction at low temperature are evident. But too low a temperature will slow down the polymerization rate and lengthen the polymerization time. It has been reported that using the same initiating system, polymerization of styrene and MMA at 40°C resulted in a much longer reaction time (60 h) and polymers of low molecular weight with a broad molecular weight distribution.[4,5] Confined to the boiling point temperature of monomers (MMA, 100°C; styrene, 145.2°C), in this work the copolymerization of styrene and MMA was carried out at 70°C and 90°C and a lower than usual temperature of ATRP (80°C–130°C).[1–3]

As shown in Table I, the molecular weight of polymer II [poly(St-MMA)] increased with the conversion of monomers and the molecular weight distribution was narrow, showing the characteristics of living polymerization. Comparatively, polymerization at 90°C is more desirable, as evidenced by a higher molecular weight and narrower molecular weight distribution. This suggests that at a higher temperature, deactivation of the growing radicals is faster than at a lower temperature, which makes growing radicals tend to propagate simultaneously. So all the polymerizations hereinafter were carried out at 90°C. But it must be pointed out that the low conversion was a result of the excess of monomers, most of which acted as a solvent of SBS.

Effect of cuprous salt oxidation state

ATRP has two major drawbacks: first, the use of a halide species, RX, which often is toxic or not easily handled or obtained; and, second, the oxidation of catalyst by oxygen included in the air. On these premises, Matyjaszewski first reported reverse ATRP using conventional radical initiator AIBN and a transition metal in higher oxidation.[3] But later Matyjaszewski also found that reverse ATRP initiated by peroxides (BPO) differed greatly from azo initiators (AIBN).[6,7] Based on the above facts, the effects of different oxidation states of a transition metal on the ATRP initiated by BPO were investigated in the work, as shown in Table II.

Similar to the experimental results of a previous work,[6] with an increased amount of CuCl₂, the poly-

TABLE II
Effect of Cuprous Salt Oxidation State

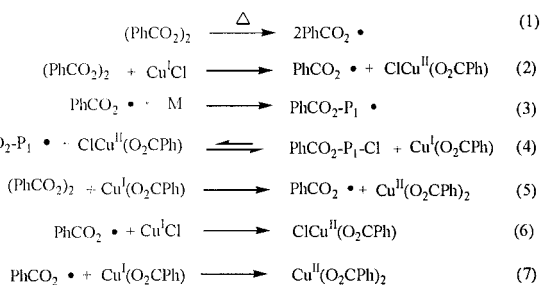| CuCl$_2$/CuCl[a]	Conversion (%)	M_n II	M_w II/M_n II
0.00/1.00	15.42	24100	1.412
0.25/0.75	14.78	23300	1.442
0.50/0.50	13.27	21300	1.461
0.75/0.25	12.06	18400	1.622
1.00/0.00	10.14	13500	1.901

[a] BPO:CuCl:bpy = 1:1:3 (mol); BPO:St:MMA = 1:500:50 (mol).
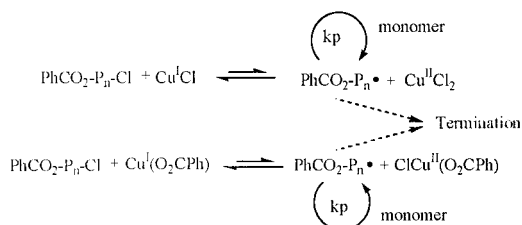[b] Subscript II: polymer II.

merization processes became more and more badly controlled, yielding polymers with lower molecular weights and higher polydispersities. Schemes 1 and 2 (the bpy ligand was omitted for simplification) show the different mechanisms of reverse ATRP initiated by BPO/CuCl and by BPO/CuCl$_2$ advanced by Matyjaszewski.[6]

As shown in Scheme 1, the benzoyloxy primary radicals are generated from the BPO initiator, either by thermal decomposition (step 1) or by induced decomposition through the electron-transfer process (steps 2 and 5), and the significantly faster electron-transfer process makes the induced decomposition the dominant pathway to generating the benzoyloxy primary radicals. In addition to the formation of oligomers with benzoate tail groups (some phenyl tail groups from decarboxylation can also be formed) and chloride head groups, the initiation process generates Cu^I(O$_2$CPh), which can participate in the induced decomposition of the BPO initiator and results in the formation of Cu^{II}(O$_2$CPh)$_2$. Because Cu^{II}(O$_2$CPh)$_2$ does not reversibly deactivate the growing radicals as
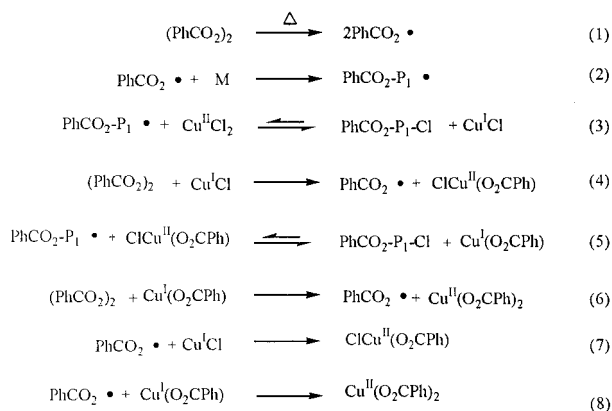
Initiation:

$$(PhCO_2)_2 \xrightarrow{\Delta} 2PhCO_2 \bullet \tag{1}$$

$$(PhCO_2)_2 + Cu^ICl \longrightarrow PhCO_2 \bullet + ClCu^{II}(O_2CPh) \tag{2}$$

$$PhCO_2 \bullet + M \longrightarrow PhCO_2\text{-}P_1 \bullet \tag{3}$$

$$PhCO_2\text{-}P_1 \bullet + ClCu^{II}(O_2CPh) \rightleftharpoons PhCO_2\text{-}P_1\text{-}Cl + Cu^I(O_2CPh) \tag{4}$$

$$(PhCO_2)_2 + Cu^I(O_2CPh) \longrightarrow PhCO_2 \bullet + Cu^{II}(O_2CPh)_2 \tag{5}$$

$$PhCO_2 \bullet + Cu^ICl \longrightarrow ClCu^{II}(O_2CPh) \tag{6}$$

$$PhCO_2 \bullet + Cu^I(O_2CPh) \longrightarrow Cu^{II}(O_2CPh)_2 \tag{7}$$

Propagation:

$$PhCO_2\text{-}P_n\text{-}Cl + Cu^ICl \rightleftharpoons PhCO_2\text{-}P_n\bullet + Cu^{II}Cl_2 \xrightarrow{monomer, kp} \cdots \longrightarrow Termination$$

$$PhCO_2\text{-}P_n\text{-}Cl + Cu^I(O_2CPh) \rightleftharpoons PhCO_2\text{-}P_n\bullet + ClCu^{II}(O_2CPh) \xrightarrow{monomer, kp}$$

Scheme 1 Mechanism of reverse ATRP initiated by BPO/CuCl.

$$(PhCO_2)_2 \xrightarrow{\Delta} 2PhCO_2 \bullet \tag{1}$$

$$PhCO_2 \bullet + M \longrightarrow PhCO_2\text{-}P_1 \bullet \tag{2}$$

$$PhCO_2\text{-}P_1 \bullet + Cu^{II}Cl_2 \rightleftharpoons PhCO_2\text{-}P_1\text{-}Cl + Cu^ICl \tag{3}$$

$$(PhCO_2)_2 + Cu^ICl \longrightarrow PhCO_2 \bullet + ClCu^{II}(O_2CPh) \tag{4}$$

$$PhCO_2\text{-}P_1 \bullet + ClCu^{II}(O_2CPh) \rightleftharpoons PhCO_2\text{-}P_1\text{-}Cl + Cu^I(O_2CPh) \tag{5}$$

$$(PhCO_2)_2 + Cu^I(O_2CPh) \longrightarrow PhCO_2 \bullet + Cu^{II}(O_2CPh)_2 \tag{6}$$

$$PhCO_2 \bullet + Cu^ICl \longrightarrow ClCu^{II}(O_2CPh) \tag{7}$$

$$PhCO_2 \bullet + Cu^I(O_2CPh) \longrightarrow Cu^{II}(O_2CPh)_2 \tag{8}$$

Scheme 2 Mechanism of initiation using BPO/CuCl$_2$.

ClCu^{II}(O$_2$CPh) and Cu^{II}Cl$_2$, initiator efficiency is reduced. The benzoyloxy radicals may also oxidize CuCl and Cu^I(O$_2$CPh) to the corresponding Cu(II) species (steps 6 and 7), resulting in the decrease of initiator efficiency and the consumption of active catalyst. Propagation proceeds similarly to conventional ATRP, with the produced Cu^I(O$_2$CPh) and the remaining CuCl acting as the catalyst to generate radicals and reversibly form CuCl$_2$ and ClCu^{II}(O$_2$CPh) as deactivators.

In contrast, CuCl$_2$ does not accelerate the decomposition of BPO (Scheme 2). However, it deactivates the growing radicals and generates CuCl *in situ*, which then induces the decomposition of BPO (steps 3 and 4). After deactivation of the growing radicals by ClCu^{II}(O$_2$CPh), the newly formed Cu^I(O$_2$CPh) also participates in the induced decomposition of BPO. As a result, the intermediate Cu(I) species, both CuCl and Cu^I(O$_2$CPh), is reoxidized to Cu(II) species by BPO. In other words, for the BPO/CuCl$_2$ system, there are almost no or only little Cu(I) species for activation, and the polymerization is ill-controlled.

Effect of initiating system composition

Using the BPO/CuCl/bpy initiating system, the effects of different ratios of BPO/CuCl/bpy were also studied. The results, shown in Table III, indicate that polymerization with BPO:CuCl:bpy = 1:2:4 is less desirable than BPO:CuCl:bpy = 1:1:3 because the polymerization of the former reaches a little higher conversion, yielding polymer II with higher molecular

TABLE III
ATRP of St and MMA Initiated with Different BPO:CuCl:bpy

BPO:CuCl:bpy[a]	Conversion (%)	M_n II	M_w II/M_n II
1:2:4	15.86	25300	1.268
1:1:3	15.42	24100	1.412

[a] Molar ratio.

TABLE IV
Effect of MMA Content on ATRP

MMA content[a]	Conversion (%)	M_n II	M_w II/M_n II
0.00	11.82	16500	1.397
0.05	13.21	21900	1.452
0.10	15.42	24100	1.412
0.15	16.87	28400	1.360

[a] Molar ratio to styrene.

Figure 1 FTIR spectrum of SBS/poly(St-MMA).

weight and narrower molecular weight distribution. This can be explained as follows: in a heterogeneous system, increasing catalyst and amount of ligand means increasing the actual concentration of catalyst in the system and decreasing the proportion of the Cu(I) species transferred to $Cu^{II}(O_2CPh)_2$ because of the oxidation of BPO.

In addition to the unsubstantial differences shown in Table III, given the prices of catalyst and ligand and how inconvenient it is to remove them in an aftertreatment process, it can be seen that polymerization with an initiating system of BPO:CuCl:bpy = 1:1:3 is preferable.

Effect of comonomer content

ATRP works well with a broader class of monomers and offers a more general and efficient way to make various tailor-made polymers. Therefore, it is the best way to change the composition of comonomers to prepare copolymer as a component in TIPN, thus changing the architecture, morphology, and properties of TIPN. In this study, a small amount of polar monomer, MMA, was introduced into the polymerization system, which contributed a lot, not only to the polymerization rate and living character of the polymerization, but also to the TIPN properties.

Table IV shows that the more MMA in the initial mixed-monomer feed, the higher the monomer conversion and poly(St-MMA) molecular weight. This might result from the difference in polymerizability between styrene and MMA.[8] In homopolymerization with the same initiating system and experimental conditions, MMA was able to be polymerized much faster than styrene. The energy difference of C—Cl bonds between that formed by styrene and Cl and that formed by MMA and Cl may be responsible for the difference in polymerizability mentioned above. In another way, electrophilic PMMA radicals are scavenged less efficiently by electrophilic $CuCl_2$ than by nucleophilic PSt radicals because of the different polar properties of the transition states.[3]

Figure 1 shows the FTIR spectrum of the TIPN. The characteristic absorption peaks of the polystyrene chain (3059, 3025, 758, and 699 cm^{-1}), the polybutadiene chain (910 and 966 cm^{-1}), and carboxyl (1728
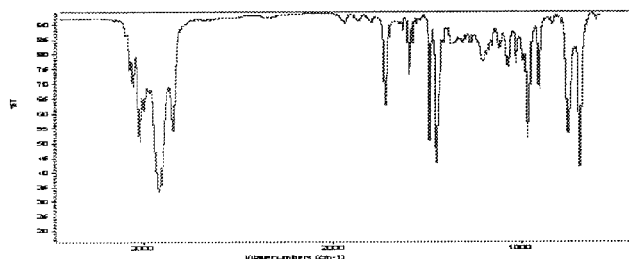
cm^{-1}) suggest that both styrene and MMA took part in the polymerization.

A gel permeation chromatogram (GPC) of the TIPN is shown in Figure 2. The bimodal chromatogram [one for poly(St-MMA), the other for SBS] indicates that both styrene and MMA were polymerized into the copolymer rather than into each homopolymer, respectively. Therefore, in this work, by the sequential method, TIPN comprised of both narrow moleculardistribution-components was successfully prepared. More results on copolymer composition, sequential structure, and monomer reactivity ratio will be involved in further reports.

Effect of polymerization time

Table V presents the results of the kinetic studies of bulk polymerization at 90°C [BPO:CuCl:bpy = 1:1:3 (mol), St:MMA = 10:1 (mol)]. It can be seen that the conversion of monomers increased with polymerization time within 8 h but changes little after 8 h, as does the molecular weight of polymer II, poly(St-MMA). The polydispersities of polymer II increased a little remained low (<1.5) during the entire polymerization. The results indicate that the molecular weight of polymer II cannot increase with polymerization time infi-
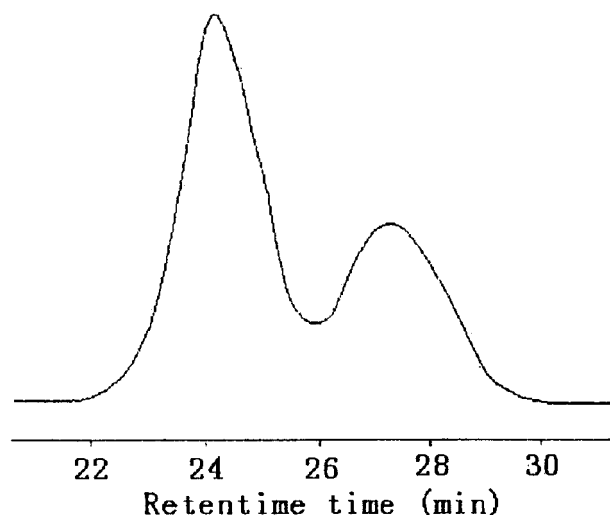

Figure 2 GPC curve of SBS/poly(St-MMA).

TABLE V
Dependence of Molecular Weight and Polydispersities on Polymerization Time

Polymerization time (h)	Conversion (%)	M_n IIth[a]	M_n II	M_w II/M_n II	f[b]
2	4.32	4924	16500	1.397	0.298
4	7.88	8983	18900	1.386	0.475
6	13.68	15595	21100	1.346	0.728
8	15.42	17579	24100	1.412	0.729
10	15.43	17595	24100	1.413	0.730
12	15.58	17761	24100	1.476	0.736

[a] Theoretical molecular weight of polymer II, M_n IIth = mass of monomers mixture/(mole of BPO/2)*Con%
[b] Efficiency of initiator, f = M_n IIth/M_n II.

nitely. This can partially be ascribed to the presence of trace impurities in the system, which will inevitably cause the abnormal termination and chain transfer of the growing chain radicals because of their relatively higher reactivity to monomers. It can also be ascribed to the side reaction of the exchange of Cl^- on the polymer chain ends with $(O_2CPh)^-$ of the copper complex, that is, $Cu^I(O_2CPh)$, $Cu^{II}(O_2CPh)_2$, and $ClCu^{II}(OCPh)$.[6]

It can also be seen that the initiator efficiency was low, only about 0.73, even at the end of polymerization. This may be result from the following: (1) as shown in Scheme 1, initiation steps generated $Cu^I(O_2CPh)$, $ClCu^{II}(O_2CPh)$, and $Cu^{II}(O_2CPh)_2$ that reduced initiator efficiency directly; (2) in addition to monomers, the benzoyloxy primary radicals could also be captured by CuCl and $Cu^I(O_2CPh)$, shown as steps 6 and 7 in scheme 1,, resulting in a decrease in initiator efficiency; and (3) it is know that the aromatic substitution reaction of the benzoyloxy radical is strongly reversible, but the intermediate radical can be trapped by an oxidizing reagent such as $CuCl_2$. This possible pathway as a side reaction to the initiation process is shown in Scheme 3.[6] In our studies a ligand such as bpy was used to complex copper species, and this should decrease the Cu(II) species redox potential. Nevertheless, the pathway shown in Scheme 3 may be additionally responsible for the low efficiency of BPO.

It is difficult to quantify the actual amount of BPO initiating the polymerization. In other words, because of the complexity of the system, there is no way to accurately measure how much benzoyloxy primary radicals generated either by the thermal decomposition or the induced decomposition was built into the copolymer of poly(St-MMA). Based on the mechanism shown in Scheme 1, in the calculation of M_nII(th), it was assumed that at most half of the benzoyloxy primary radicals from BPO was combined into polymer II. Therefore, the theoretical molecular weight of polymer II, M_nII(th), was much lower than the result of the GPC measurement, as shown in Table V.
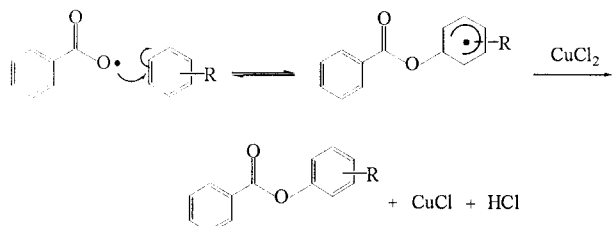
CONCLUSIONS

By sequential method, SBS as polymer I, poly(St-MMA) polymerized by ATRP as polymer II, and the TIPN of SBS/poly(St-MMA) were successfully prepared. The following conclusions were reached:

1. Consistent with the characteristics of "living"/controlled polymerization, the molecular weight of polymer II increased linearly with polymerization time, and the polydispersities remained low (< 1.5) during the entire polymerization.
2. The optimal polymerization condition was reached: polymerization at 90°C with BPO:CuCl:bpy = 1:1:3.
3. An FTIR spectrum and GPC chromatograph indicate that poly(St-MMA) was produced; therefore, the molecular weight distributions of both components of the TIPN were narrow.

Scheme 3 Aromatic substitution reaction of the benzoyloxy radical.

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