

Synthesis and Properties of Novel Macromolecular Coupling Agents Prepared by ATRP

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ABSTRACT: Novel block and graft macromolecular coupling agents with well-defined structures have been synthesized successfully by atom transfer radical polymerization (ATRP). The molecular weights and molecular weight distributions of those functional copolymers can be controlled because of the living/controlled ATRP. The structures and composition of block and graft copolymers with the monomers of butyl acrylate (BA), styrene (St), and 3-methacryloxypropyltrimethoxyl silicon (KH-570) have been characterized by mean of ¹H NMR, IR, GPC, and UV. Because the KH-570 of macromolecular coupling agents owns strong affinity to surface hydroxyl of fillers, inorganic fillers that were treated by the macromolecular coupling agents possess some new properties, for example increasing the effect between matrix and fillers of composites. The mechanical

properties and morphology of composites with macromolecular coupling agents have been investigated by the dynamic mechanical spectra and SEM. The results showed that the damping value and compatibility of composites with macromolecular coupling agents were improved greatly when compared with that of composite with small molecular coupling agent. Furthermore with different contents of BA, St, and KH-570 in the macromolecular coupling agents, the damping value of the composites are different. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3919–3926, 2006

Key words: atom transfer radical polymerization (ATRP); macromolecular coupling agent; interpenetrating polymer networks (IPNs); compatibility; damping

INTRODUCTION

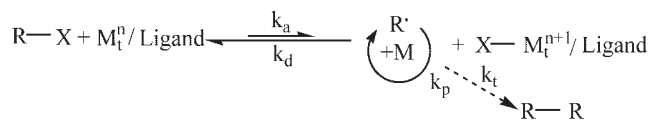
Atom transfer radical polymerization (ATRP) is a kind of "living"/controlled radical polymerization, which is based on a reversible activation–deactivation process of the terminal C-halogen bond of the growing chains by a transition metal complex. It has made significant progress since Matyjaszewski and Wang have first studied it in 1995.¹ Many scientists pay more attention to the mechanism, monomer, initiator, ligand, and catalyst of ATRP.²

Scheme 1 shows the mechanism of ATRP. The polymers with low polydispersities and predetermined molecular weights could be synthesized by ATRP. ATRP tolerated various functionalities in its monomeric parts without disturbing the polymerization. The terminal group of polymer that was prepared by ATRP is halogen atom and another end is also prescient, where both come from initiator.³ In other words, polymers synthesized by ATRP own well-defined structures. Therefore, ATRP may be an effective way to prepare architecturally functional polymers or

oligomers. Since the terminal bond of C—X is relatively stable, the halogenated polymers can be isolated, dried, and stored while keeping the halogen available at the chain end. Thus, the bond of C—X can be reactivated by a freshly added catalyst in the presence of monomer, which opens the way to synthesize block copolymers as previously reported by Sawamoto.⁴ Many scientists have studied the diblock, triblock, and comb copolymers with well-defined structures.^{5–7} Those well-defined structures of copolymers have elicited fascination not only for theoreticians modeling phase behavior but also in the physical realm for studying morphological transitions.^{8–14} Furthermore, the block and graft copolymers may be used as functional materials such as interpenetrating polymer networks (IPNs), damping materials, and the matrix of composites.

IPNs allow mutual enhancement of the properties of two (or more) combined polymers, and have been used in many fields.¹⁵ The composites with IPNs fillers have important roles in modifying the properties of various polymers. The properties of composites, such as thermal stability and rigidity, are affected by fillers, depending on their concentration, particle size, shape, and interaction with the matrix.¹⁶ Fillers can form a boundary layer with the matrix that is different from both the filler and the matrix. The properties of

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Scheme 1 The mechanism of ATRP (R—X: initiator; X: Cl, Br; M: monomer; M_t : catalyst).

composite are dependent on the boundary layer, and the strength of the layer depends on the interaction of the particles with the matrix. Coupling agents can bond with surface hydroxyl of inorganic fillers and at the same time it can affect with organic matrix, which include physical and chemical action. Because traditional coupling agent is small molecule, the effect between filler and matrix is feeble. Recently, polymeric surfactant^{17,18} has attracted much attention because of the intense action with matrix. Macromolecular coupling agents^{19,20} were so-called “macromolecular bridge” with particular structure. The fillers modified with macromolecular coupling agent possess structures of inorganic core and organic shell. The antenniform organic shell that is composed of macromolecules can strongly tangle with organic matrix of composite, which increased the thickness of boundary layer between fillers and matrix. Graft and block macromolecular coupling agents are outstanding in this field, because those copolymers own vivid structure and particular properties. Many scientists have studied the synthetically methods, structure, and properties of macromolecular coupling agent, but few reported the macromolecular coupling agent with well-defined structures, because living polymerizations based on anionic, cationic, or group transfer are very sensitive to moisture and impurities and thus very difficult to operate. But ATRP is preferred method that is known to impart a good control to the polymerization of styrene (St), acrylate (methacrylate) monomers, and so on at the same time using easily accessible experimental conditions. In this article, diblock, triblock, and graft macromolecular coupling agents with well-defined structures were prepared successfully by ATRP. The structures and composition of macromolecular coupling agents were characterized by means of ¹H NMR, GPC, UV, and IR. The results indicate that the macromolecular coupling agents possess well-defined structures. The mechanical properties and morphology of composites with macromolecular coupling agents were studied by dynamic mechanical spectra and scanning electron microscopy (SEM). The results show that the compatibilities and damping value of composites with block and graft macromolecular coupling agents are improved greatly when compared with that of composite with small molecular coupling agent.

EXPERIMENTAL

Materials

Styrene (St), *n*-butyl acrylate (BA), and *n*-butyl methacrylate (BMA) supplied by Shenyang Chemical (A.R.) were extracted with 5% solution of sodium hydroxide, stirred over calcium hydroxide for 24 h, and distilled under vacuum and stored at -15°C before use. Toluene purchased from Beijing Chemical (A.R.) was dried by calcium hydroxide for 24 h, and distilled. CuCl provided by Shanghai Chemical (A.R.) was purified by stirring in acetic acid, filtered, and washed with ethanol and dried. Carbon tetrachloride purchased from Beijing Chemical (A.R.), was washed with diethyl ether and solution of sodium hydroxide and dried with P_2O_5 for 24 h, then distilled. *N*-bromosuccinimide (NBS) and azodiisobutyronitrile (AIBN) from Shanghai Chemical (AR) were used without purification. 2,2'-Bipyridine (bpy, A.R.) and SiO_2 (C.P.) were provided by Beijing Chemical, DL-ethyl-bromopropionate (99%) was purchased from ACROS, and 3-methacryloxypropyltrimethoxyl silicon (C.P.) was provided by Nanjing Chemical, and all were used directly without purification.

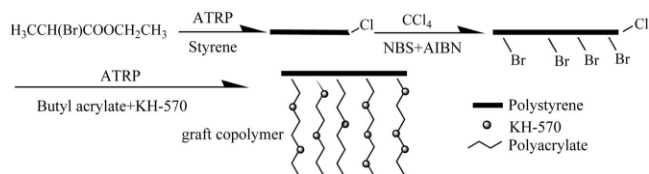
Equipment

The ¹H NMR spectra performed on a Bruker AV400 instrument with CDCl_3 as the solvent. The molecular weights and molecular weight distributions were measured on Waters 410 GPC (Guard, 10^5 , 10^3 , and 10^2 Å) with THF as the eluent and polystyrene as standard. The infrared data (IR) were recorded on a Nicolet FT/IR-410 spectrophotometer. The ultraviolet spectrum (UV) was recorded on a Shimadzu UV-Vis UV-3100 spectrometer. The dynamic mechanical spectra (model GDP-3 supplied by Jilin university instrumental factory) were recorded, using an automatic tensional braid analysis system with a heating rate of 2 K/min, frequency 0.1–1 Hz, and temperature from 302 to 403 K. Plots of the log change in the swing, $\ln(A_1/A_2)$, against temperature were obtained. The Braids of dynamic mechanical analysis made of fiberglass were immersed into the sample and dried under vacuum oven for 48 h at 60°C before used. The sample of morphology was dried under vacuum for 2 days and examined by scanning electronic microscopy using a Hitachi (Japan) X-650 SEM instrument.

Synthesis

Synthesis of polystyrene with low polydispersities

A bottom flask was charged with CuCl and bpy. The flask was sealed and cycled between vacuum and argon thrice to remove oxygen. Then 5 mL of degassed St and 42.7 μL DL-ethyl-bromopropionate were added



Scheme 2. The reactive routes of graft macromolecular coupling agents.

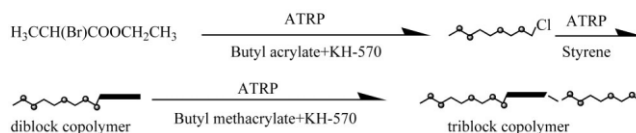
in the flask by syringe. The flask was immersed in a 120°C oil bath. After 6 h, the polymerization solution was terminated by using a hydrohalite bath. The polymer was diluted with THF and precipitated from the solution of methanol and deionized water. After being dissolved and precipitated for three times, the product was dried at 60°C under vacuum for 24 h.

Synthesis of graft macroinitiator²¹

The proper quantity of NBS, AIBN, and polystyrene with low polydispersities were dissolved in 20 mL CCl₄ and refluxed for 6 h. The solution was filtrated to remove the deposition, and concentrated by distillation. After being dissolved in THF and precipitated in the solution of methanol and deionized water for three times, the bromized polystyrene was dried at 60°C under vacuum for 24 h.

Synthesis of graft macromolecular coupling agents

Proper quantity macroinitiator of bromized polystyrene, CuCl, and bpy were added in a flask with magnetic stirring. The flask was sealed and cycled between degassed and vacuum-argon thrice. Then degassed 3-methacryloxyl-propyltrimethoxyl silicon, BA, and toluene were added in the flask by syringe. The flask was immersed into a 90°C oil bath for 6 h. The polymerization was terminated by using a hydrohalite bath. After being dissolved in THF and precipitated from the solution of methanol and deionized water for



Scheme 3. The reactive routes of block macromolecular coupling agents.

three times, the product was dried at 60°C in under vacuum for 24 h (Scheme 2).

Synthesis of diblock and triblock macromolecular coupling agents

The surplus monomers were distilled under vacuum after the first polymerization (BA and KH-570) was terminated. Proper quantity and degassed of next monomers (St) were introduced in the system by syringe. Then the flask was immersed into a 120°C oil bath with stirring for 10 h. The synthesis of triblock macromolecular coupling agent is same as diblock polymer except the monomers (5 mL BMA and 0.5 mL KH-570) and the reactive temperature (80°C) (Scheme 3). Table I shows all the materials used in the experiments.

RESULTS AND DISCUSSION

As references reported,² DL-ethyl-bromopropionate (initiator), CuCl (catalyst), and 2,2'-bipyridine (ligand) were employed in ATRP of BA and St that had been proved its living/controlled polymerization. Since the terminal bond of C—X is relatively stable, the halogenated polymers can be used as macroinitiator to synthesize block copolymers. The polyacrylate including KH-570 was used as macroinitiator for synthesis of block macromolecular coupling agents (Scheme 3). After the polystyrene had been synthesized by ATRP, bromination was carried out using the polystyrene in CCl₄ in the presence of NBS and AIBN. Then the

TABLE I
Materials Used in the Preparation of the Macroinitiator and Macromolecular Coupling Agents

Sample	BA (mL)	St (mL)	Initiator	KH-570 (mL)	CuCl (mg)	bpy (mg)	NBS (mg)	AIBN (mg)
Pst	—	5	42.7 μL	—	33.8	160	—	—
Graft initiator (a)	—	—	0.5 g	—	—	—	42	7
Graft initiator (b)	—	—	0.75 g	—	—	—	171	26
Graft initiator (c)	—	—	0.87 g	—	—	—	299	46
Diblock a	5	5	50.5 μL	0.5	40	213	—	—
Diblock b	5	10	50.5 μL	0.5	40	213	—	—
Diblock c	5	2.5	50.5 μL	0.5	40	213	—	—
Triblock	5	5	50.5 μL	1	40	213	—	—
Graft polymer a	3.5	—	0.5 g	0.35	47	224	—	—
Graft polymer b	3.5	—	0.5 g	0.35	47	224	—	—
Graft polymer c	3.5	—	0.5 g	0.35	47	224	—	—

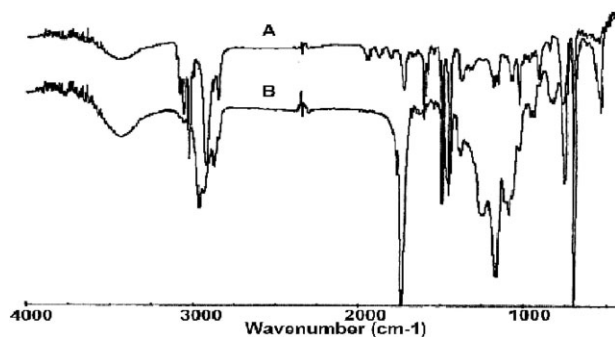


Figure 1 The IR spectra of (a) graft macroinitiator and (b) graft copolymer.

brominated polystyrene was used as macroinitiator for synthesis of graft macromolecular coupling agents (Scheme 3).

From the IR spectrum of diblock macromolecular coupling agent, the absorption peaks at 3025, 3060, 1601, and 1493 cm^{-1} are attributed to the polystyrene. The absorption peak of carbonyl group at 1734 cm^{-1} is assigned to the PBA and KH-570. The absorption peak at 1089 cm^{-1} is attributed to the group of $-\text{Si}(\text{OCH}_3)_3$. In fact, the IR spectrum of graft macromolecular coupling agent is same as block macromolecular coupling agent except the intensity of absorption. Figure 1 is the IR spectra of graft initiator (a) and graft copolymer (b). Comparing with (a), the absorptions at 1700–2000 cm^{-1} of (b) are attributed to polystyrene disappeared and a strong absorption at 1734 cm^{-1} is attributed to ester appeared because the graft macroinitiator initiated the monomers of BA and KH-570. In addition, the new absorption peak at 1089 cm^{-1} is attributed to the group of $-\text{Si}(\text{OCH}_3)_3$. From those data, we can affirm that the block and graft copolymers are composed of polystyrene, PBA, and KH-570.²²

Figure 2 is the UV spectrum of diblock macromolecular coupling agent. In the spectrum (a), the absorption at 238 nm is attributed to $n \rightarrow \pi^*$ transition of ester group. The absorption peaks at 260 and 286 nm are due to the transition of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of St units, respectively. Compared with (a) the absorption peak at 238 nm of (b) disappeared because the content of polystyrene is so high that the peak has been superposed upon. All those data indicate that the macroinitiator of PBA has initiated the monomer of St. Figure 3 is the UV spectra of graft macroinitiator and graft macromolecular coupling agent. The absorption peaks at 253 and 283 nm of (a) are due to the transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of St units, respectively. Comparing with (a) the absorption peak at 283 nm of (b) disappeared because the polystyrene was partly substituted by bromine. The absorption peak at 240 nm of (c) is attributed to the transition $n \rightarrow \pi^*$ of PBA and KH-570. The peak at 277 nm is assigned to phenyl group of St. From those data the monomers of BA and KH-570

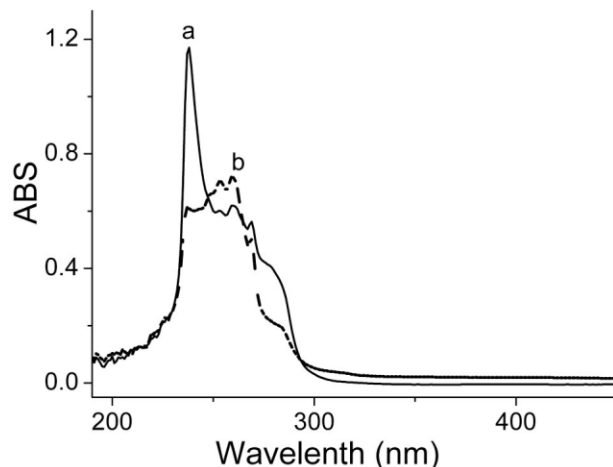


Figure 2 The UV spectra of (a) P(BA-co-KH-570)-b-St $V_{\text{BA}}:V_{\text{KH-570}}:V_{\text{St}} = 5:0.5:2.5$ and (b) P(BA-co-KH-570)-b-St $V_{\text{BA}}:V_{\text{KH-570}}:V_{\text{St}} = 5:0.5:10$.

were initiated by brominated polystyrene. Graft macromolecular coupling agents were synthesized successfully by ATRP.

Figure 4 shows the ^1H NMR spectra of the polystyrene (a) prepared by ATRP, the brominated polystyrene (b), and graft macromolecular coupling agents 4(c). The resonances at 6.0–7.5 ppm are assigned to the CH of aromatic protons in the St units of polystyrene. The resonances at 1.0–2.0 ppm are assigned to the CH_2 and CH of St units. The resonance at 4.0 ppm is assigned to the $-\text{OCH}_2$ of initiator, which suggested the polystyrene was synthesized by ATRP [Fig. 4 (a)]. After bromination, the intensity of the CH resonance (1.9 ppm) decreased significantly due to benzylic bromination [Fig. 4 (b)].²¹ In the ^1H NMR spectrum of graft macromolecular coupling agents [Fig. 4 (c)], the resonances at 6.2–7.5 ppm are assigned to the CH of aromatic protons in the St units of graft macromolec-

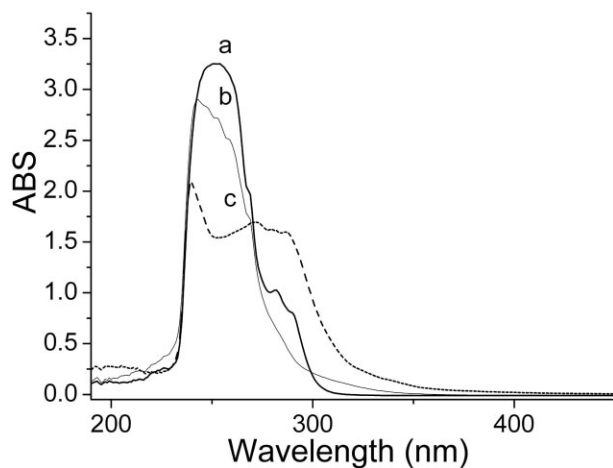


Figure 3 The UV spectra of (a) polystyrene; (b) brominated polystyrene; and (c) graft copolymer.

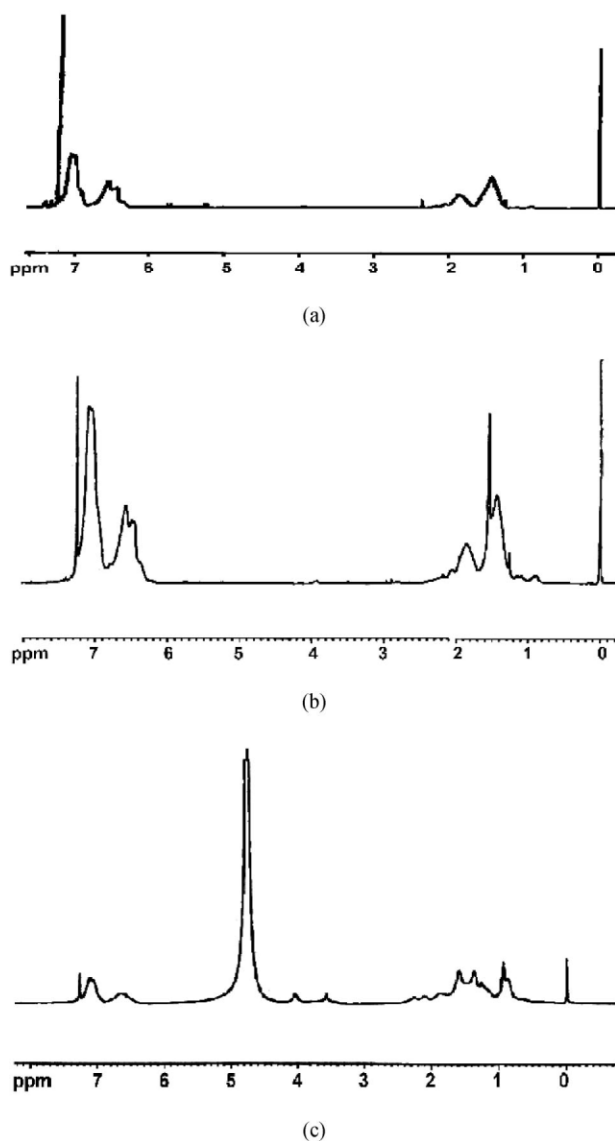


Figure 4 (a) The ¹H NMR spectra of polystyrene prepared by ATRP. (b) The ¹H NMR spectra of brominated polystyrene. (c) The ¹H NMR spectra of graft macromolecular coupling agent.

ular coupling agent, and the resonance at 4.0 ppm is attributed to the protons of $-\text{OCH}_2$ in PBA and KH-570. Although there is overlap to a certain extent, the spectrum of macromolecular coupling agent is different from polystyrene-*co*-polybutylacrylate because of KH-570. In addition, a strong resonance at 4.7 ppm is attributed to the KH-570 inside the graft macromolecular coupling agent appeared. From the data of IR, UV, and ¹H NMR, the functional copolymers are block or graft copolymers that are composed of St, butyl (meth)acrylate, and KH-570 unites.

Table II shows the data of GPC. It shows that all the block and graft copolymers were of low molecular weight distributions because ATRP possess living/controlled properties. There was an increase in the

molecular weights of the copolymers comparing with the original macroinitiator. Increases in the molecular weights of the products when compared with the macroinitiators confirm block and graft copolymer formation.²³ But the designed molecular weights and actual molecular weights of copolymers are different. Three factors important to that are as follows. First, because the copolymers are composed of polyacrylate, polystyrene, and KH-570, the polyacrylate brings error of test with standard sample (polystyrene). Second, the KH-570 inside the copolymer affects immovable phase of GPC also. Third the spatial structure of functional copolymer is complex. All these will spend more reserved time in the GPC. Thus, the tested molecular weights are less than the designed molecular weights.

The composite of damping materials with the matrix of IPNs from methylmethacrylate, methylethacrylate, methylbutylacrylate, and St²⁴ were improved by silicon dioxide that were treated by KH-570, block, and graft macromolecular coupling agents, respectively. (The content of filler is 20% wt and the content of coupling agent is 0.2% wt.) Figure 5 represents the dynamic mechanical analysis of composites. At zero external force $\ln(A_n/A_{n+1})$ denotes the inner wastage of the sample. The IPNs that are the matrix of composite consist of rigid polystyrene and flexible polymethacrylate. From Figure 5, the glass transition temperature (T_g) of composite at low temperature is attributed to the polymethacrylate and at high temperature it is attributed to polystyrene. The low T_g of the composite with diblock macromolecular coupling agent shifts to high temperature (a: 333°C; b: 323°C; and c: 333°C) compared with that of the composite with KH-570 (d: 315°C) and the high T_g of the composite with diblock macromolecular coupling agent shifts to low temperature about 10°C, which suggests that the compatibility of composite with diblock macromolecular coupling agent is improved greatly. Furthermore, the damping values of the composites with diblock macromolecular coupling agents are increased. This is because the fillers that are treated by macromolecular coupling agents possess structures of inorganic core and organic shell. The antenniform organic shell that is composed of macromolecules can entwine strongly with organic matrix. At the same time, the flexible polyacrylate in block macromolecular coupling agent contains some KH-570, which can react with the exterior hydroxyl of silicon dioxide, and the physical effect of matrix with coupling agent is strong, which increased the thickness of boundary layer between the matrix and fillers. On the basis of aforementioned results, in the composite the modified filler by macromolecular coupling agents has similar effect to that of a crosslinking agent. On one hand, the intermolecular friction increased and the movement of macromolecular chains of the

TABLE II
The Data of Block and Graft Copolymer

Sample	M_n	M_{th}	M_n/M_w	Content of Br (mol %)
Polystyrene	10,400	10,000	1.30	–
(BA-co-KH-570)-b-St $V_{BA}:V_{KH-570}:V_{St} = 5:0.5:5$	15,500	24,600	1.3	–
(BA-co-KH-570)-b-St $V_{BA}:V_{KH-570}:V_{St} = 5:0.5:10$	18,900	36,200	1.3	–
(BA-co-KH-570)-b-St $V_{BA}:V_{KH-570}:V_{St} = 5:0.5:2.5$	14,200	18,700	1.2	–
(BA-co-KH-570)-b-St-b-BMA $V_{BA}:V_{KH-570}:V_{St}:V_{BMA} = 5:1:5:5$	21,700	46,200	1.9	–
Macromolecular initiator (PSt)	10,530	10,000	1.38	6.6 (a)
	11,400	10,000	1.38	9.9 (b)
	11,560	10,000	1.38	12.4 (c)
Graft polymer a	20,100	53,200	1.40	Initiator a
Graft polymer b	17,000	76,300	1.42	Initiator b
Graft polymer c	14,000	92,700	1.45	Initiator c

M_n , the molecular weights from GPC; M_{th} , the theoretic molecular weights. The contents of Br% were obtained by titration.

matrix is restricted. On the other hand, the decrease in free volume of the matrix accelerates phase separation and limits the motion of some macromolecular chains of matrix so that the damping of composite decreases.²⁵ Thus, under mild degree of crosslinking the filler can improve the compatibility and damping property of composite. The KH-570 in block macromolecular coupling agents increased the effect between the silicon dioxide and the matrix because dimensional structures of functional block copolymers are propitious to increase the interplay between macromolecular coupling agents and matrix. The compatibility of composites with diblock macromolecular coupling agents was

improved for the T_g to shift inside. Figure 6 shows the dynamic mechanical spectra of composite with triblock macromolecular coupling agents. The damping property of composite with triblock macromolecular coupling agent is better than that of the composites with diblock macromolecular coupling agents and KH-570, because the functional triblock macromolecular coupling agent contains flexible polybutyl methacrylate, polybutyl acrylate, and rigid polystyrene. Furthermore, the content of KH-570 in triblock copolymers is more than that of diblock copolymers. It shows that the T_g indicates the compatibility of composite with triblock functional copolymer was im-

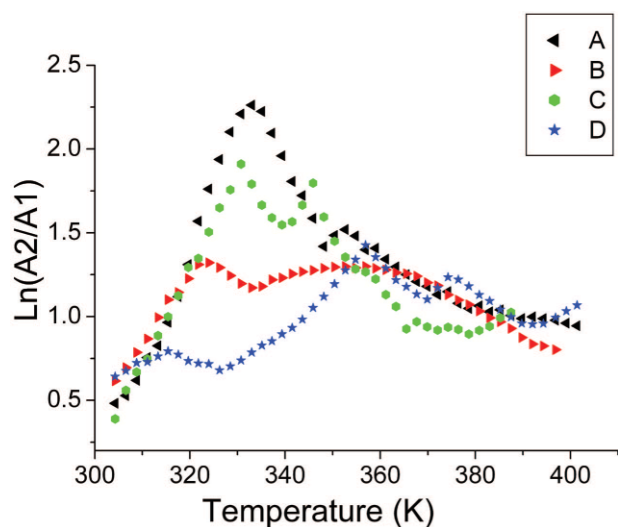


Figure 5 The dynamic mechanical spectra of composite with (a) BA:KH-570:St = 5:0.5:5; (b) BA:KH-570:St = 5:0.5:10; (c) BA:KH-570:St = 5:0.5:2.5; and (d) KH-570. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

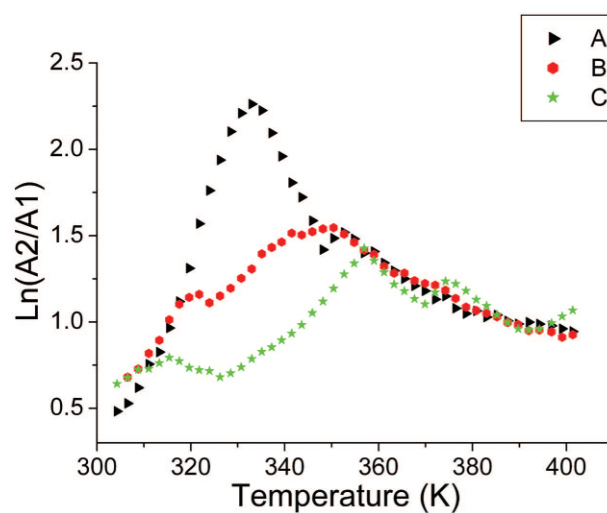


Figure 6 The dynamic mechanical spectra of composite with (a) BA:KH-570:St = 5:0.5:5; (b) BA:KH-570:St:BMA = 5:1:5:5; and (c) KH-570. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

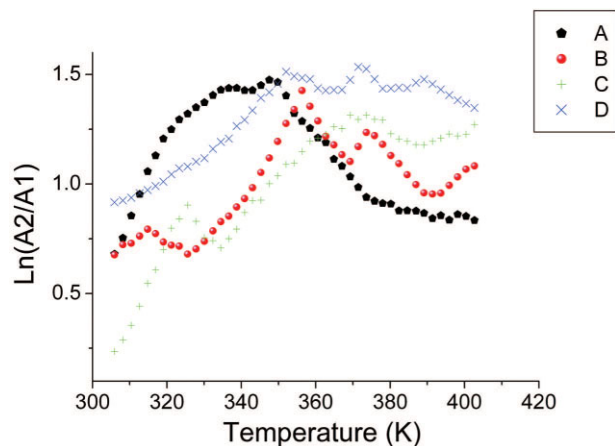


Figure 7 The dynamic mechanical spectra of composite with graft coupling agents (a) 9.94%; (b) KH-570; (c) 12.4%; and (d) 6.88%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

proved greatly. Combining the value of damping the composite with triblock macromolecular coupling agent is valuable damping material. The difference between diblock copolymer and triblock copolymer is that triblock copolymer possesses longer flexible macromolecular chain than that of diblock copolymer. Thus, the KH-570 can enhance the intensity of effect between matrix and antenniform organic shell of modified fillers.

As we can control the content of bromine by replacing polystyrene, the graft macromolecular initiator with multigroups were synthesized. Three kinds of graft macromolecular coupling agents were synthesized and applied in composite. Figure 7 represents the dynamic mechanical analysis of composite with graft macromolecular coupling agent. Curve (a) (the percentage of graft is 9.94%) shows one broad T_g (340°C) and high damping value, which indicates compatibility of the composite is improved greatly and is suitable to be used as damping materials. Curve (c) (the percentage of graft is 12.4%) shows good compatibility but low damping value because of high crosslinking degree of the composite. Curve d (the percentage of graft is 6.88%) shows high damping value but poor compatibility because of low crosslinking degree of the composite. The glass transition region T_g of composites with graft coupling agents shifts to high temperature about 10–50°C compared with that of composite with small molecular coupling agent (curve b). This is because the content of flexible polyacrylate in graft copolymer is so high that the physical affect between matrix and macromolecular coupling agent is strong, which increased the thickness of boundary layer. Furthermore, the spatial structure of graft macromolecular coupling agent (especially b) is more suitable to entwine with the matrix.

Figure 8 shows the spectra of the dynamic mechanical analysis of composites with (a) diblock, (b)

triblock, and (c) graft macromolecular coupling agents. The compatibility and damping of composite with triblock and graft macromolecular coupling agent are better than that of composite with diblock copolymer because of the content of KH-570 and spatial structure of macromolecular coupling agents. But the compatibility of composite with graft macromolecular coupling agent is the best, which indicates the affect between modified filler and matrix is the strongest and the boundary layer is the thickest. The intermolecular friction of matrix increased and the movements of macromolecular chains of matrix were restricted. Thus, the damping value and compatibility of composite with graft macromolecular coupling agent are improved greatly.²⁶

Figure 9 shows scanning electron photomicrographs of composites. The (a) is the composite with modified silicon dioxide by KH-570. The (b) is the composite with modified silicon dioxide by graft macromolecular coupling agent and (c) is the composite with modified silicon dioxide by triblock macromolecular coupling agent. From Figure 9, the black copolymer matrix phase constitutes the continuous phase and the white filler phase constitutes a dispersed phase. In the Figure 9(a), the interface of the two phases is very clear. Furthermore, there are aggregates, because the action of filler with matrix is so weak that the boundary layer of composite is very thin. From Figures 9(b) and 9(c), we can see that with the addition of fillers that were modified by triblock and graft macromolecular coupling agents, the interface is faint. This is because the macromolecular coupling agent combined greatly with the matrix and with the silicon dioxide. Furthermore, the compatibil-

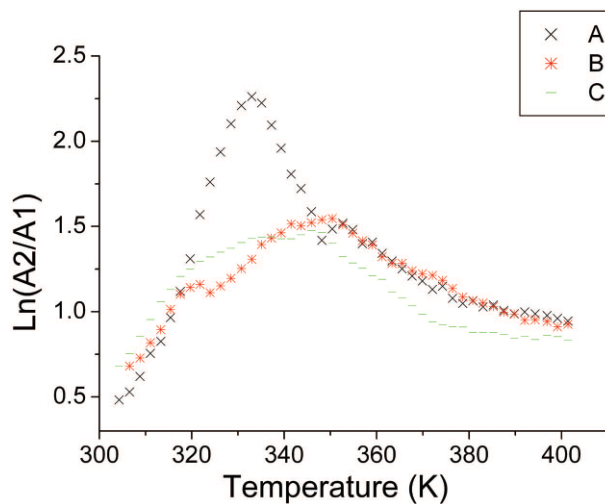


Figure 8 The dynamic mechanical spectra of composite with macromolecular coupling agents (a) diblock; (b) triblock; and (c) graft. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

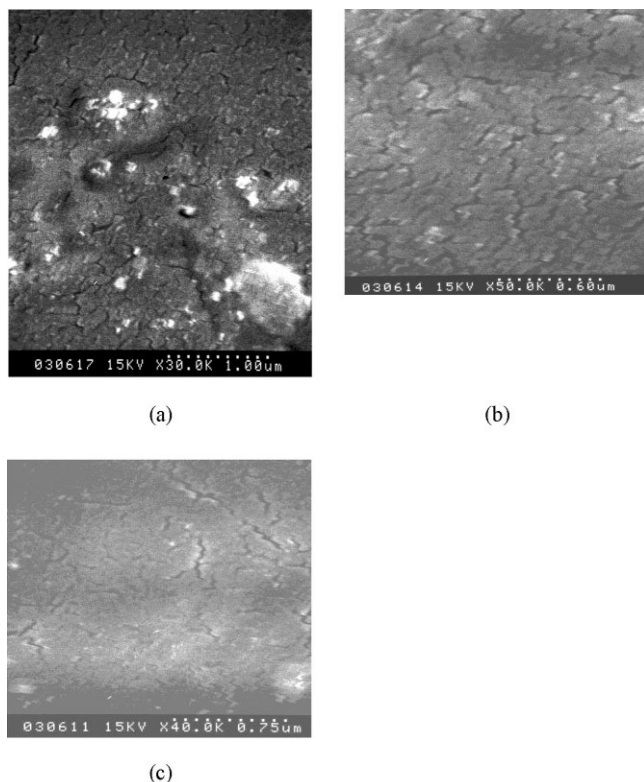


Figure 9 The SEM of composite with (a) KH-570; (b) graft macromolecular coupling agent; and (c) triblock macromolecular coupling agent.

ity of the system that was formed by modified silicon dioxide and matrix was excellent. The filler dispersed in the IPNs homogeneously and aggregates did not appear. This is because of the exclusion interaction between the particles, which were modified by macromolecular coupling agent, was increased. Another reason is that the boundary layer of composites was thicker than that of ordinary composites, which is consistent with the results of dynamic mechanical analysis.

CONCLUSIONS

Novel macromolecular coupling agents were synthesized successfully by ATRP. The ^1H NMR, GPC, UV, and IR were used to characterize the structures and composition of macromolecular coupling agents. The composites were composed of matrix (IPNs) and the

silicon dioxide that were treated by diblock triblock and graft macromolecular coupling agents. The morphology and properties of composites were characterized by SEM and dynamic mechanical spectra. The results show that the action of modified particles was similar to that of a crosslinking agent. The compatibility and damping value of the composites with macromolecular coupling agents were improved greatly. This kind of novel macromolecular coupling agent may be used in many fields such as bond, coating, and damping materials.

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