Characterization of End-Functionalized Styrene–Butadiene–Styrene Copolymers and Their Application in Modified Asphalt

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ABSTRACT: End amino, carboxylic acid, and hydroxyl functionalized styrene–butadiene–styrene (SBS) triblock copolymers were prepared with 1,5-diazabicyclo[3.1.0]hexane, carbon dioxide, and epoxy ethane as capping agents, respectively. The effects of the end polar groups on the morphology and dynamic mechanical properties were investigated. Transmission electron microscopy images suggested that the group at the end of the polystyrene (PS) segment made the morphology of the PS domains disordered and incompact. Dynamic mechanical results showed that the storage and loss modulus increased after SBS was end-functionalized. End amino and carboxylic acid groups improved the compatibility and storage stability of SBS-modified asphalt. However, the effect of the end-hydroxyl group on the improvement of the storage stability of SBS-modified asphalt was not obvious. The differential scanning calorimetry analysis of SBS-modified asphalt further showed that the compatibility and storage stability of SBS-modified asphalt were improved by the attachment of amino or carboxylic acid groups through the anionic polymerization method. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 8–16, 2007

Key words: anionic polymerization; block copolymers; compatibility; microstructure

INTRODUCTION

Styrene–butadiene–styrene (SBS) triblock copolymers are widely used as asphalt modifiers.[1,2] The physical and mechanical properties of conventional asphalt compositions can be improved by the addition of SBS.[3,4] SBS exhibits a two-phase morphology consisting of glassy polystyrene (PS) domains and rubber polybutadiene (PB) when the temperature is between the glass-transmission temperatures of the polybutadiene segments ($T_{g,\mathrm{PB}}$) and the polystyrene segments ($T_{g,\mathrm{PS}}$). Therefore, SBS exhibits an elastomeric network. In general, one of the critical aspects of SBS-modified asphalt is storage stability. Several ways of solving this problem have been investigated, including physical and chemical means.[5–7] In the latter case, the chemical modification of SBS through the grafting of carboxylic acid groups and epoxy PB has been studied to improve the storage stability.[7–9]

The end functionalization of SBS by *in situ* anionic polymerization technology is an effective method for attaching polar groups to the end of the SBS molecular chain. Polar groups can be attached to polymer chains both by a functionalized initiator and by a terminating agent, which have attracted widespread commercial and academic interest.[10–12] The end functionalization of synthetic polymers is of great interest because the reactive polymers are highly valuable intermediates for the synthesis of copolymers of complex structures[13] and compatibilizers for polymer blends.[14]

The methodology of living anionic polymerization is particularly suitable for the synthesis of well-defined chain-end-functionalized polymers with controllable molecular weights, narrow molecular weight distributions, and quantitative degrees of end functionality.[10] In this study, we synthesized SBS copolymers using 1,5-diazabicyclo[3.1.0]hexane, carbon dioxide (CO_2), and epoxy ethane as capping agents.

The introduction of carboxy groups at the end of polymer chain ends is of considerable interest because these groups undergo a variety of reactions and the polymers can transform readily into ionomers with carboxylate anions.[15] Soobum and Chang[16] studied the special phase transition in styrene–isoprene–styrene triblock copolymers end-capped with carboxylic acid groups or sodium carboxylate groups and further investigated the strong ionic associations and increased repulsive segment–segment interactions in the block copolymers. Milkovich[17] prepared star block styrene–butadiene copolymers having carboxylic acid groups associated with the nucleus and found that they were more compatible with polar fillers than uncarboxylated equivalents. Quirk and Jinh-Jing[18] reported the prepar-

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ation of end-hydroxyl PS using anionic polymerization and found that epoxy ethane was an effective capping agent for the synthesis of the end-functionalized polymer. The end-hydroxyl polymer was also applied to improve the compatibility of polymer blends by Jerome et al.[19]

Although numerous studies have focused on the anionic polymerization of end-functionalized polymers,[20–22] only a limited number of works have dealt with the synthesis of SBS by the end-capping reaction of a Schiff base.[23,24] Koning et al.'s[25] and Klaus's[26] studies have shown that 1,5-diazabicyclo[3.1.0]hexane is an effective end-capping agent for anionic polymerization, but to the best of our knowledge, little has been reported on the synthesis of end-amino-functionalized SBS triblock copolymers.

In this study, we report a kind of end-functionalized, SBS-modified asphalt (PMA) and discuss the storage stability of these blends. End-functionalized groups were attached to SBS with 1,5-diazabicyclo[3.1.0]hexane, CO_2, and epoxy ethane as capping agents according to anionic polymerization technology. Amino, carboxylic acid, and hydroxyl groups were designed for the molecular end of SBS.

We study their special transmission electron microscopy (TEM) and dynamic mechanical properties. At the same time, end-functionalized SBS is applied to improve the storage stability of SBS-modified asphalt. The compatibility of the aforementioned end-functionalized SBS and nonfunctionalized SBS-modified asphalt is compared.

EXPERIMENTAL

Materials

Butadiene, styrene, cyclohexane, and n-butyllithium (n-BuLi) were obtained from Beijing Yanshan Petrochemical Corp. (Beijing, China). Styrene and cyclohexane were dried with molecular sieves to keep the water concentration below 5 ppm and were purged with highly purified nitrogen for more than 15 min before use to keep the oxygen concentration below 10 ppm. Tetrahydrofuran (THF) was refluxed over calcium hydride for more than 4 h and then distilled under the protection of N_2. The purity of THF was checked with gas chromatography. The concentration of n-BuLi was calibrated by the Gilman double titration method.[15]

For the synthesis of 1,5-diazabicyclo[3.1.0]hexane, see refs. 26 and 27. The purity was analyzed by gas chromatography/mass spectrometry, and it was 95.8%.

AH-90 paving asphalt was obtained from Liaoning Huanxiling Asphalt Factory (Panjin, Liaoning, China). The physical properties of this asphalt were as follows: penetration = 88 dmm (25°C, ASTM Standard D5) and softening point = 49.5°C (ASTM Standard D36). The composition of AH-90 asphalt could be described as follows: saturates (6.1 wt %), aromatics (41.7 wt %), resins (39.6 wt %), and asphaltenes (12.6 wt %).

Polymerization procedures

A 5-L stainless reactor, which was dried and purged with nitrogen, was charged with cyclohexane and styrene, and the temperature was maintained at 50°C with a water bath. THF and n-BuLi were added with a syringe to first polymerize the styrene monomer. About 45 min after the addition of n-BuLi, the temperature of the water bath was increased to 70°C, and butadiene monomer was added to the reactor. After the copolymerization of the styrene and butadiene monomers for 1 h at 70°C, a designated amount of styrene was added to the reactor, and the polymerization proceeded for 45 min. At the end of the polymerization, 1,5-diazabicyclo[3.1.0]hexane in a ratio of 1 : 1 to the living chain was added to the reactor at 35°C and reacted for 30 min. Then the color of the solution changed from red to pink. A small amount of ethanol was added to terminate the living polymers, at which point the color of the solution changed from pink to colorless. An aging-resistant agent (2,6-dibutyl-4-methylphenol) was added (1 wt % with respect to the dry rubber, ca. the total weight of the monomers participating in the copolymerization), and the reactor temperature was then lowered to 20°C. The solution was precipitated by the addition of an excess amount of alcohol, and the precipitated polymer, end-amino-functionalized styrene–butadiene–styrene (SBS–N), was dried in a vacuum oven at 40°C to a constant weight. The overall polymerization is shown in Scheme 1.

SBS copolymers initiated with n-BuLi were further subjected to carbonation to end-cap the PS end blocks with carboxylic acid groups by the introduction of high-purity gaseous CO_2. The carbonation of SBS was carried out with the following procedures. After polymerization, a polar additive, N,N,N,N-Tetramethylethylenediamine (TMEDA), was added to the solution of SBS by a syringe, and the polymerization solution was lowered to about 10°C. CO_2 gas at a constant pressure of 0.1 MPa was passed into the reactor, after which the CO_2 gas reacted with the polymeric organolithium compound in the solution without stirring. As the reaction progressed, a gradual discoloration of the red living anionic solution was observed. After 12 h, the solution was pressured out of the reactor by N_2 pressure. Immediately after that, about 1 mL of hydrochloric acid/methanol (1/1 v/v) was added to the polymer solution, and the mixture was stirred to hydrolyze the polymeric lithium carboxylate salt, yielding the SBS copolymer end-capped with the —COOH group. The precipitated polymer, end carboxylic acid functionalized styrene–butadiene–styrene (SBS–COOH),
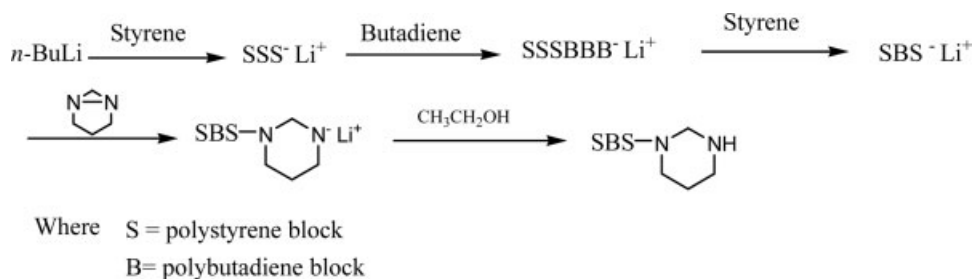
Scheme 1

was dried in a vacuum oven. The overall polymerization is shown in Scheme 2.

The hydroxylation of SBS was carried out with epoxy ethane as a capping agent. After the copolymerization of SBS, the temperature of the polymerization solution was lowered to about 10°C. Epoxy ethane (the molar ratio of epoxy ethane to SBS was 5) was added to the polymerization solution. After 12 h, the solution was pressured out of the reactor by N_2 pressure. Immediately after that, about 1 mL of hydrochloric acid/methanol (1/1 v/v) was added to the polymer solution, and the mixture was stirred to produce end-hydroxyl styrene–butadiene–styrene (SBS–OH).

Preparation of SBS-modified asphalt

Asphalt (250 g) was heated to 160°C in a small container until it flowed fully. SBS (16 g) was mixed into asphalt at a stirring rate of 3750 rpm for 45 min; sulfur (2 wt % with respect to the mass of SBS) was added to the blends to improve the storage stability, and the stirring was continued for 60 min at a speed of 3750 rpm for 60 min.

Characterization

The molecular weight was determined by gel permeation chromatography (GPC; Maxims 820, Waters, Glenside, PA) with three Waters μ-Styragel columns (10^3, 10^4, and 10^5 Å) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in the solvent THF. The GPC instrument was calibrated with monodisperse PS standards.

The composition of the polymers was analyzed by ^{1}H-NMR (AM-400, Bruker, Karlsruhe, Baden-Wurt-

temburg, Germany) spectroscopy at room temperature. The sample was dissolved in chloroform ($CDCl_3$) to prepare a solution with a concentration of 150 mg/mL. ^{1}H-NMR spectra were used to calculate the contents of the vinyl and 1,4-microstructures of SBS.[21] The percentages of the styrene block and the microstructure of the butadiene portion were calculated according to ref. 28.

The concentration of the amine at the polymer chain ends was determined by acid–base titration as follows.[26,29,30] The polymer sample was dissolved in a 1/1 (v/v) mixture of $CDCl_3$ and glacial acetic acid, and the solution was titrated with standard $HClO_4$ in glacial acetic acid with crystal violet as the indicator. The degree or functionality of amination was evaluated by a combination of the amine content by the titration, and the number-average molecular weight was determined by GPC.

The concentration of carboxyl chain ends in SBS–COOH was determined by the titration of a polymer solution in toluene with $0.01M$ potassium hydroxide (KOH) in methanol to the phenolphthalein end point.[31]

Dynamic mechanical properties were measured with a TA 2980 DMA dynamic mechanical analyzer (New Castle, DE) with a multifrequency film tension module. The specimens ($1.5 \times 4.5 \times 20$ mm^3) were cut from the center of the samples. A temperature sweep at 5°C/min from −150 to 150°C at a frequency of 1 Hz was used to determine the loss factor (tan δ) for all samples in addition to the dynamic modulus. $T_{g,PB}$ and $T_{g,PS}$ were measured from the inflection point in a plot of tan δ versus the temperature.

TEM analysis was carried out on a Tecnai G^{2}20 transmission electron microscope (FEI Co., Hillsboro, OR) at an acceleration voltage of 200 kV. Ultrathin sections of the sample were prepared with a Leica
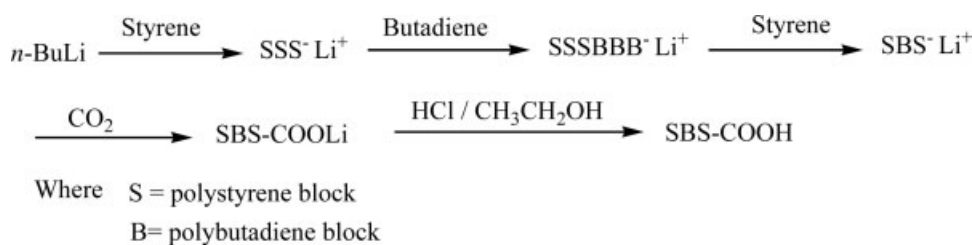
Scheme 2

TABLE I
Molecular Characteristics of SBS and End-Functionalized SBS

	$M_n \times 10^{4a}$	$M_w/M_n{}^b$	Styrene (%)	1,2 (%)	$T_{g,PS}$ (°C)	$T_{g,PB}$ (°C)	Functionality
SBS	8.1	1.04	29.8	13.7	99.39	−79.07	0
SBS–N	8.1	1.04	29.8	13.7	100.32	−77.93	0.96
SBS–COOH	8.3	1.05	29.6	12.8	99.98	−73.68	0.92
SBS–OH	9.2	1.07	29.5	13.8	99.29	−74.28	—

[a] Number-average molecular weight.
[b] Weight-average molecular weight/number-average molecular weight.

Ultracut UCT with an EMFCS cryoattachment (Leica, Bannockburn, IL) at −120°C. Cross sections with a thickness of 50 nm were obtained with a diamond knife.

The storage stability of the asphalt binders was tested as follows.[3] Each sample was poured into a glass tube 25 mm in diameter and 140 mm high. It was stored vertically at 163°C in an oven for 48 h, and then the tube containing the modified asphalt was cooled at −10°C for 4 h and cut horizontally into three equal sections. The difference in the softening points between the top and bottom sections of the tube was measured. The smaller the difference was of the softening points, the better the storage stability was of the SBS-modified asphalt.

To determine the storage stability of PMA, calorimetric measurements were performed on a differential scanning calorimeter (Netzsch, Burlington, MA). A constant heating rate of 10°C/min was employed to heat PMA from −60 to 60°C. Approximately 10-mg samples at the top and bottom of PMA were used in differential scanning calorimetry (DSC) analysis.

RESULTS AND DISCUSSION

Synthesis and structure of end-functionalized SBS

1,5-Diazabicyclo[3.1.0]hexane can be capped to polystyryllithium effectively and produce end-amino-functionalized PS.[25,26] The actual reaction between the active SBS anionic center and 1,5-diazabicyclo[3.1.0]-hexane is finished by the termination of polystyryllithium, which inspired us to apply it to the synthesis of end-amino SBS. Table I lists the compositions and structures of the prepared SBS samples. In the sequential SBS polymerization process, the PS block was made first, followed by the addition of butadiene to the living polystyryllithium chain end. The preparation of SBS was completed by the further addition of a second quantity of styrene in an amount equal to that of the first styrene usage. At the end of the polymerization, half of the solution was transferred to another reactor under the protection of N_2. Ethanol was used to terminate the active SBS anion. To the rest of the solution, 1,5-diazabicyclo[3.1.0]hexane with a ratio of 1 : 1 to the living chain was added to the reactor and reacted for 30 min. Then, ω-amino SBS (SBS–N) was

prepared by *in situ* anionic polymerization technology. The GPC spectra of SBS before and after functionalization are analyzed in Figure 1. The end amino group has few effects on the molecular weight and its distribution. Because the functionalized group is attached to SBS at the end of polymerization, it will not influence its microstructure. The microstructure of SBS–N was estimated by ^{1}H-NMR, and the vinyl content was calculated according to ref. 15. The functionality of amine, which was determined by the molar ratio of end-functionalized SBS to total SBS, was found to be over 0.95.

CO_2 can be used in the anionic end-capping reaction. However, a byproduct with a double molecular weight, which is produced by the coupling reaction of CO_2, has impaired the quality of the end-functionalized polymer. As Quirk et al.[31] reported, a polar modifier was effective in reducing the coupling byproduct and improving the functionalized product. In our research, TMEDA was added before the introduction of CO_2 to decrease the byproduct. The GPC spectrum of SBS with increasing amounts of TMEDA is shown in Figure 2. The area of coupled SBS (double molecular weight) decreases with the increase in TMEDA. The content of uncoupled SBS and the corresponding efficiency of carbonation analyzed by titration are summarized in Table II. From Table II, it can
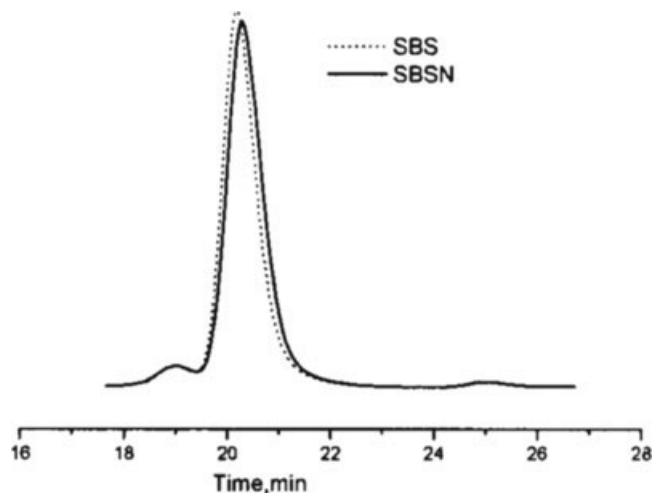

Figure 1 GPC chromatograms of SBS before and after end functionalization with amino groups.
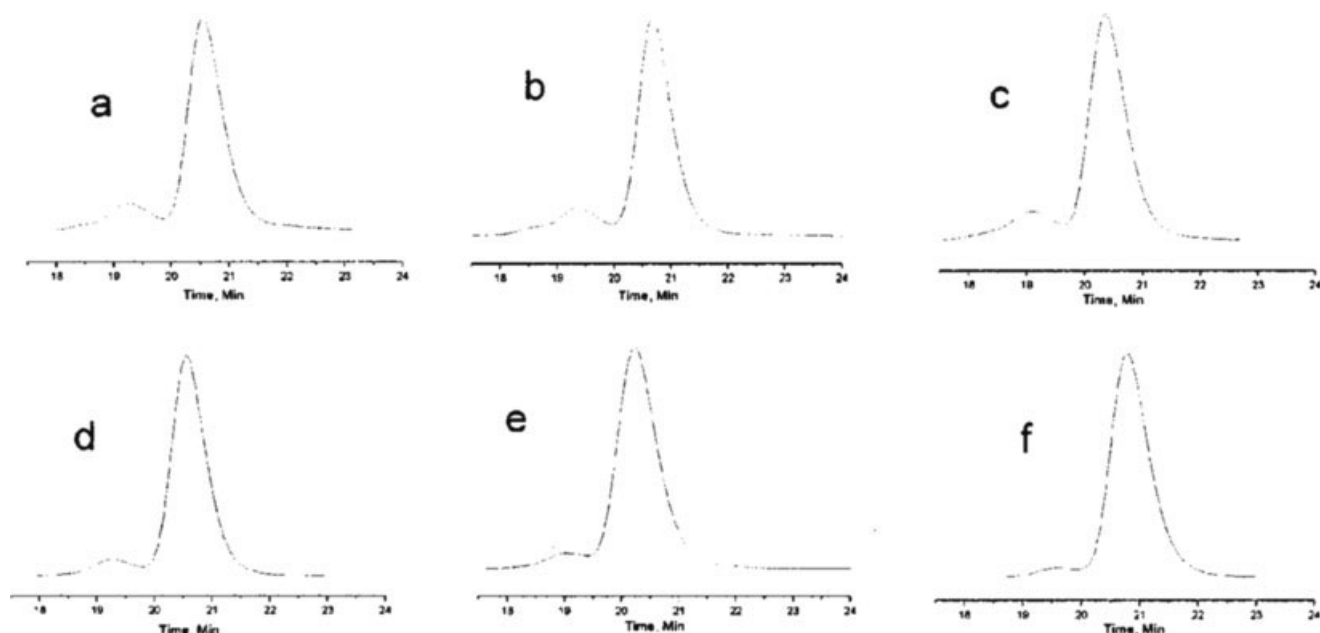
Figure 2 GPC chromatograms of SBS–COOH with different amounts of TMEDA (TMEDA/Li): (a) 0, (b) (1.0, (c) 5.0, (d) 10.0, (e) 20.0, and (f) 40.0.

be concluded that the uncoupled living SBS center transfers to carboxylic acid quantitatively and that the addition of TMEDA can increase the efficiency of carbonation. Table I contains the composition and molecular weights of the prepared samples, as determined from the stoichiometry of the reaction mixtures. SBS–COOH was prepared with n-BuLi as the initiator and THF as the polar modifier (the molar ratio of THF to SBS was 1.0). The functionality of carbonation, which was determined by the molar ratio of end-functionalized SBS to total SBS, was found to be over 0.92.

During the actual preparation of SBS–OH, the usage of epoxy ethane is relatively small, and this makes it difficult to study the reaction between epoxy ethane and active anionic centers. At the same time, it is difficult to determine the efficiency of the hydroxyl group at the end of the macromolecule. However, by studying the low-molecular-weight model polymer, we could accurately estimate the end-hydroxyl group through the ^{1}H-NMR method. Because the actual reaction between the active SBS anionic center and epoxy ethane is finished by the termination of polystyryllithium, low-molecular-weight PS has been designed to investigate the reaction activity of epoxy ethane. The ^{1}H-NMR spectrum of end-hydroxyl PS is shown in Figure 3. The proton (H) appearing at 3.2 ppm is characteristic of methylene hydrogen bonded to the carbon that is adjacent to the hydroxyl group. The GPC spectra of SBS before and after functionalization are analyzed in Figure 4. The end-hydroxyl group has few effects on the molecular weight and its distribution. The composition and molecular weights of SBS–OH are summarized in Table I.

Morphology of end-functionalized SBS

TEM of the prepared SBS copolymer is shown in Figure 5. Both end-functionalized SBS and nonfunctionalized SBS show that microphase separation of the PS block forms discrete domains in the continuous PB phase. As we know, the morphology formation in block copolymers is influenced by different factors.[32] The monomer type, chemical composition, and molecular features play significant roles. The end functionalization of SBS does little to change the molecular weight and composition of the block copolymer. We are left to explore the effects of end groups on the morphology of SBS.

In the case of SBS, PS cylinders are clearly arranged in a uniform lattice in the PB matrix. In contrast, end-functionalized SBS shows perforated layers with disordered and zonal PS domains dispersed in the PB matrix. This change can be attributed to the increase in the interfacial tension between PB and PS blocks, which is affected by the introduction of polar end groups.

Dynamic mechanical properties of end-functionalized SBS

The tan δ, storage modulus (E'), and loss modulus (E'') values versus the temperature for SBS and end-func-

TABLE II
Content of Uncoupled SBS and Corresponding Efficiency of Carbonation

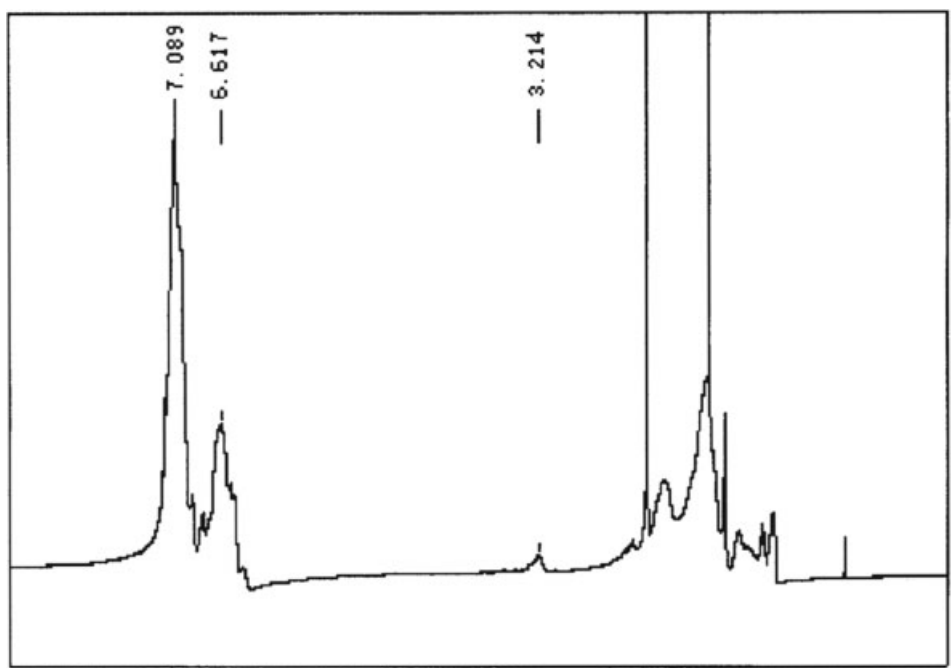| TMEDA/Li	0	1	2	5	10	20
Uncoupled SBS (%)	82.0	84.9	86.2	91.9	93.8	96.5
Efficiency of carbonation (%)	83.5	86.7	87.97	92.39	92.4	98.3

Figure 3 ^{1}H-NMR spectrum of end-hydroxyl PS.

tionalized SBS are potted in Figure 6. In Figure 6, two transitions can be observed. The low-temperature transition is characteristic of the PB domains, whereas the higher temperature transition is characteristic of the PS domains. The molecular mobility can be well characterized by the position of the glass-transition temperatures of the components. $T_{g,PB}$ and $T_{g,PS}$ can be analyzed from the inflection point in a plot of tan δ versus the temperature. $T_{g,PB}$ and $T_{g,PS}$ are listed in Table I. It is obvious that $T_{g,PB}$ and $T_{g,PS}$ are influenced slightly after they are end-functionalized.

In addition, another effect can be observed. E' and E'' of the end-functionalized block copolymers are much higher than those of nonfunctionalized SBS, and a considerable increase can be observed after the temperature is increased over $T_{g,PB}$. This change identifies the improvement of the end-functionalized group in the molecular interaction.

Application of end-functionalized SBS in modified asphalt

Because of the differences in the solubility parameters and densities between SBS and asphalt, phase separation takes place in PMA.[33] SBS dispersed in asphalt usually accumulates and floats on top of the asphalt, especially at high temperatures. According to an evaluation of the storage stability of SBS-modified asphalt, as mentioned in the Experimental section, the softening point of the top section of modified asphalt after a period of storage becomes much higher than that of the bottom section if the blend of SBS and asphalt is

unstable. Table III shows the storage stability of SBS-modified asphalt under the same blending conditions. The modified asphalt with end amino and carboxylic acid group SBS shows a lower difference in the softening points between the top and bottom sections, and this means good storage stability. However, the end-hydroxyl group cannot reduce the difference in the softening points obviously and makes few contributions to the improvement of the storage stability. These results suggest that the attachment of amino and carboxylic acid group to SBS could improve the storage stability of modified asphalt.
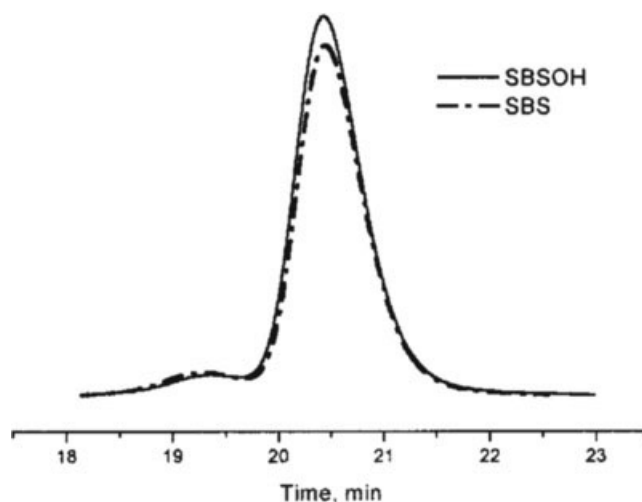

Figure 4 GPC chromatograms of SBS before and after end functionalization with hydroxyl groups.
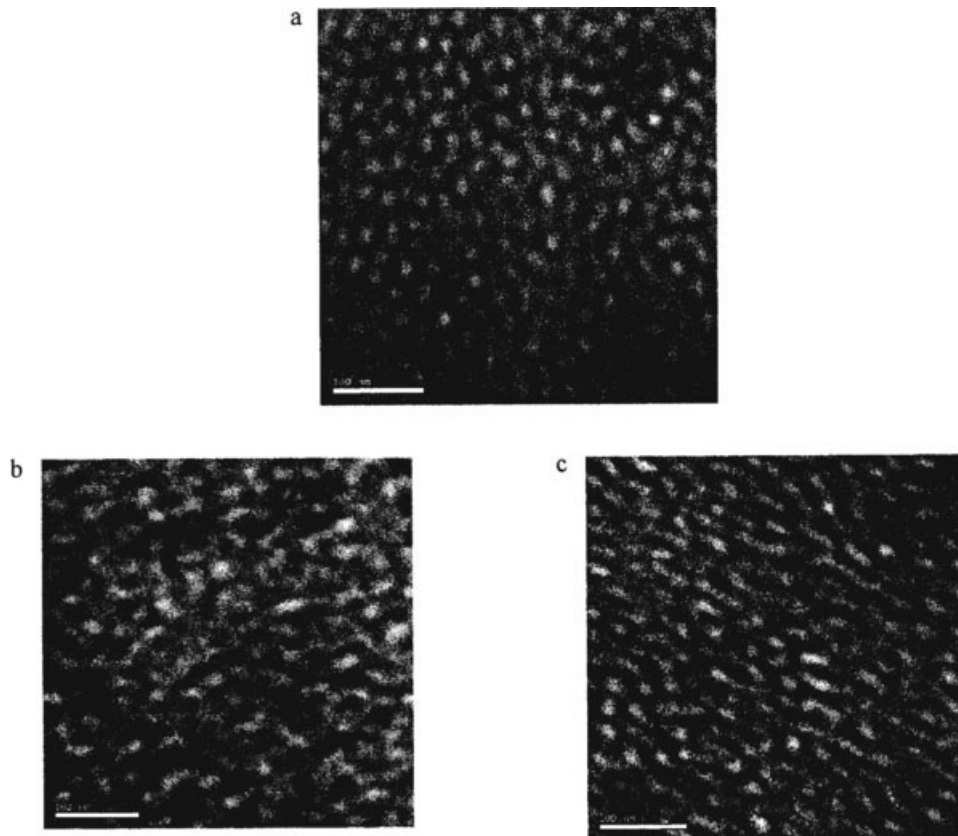
Figure 5 TEM images of SBS and end-functionalized SBS: (a) SBS, (b) SBS–COOH, and (c) SBS–N.

DSC analysis could be used to investigate the compatibility and storage stability of SBS-modified asphalt.[34] Commonly, asphalt consists of saturates, aromatics, resins, and asphaltenes. On the DSC curves of SBS-modified asphalt, the absorbing peaks of these components overlap to form broad peaks. Generally,
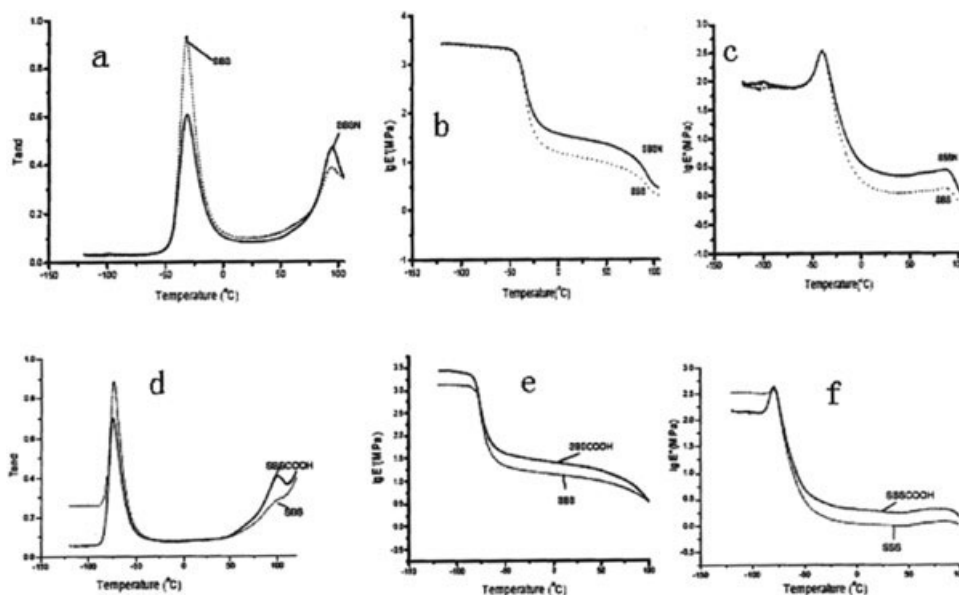

Figure 6 Dynamic mechanical analysis of SBS before and after end functionalization: (a) tan δ vs the temperature of SBS–N, (b) lg E' versus the temperature of SBS–N, (c) lg E'' versus the temperature of SBS–N, (d) tan δ vs the temperature of SBS–COOH, (e) lg E' versus the temperature of SBS–COOH, and (f) lg E'' versus the temperature of SBS–COOH.

TABLE III
Softening Point at the Top and Bottom Sections of SBS-Modified Asphalt

Softening point (°C)	SBS-modified asphalt	SBS–OH-modified asphalt	SBS–N-modified asphalt	SBS–COOH-modified asphalt
Top	91.0	84	65	59.5
Bottom	59.5	64	63.5	59.3
Difference	31.5	20	1.5	0.2

PMA with large absorbing peaks (the area of the absorbing peaks is large) on DSC curves will have more components conducting phase transmission in the designated range of temperatures, and this means that the blends have poor stability.[34] Thus, the stable PMA blends have smooth DSC curves, and the area of the absorbing peaks is relatively small. At the same time, by comparing the areas of the absorbing peaks at the top and bottom sections of SBS-modified asphalt, we can estimate the storage stability of PMA.

The DSC curves of end-functionalized and nonfunctionalized SBS-modified asphalt in the temperature range of −60 to 60°C are presented in Figure 7. The curves of end amino and carboxylic acid SBS-modified asphalt are smoother than those of nonfunctionalized SBS. However, the curve of the end-hydroxyl-group

SBS-modified asphalt is still rough, similar to that of nonfunctionalized SBS.

Both the softening point and DSC analysis suggest that the attachment of amino and carboxylic acid groups to the end of SBS could improve the storage stability of PMA. However, the end-hydroxyl group at the end of SBS is not effective in improving the storage stability.

CONCLUSIONS

End amino, carboxylic acid, and hydroxyl functionalized SBS was prepared with 1,5-diazabicyclo[3.1.0]hexane, CO_2, and epoxy ethane as the capping agents, respectively. Because the end groups were attached to
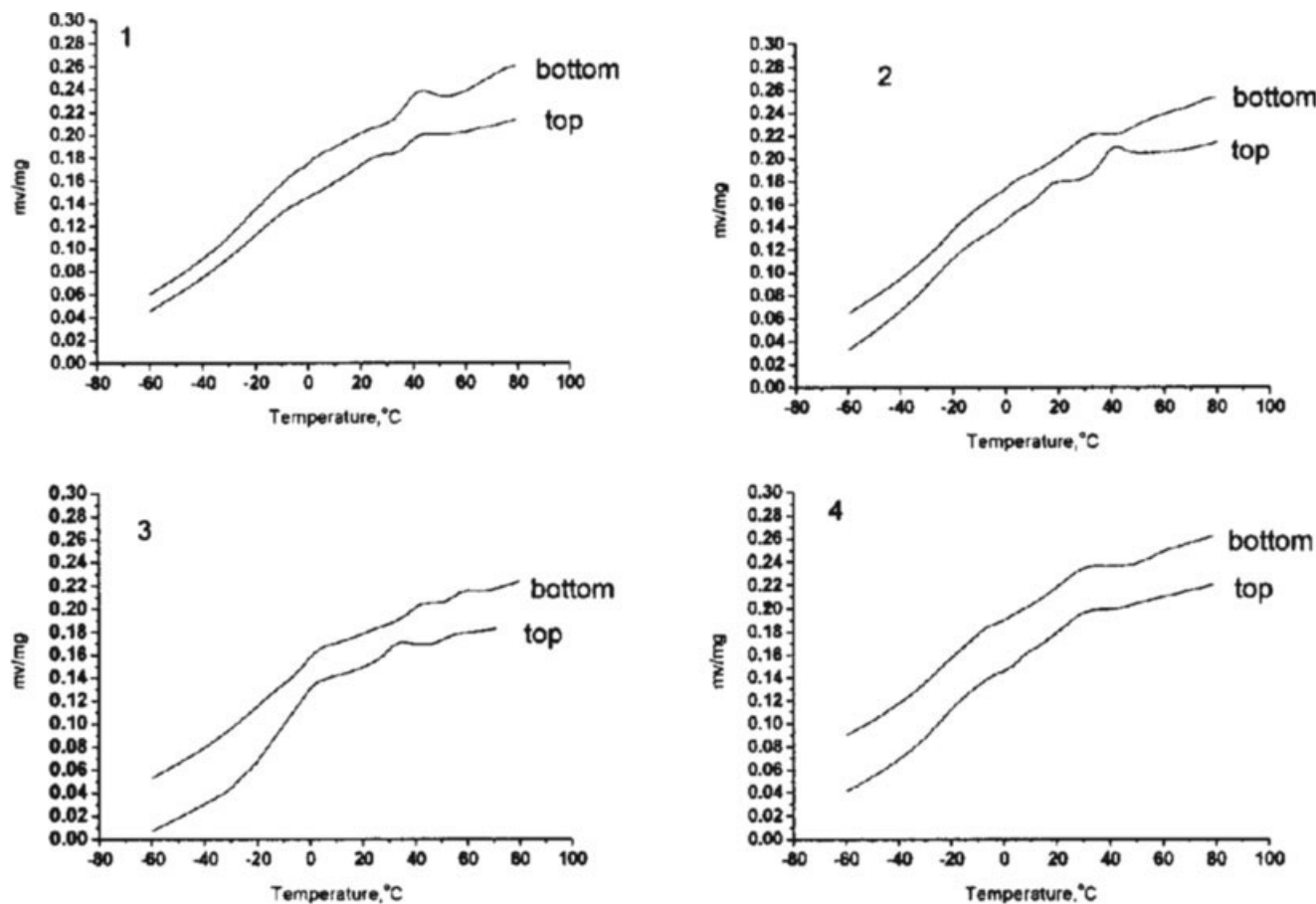

Figure 7   DSC curves of SBS-modified asphalt: (1) SBS, (2) SBS–OH, (3) SBS–N, and (4) SBS–COOH.

SBS by an *in situ* anionic polymerization method, it could attract widespread commercial and academic interest. The introduction of end groups did not alter the structure and composition of SBS. Dynamic mechanical analysis suggested that $T_{g,\text{PB}}$ and $T_{g,\text{PS}}$ were influenced slightly after SBS was end-functionalized and E' and E'' increased correspondingly. A TEM image of end-functionalized SBS suggested that the shape of the PS domains changed from uniform spheres in SBS to disordered, incompact strips in end-functionalized SBS.

By comparing the softening points and DSC curves of end-functionalized and nonfunctionalized SBS-modified asphalt, we concluded that end amino and carboxylic acid were useful in improving the storage stability and compatibility of SBS-modified asphalt.

References

1. Adedeji, A.; Grenfelder, T.; Bates, F. S.; Macosko, C. W. Polym Eng Sci 1996, 36, 1707.
2. Masson, J.-F.; Pelletier, L.; Collins, P. J Appl Polym Sci 2001, 79, 1034.
3. Wen, G.; Zhang, Y.; Zhang, Y.; Sun, K.; Fan, Y. Polym Test 2002, 21, 295.
4. Masson, J. F.; Collins, P.; Robertson, G. Energy Fuels 2003, 17, 714.
5. Jew, P.; Shinizu, J. A.; Svazic, M.; Woodhams, R. T. J Appl Polym Sci 1986, 31, 2685.
6. Fawcett, A. H.; Mcnally, T.; Mcnally, G. M.; Andrews, F.; Clarke, J. Polymer 1999, 40, 6337.
7. Engel, R.; Vidal, A.; Papirer, E.; Grosmangin, J. J Appl Polym Sci 1991, 43, 227.
8. Kluttz, R. Q.; Erickson, J. R. U.S. Pat. 5,451,619 (1996).
9. Hesp, S.; Liang, Z.; Woodhams, R. T. U.S. Pat. 5,494,966 (1996).
10. Hsieh, H. L.; Quirk, R. P. Anionic Polymerization: Principle and Practice; Marcel Dekker: New York, 1996.
11. Young, R. N.; Quirk, R. P.; Fetter, L. J. Advances in Polymer Science: Anionic Polymerization of Non-polar Monomers Involving Lithium; Spring Berlin: Heidelberg, 1984.
12. Quirk, R. P.; Yin, J.; Cuo, S. H.; Xiao, W.; Summers, G.; Kim, J.; Zhu, L. F.; Schock, L. E. Makromol Chem Macromol Symp 1990, 32, 47.
13. Lee, M.; Cho, B. K.; Lin, W. C. Chem Rev 2001, 101, 3869.
14. Jones, T. D.; Macosko, C. W.; Moon, B.; Hoye, T. R. Polymer 2004, 45, 4189.
15. Fetter, L. J.; Grasessley, W. W.; Hadjichristidis, N.; Kiss, A.; Pearson, D. S.; Younghouse, L. B. Macromolecules 1988, 21, 1644.
16. Soobum, C.; Chang, D. H. Macromolecules 2003, 36, 6220.
17. Milkovich, R. U.S. Pat. 4,417,029 (1983).
18. Quirk, R. P.; Jing-Jing, M. J Polym Sci Part A: Polym Chem 1988, 26, 2031.
19. Fallais, J.; Devaux; Jerome, R. J Polym Sci Part A: Polym Chem 1998, 26, 2031.
20. Katsuhiko, T.; Akira, H.; Nakahama, S. Macromol Chem Phys 1995, 196, 1687.
21. Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. Macromolecules 1998, 31, 3759.
22. Fallais, J.; Jerome, R. J Polym Sci Part A: Polym Chem 2000, 38, 1618.
23. Hall, J. E.; Lawson, D. F. Eur. Pat. EP 069355 (1995).
24. Klaus, K. U.S. Pat. 4,816,520 (1989).
25. Koning, C.; Ikker, A.; Boggreve, R.; Leemans, L.; Moller, M. Polymer 1993, 34, 4410.
26. Klaus, K. U.S. Pat. 4,753,991 (1988).
27. Koptelov, Y. B.; Kim, M. K.; Molchanovm, A. P.; Kostikov, R. R. Russ J Org Chem 1999, 35, 1182.
28. Sardelist, K.; Michels, H. J.; Allen, G. Polymer 1984, 25, 1011.
29. Ueda, K.; Hirao, A.; Nakahama, S. Macromolecules 1990, 23, 939.
30. Sela, M.; Berger, A. J Am Chem Soc 1955, 77, 1893.
31. Roderic, P. R.; Yin, J.; Lewis, J. F. Macromolecules 1989, 22, 85.
32. Huy, T. A.; Hai, L. H.; Adhikari, R.; Weidisch, R.; Michler, G.; Knoll, K. Polymer 2003, 44, 1237.
33. Rong-Ming, H. O.; Adeyinka, A. J.; David, W. G. J Polym Sci Part B: Polym Phys 1997, 35, 2857.
34. Guo, Y.; Jiang, Y. M.; Zhang, A. M. Polym Mater Sci Eng (China), 2003, 19, 144.