Macrophase Separation in Styrene−Butadiene Block Copolymers Driven by Thermooxidative Reactions

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ABSTRACT: Macroscopic phase separation has been observed in a commercial styrene-*b*-butadiene-*b*-styrene (SBS) triblock copolymer (Kraton 1102) upon exposure to atmospheric oxygen at elevated temperatures. A thermooxidative reaction occurs in the unsaturated bonds of polybutadiene segments which in turn causes the copolymer chains to break, resulting in macrophase separation between polystyrene-rich copolymer and polybutadiene segments. The macrophase separation driven by thermo-oxidative degradation has been further confirmed in as-synthesized SBS triblock and also in as-synthesized SB diblock copolymers. While the first macrophase separation proceeds, the radicals that emerged from the thermooxidative chain breakage undergo cross-linking, thereby driving phase separation to occur for a second time. The occurrence of the second phase separation may be hereafter termed “cascading phase separation”. Despite the differences in copolymer types and total molecular weights, the structure and growth dynamics of the three styrene−butadiene block copolymers are strikingly similar to each other. Of particular interest is the occurrence of the cascading macrophase separation in neat block copolymers driven by thermooxidative chain scission and cross-linking reactions.

Introduction

Phase transitions in block copolymers have been the subject of continued interest in both academia and industries.[1−5] The major reason is that block copolymers display self-organized microdomain structures that can be controlled through well-established synthesis routes.[1] The self-assembled patterns and concomitant phase transitions make the block copolymers unique that are unprecedented in other materials science disciplines such as metals and ceramics. Some typical microstructures include spherical, cylindrical, and lamellar domains with averaged domain sizes commonly in the range 50−250 nm.[1−3] Recently, a gyroid phase intermediate between cylindrical and lamellar structures has been found.[4,5] Upon variation of temperature, such a microdomain texture undergoes structural transformation from an ordered state to a disordered (isotropic) state, which is called the “order−disorder transition”. Occasionally, a block copolymer may undergo phase transition from one microdomain form to another, which is known as the “order−order transition”.[2−5]

The first commercially successful block copolymers are styrene-*b*-butadiene (SB) and styrene-*b*-butadiene-*b*-styrene (SBS) with varying topologies.[1] When polybutadiene or SBS copolymers are subjected to actual processing conditions and/or service environments, thermooxidative reactions involving chain scission and cross-linking[6−9] take place in polybutadiene chains as well as in SBS copolymers.[10,11] In a recent work on high-impact polystyrene (HIPS), Israeli and co-workers[10] observed the occurrence of thermooxidative reactions at temperatures as low as 80 °C; the reaction rate is expedited with increasing temperature. It was shown that the thermooxidative reaction starts on the surface and then penetrates into the bulk. Recently, Holjevac and Rek[11] examined the kinetics of thermooxidative degradation in HIPS as well as SBS by thermal analysis. They found that the rate of thermooxidative degradation depends on the polybutadiene content; namely, the reaction rate of the SBS block copolymer is seemingly expedited relative to the HIPS. Wang et al.[12] confirmed, through use of in situ infrared spectroscopy, the occurrence of thermal oxidative degradation of a SBS triblock copolymer during annealing at 131 °C.

Recognizing the possible degradation of butadiene blocks, researchers have paid careful attention to experiments that involve styrene−butadiene block copolymers.[13−15] For instance, in the establishment of cloud point phase diagrams of blends of polystyrene (PS)/polybutadiene (PB) and PS/SB or SBS block copolymer, it is a common practice to vacuum-seal the samples in order to prevent thermooxidative reactions.[13] The observed transition temperatures of the copolymer and the UCST coexistence curve turned out to be quite high despite the choice of the low molecular weight pairs. In an effort to avoid thermal degradation, the determination of phase diagrams has been limited only to very low molecular weight blends of homopolymers and block copolymers so that the coexistence curve would be suppressed to sufficiently low temperatures.[14,15]

Such studies on low molecular weight homopolymer/copolymer blends are interesting in their own right, but commercial utilization of these low molecular weight species, except for some pressure-sensitive adhesives, is not practical in many situations. Furthermore, not all experimental works of SB block copolymers were conducted in an oxygen-free environment, particularly industrial practices. In fact, commercially useful SB or SBS block copolymers are of relatively high molecular weights that are customarily processed in open air at elevated temperatures (>150 °C).

It is natural to witness growing interest in thermal degradation behavior of SB block copolymers subjected to thermooxidative environment. Thus, most studies have focused on the elucidation of chemical reaction steps (or mechanisms)[6−8] of thermooxidative degradation of neat polybutadiene. It was found that thermal

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oxidation in PB segments leads to chain scission and/or cross-linking. The same mechanism was hypothesized to occur in the thermooxidative degradation of SB or SBS block copolymers.[10,11] Pearce and Kwei et al. reported the thermal oxidation and photooxidation induced phase separation in blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) upon exposure to annealing (at 110 °C) and/or photooxidation at 30 °C which are supposedly in the miscible region below the lower critical solution temperature.[16,17] The molecular weight of PVME decreases with increasing oxygen uptake. The resulting PVME radicals then cross-reacted with PS that led to chain scission in PS. Since the decrease in molecular weight of an LCST system generally causes the coexistence curve to move up, the authors concluded that the change in chemical structure of PVME due to oxidation is the primary cause of phase separation.[16,17]

In this paper, the thermooxidative reaction driven macrophase segregation and morphology development in the styrene−butadiene block copolymers have been investigated by means of optical microscopy, time-resolved light scattering, thermal analysis, and gel permeation chromatography in conjunction with gel content determination. A commercial SBS block copolymer (Kraton 1102), as-synthesized SBS triblock copolymer, and as-synthesized SB diblock copolymer having different molecular weights were utilized. Emphasis has been placed on careful experimentations under conditions close to the actual processing temperatures in open air. Experimental evidence revealed that thermooxidative chain scission indeed occurs, which in turn drives macrophase separation between the styrene-rich copolymer and butadiene segments.[18] Concurrently, the cross-linking reaction takes place predominantly in the butadiene segments of the copolymer, which in turn induces a second macrophase separation.

Experimental Section

A commercial SBS block copolymer (Kraton1102) was supplied by Shell Chemical Co. According to the vendor, the weight-average molecular weight (M_w) of Kraton 1102 having 28% styrene content was about 70 000. It is worth noting that some 20% SB diblock copolymers were incorporated in Kraton 1102 (triblock) during anionic copolymerization to improve melt processability. The experimental grade SB and SBS block copolymers were received from Bridgestone/Firestone Research, Inc. These experimental grade (hereafter called as-synthesized) SB (32% styrene) and SBS (33% styrene) block copolymers have the peak molecular weights of 54 000 and 105 000, respectively, calculated using polystyrene standards.

The block copolymer films were prepared by first dissolving each polymer in toluene to obtain 5% w/w solution, and then two aliquots of the solution were spread on a glass slide to form a thin film with a thickness ca. 10 μm. All samples were left in open-air overnight and then dried in a vacuum oven for 24 h at 50 °C. These samples were further dried at 80 °C for 12 h and finally at 110 °C for 1 h in a vacuum. The film samples used for thermal analysis were prepared following the aforementioned procedure, except that the films were much thicker than that used in the microscopic studies, i.e., ca. 500 vs 10 μm.

The optical micrographs were taken on an optical microscope (model: Optiphot-2 from Nikon Corp.) equipped with a Nikon camera that was connected to an exposure controller (model: UFX-DX, Nikon). A Mettler hot stage (model FP82HT) was used for temperature control. The cloud point measurements were carried out at an arbitrary angle of 20° for most samples unless indicated otherwise. A randomly polarized 2 mW He−Ne laser (LSR2R, Aerotech) with a wavelength of 632.8 nm was utilized as a light source. The scattered light intensity was detected using a photodiode (62/3A27, Pacific Instrument). A temperature controller (model 2012, Omega) was used to control the temperature of the sample holder consisted of a heating block and a cover. The heating rate was 1 °C/min unless indicated otherwise. Time-resolved light scattering experiments were performed using a one-dimensional silicon diode Reticon detector (model 1452A, EG&G) coupled with an optical multichannel analyzer (model 1460, OMA II, EG&G).

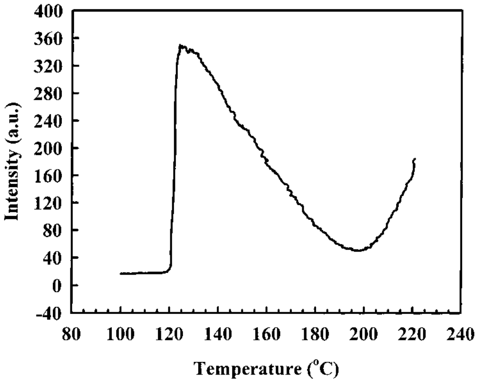

Figure 1. Change of scattered intensity of Kraton 1102 during the course of heating. The heating rate was 1 °C/min.

A Du Pont thermal analyzer, model 9900, with a heating controller, model 910, was employed in thermal investigations. Differential scanning calorimetry (DSC) curves were recorded at several isothermal temperatures. The temperature calibration was carried out based on the indium standard. Thermogravimetric analysis (TGA) measurements were conducted using a Du Pont thermogravimetric analyzer, model 951. A heating scan was undertaken at a slow heating rate (1 °C/min) in the TGA measurements.

Gel permeation chromatography (Waters) equipped with a high-pressure liquid chromatography (HPLC) pump (model 510) and a differential refractometer (model 410) was utilized in the determination of change of molecular weight and distribution with isothermal heat treatment time. Three separation columns with pore sizes of 10^2, 10^3, and 10^4 Å were utilized. Tetrahydrofuran (THF) was used to dissolve the block copolymers before and after thermal treatment (for various annealing times). The molecular weights of the dissolved copolymers were determined using polystyrene standards. Regarding the gel content determination, the samples with or without heat treatment were refluxed for 24 h using THF. The undissolved residue was weighed, and its percentage was regarded as the gel content.

Results and Discussion

Figure 1 exhibits a complex variation of the scattered intensity during the course of heating for Kraton 1102. The scattered intensity shows a sudden jump at 120−125 °C. With continued heating, the intensity decays and levels off, and then the intensity increases again. The microstructures of the block copolymers are known to be of nanosize. In order for the emerging structures to be sensed by light scattering, the average domain size must be in the range of wavelength of visible light. A natural concern is why the copolymer would cause scattering of light during the course of heating. Although light scattering data alone would be inadequate to postulate any mechanism, it is tempting to interpret the behavior such as initial rise and subsequent decay of scattered intensity as the emergence of some heterogeneous structures accompanied by phase dissolution.

To gain further insight into the emerging morphology, optical microscope pictures were taken for the Kraton copolymer as a function of time during isothermal

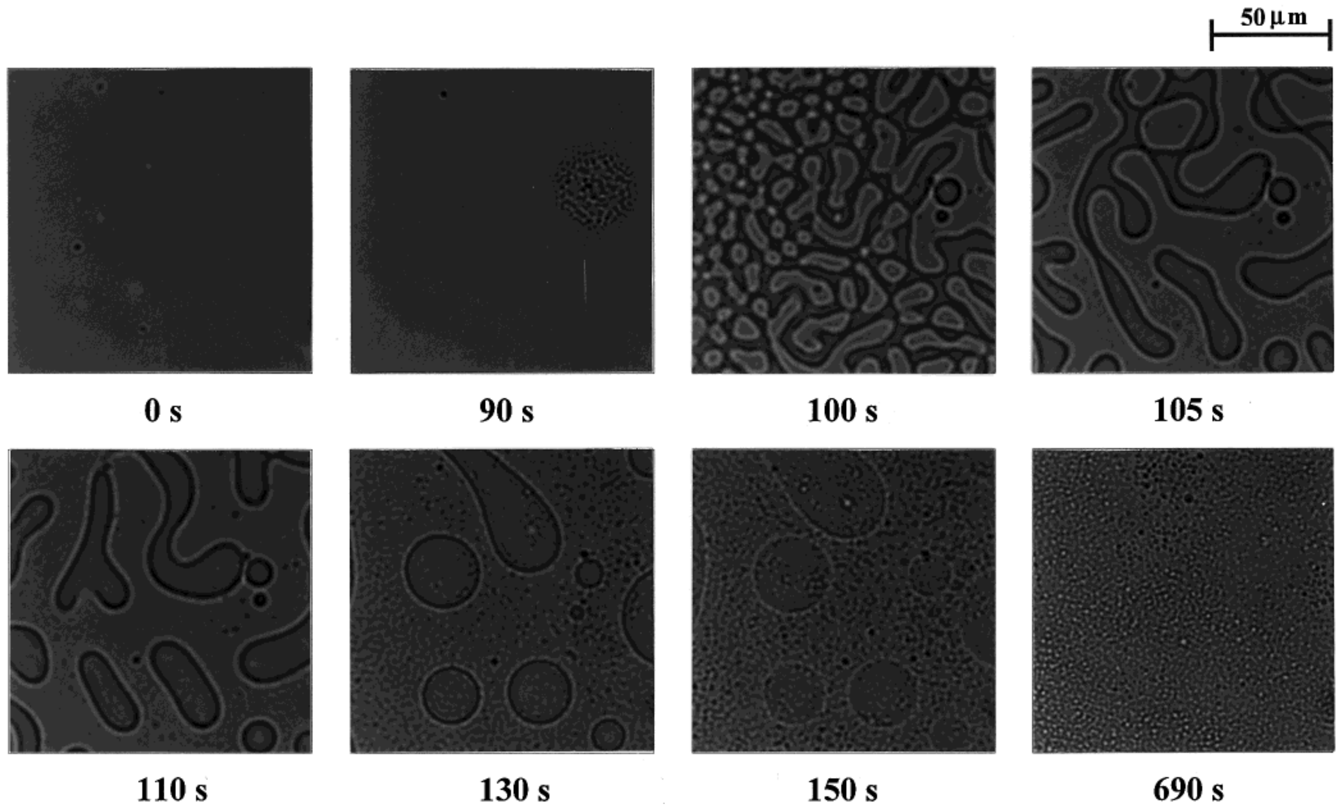

Figure 2. Optical micrographs showing temporal evolution of phase-separated morphology of Kraton 1102 subjected to heat treatment at 170 °C.

heating in open air at various temperatures from 150 to 170 °C. Figure 2 depicts the temporal evolution of domain structure of Kraton 1102 at 170 °C. There are several noteworthy observations: (i) The picture of the original copolymer film is featureless, suggestive of a homogeneous structure at least at the optical length scale, but the micron-sized phase-separated domains develop after a short induction period. (ii) The initial domain structure is, although by no means a proof for spinodal decomposition (SD), reminiscent of a SD-like bicontinuous structure. (iii) The SD-like domains grow through coalescence to larger interconnected shapes that eventually break down into droplets driven by surface tension. (iv) New tiny droplets develop in the dispersed domains as well as in the matrix suggestive of a second macrophase separation, hereafter called “cascading phase separation”. The secondary macrodomains show little or no growth in size, which are presumably fixed by chemical or physical pinning. (v) It is interesting to discern a distinct interface in the micrographs; however, the interface fades away (see at 690 s) as the refractive index contrast between the dispersed phase and the matrix diminishes at prolonged heating times. Such changing morphological behavior is quite different from the regular phase separation driven by thermal quenching.

A similar experiment was undertaken at two other temperatures of 150 and 160 °C. Within the temperature range investigated, the phase-separated structures are quite similar[16] (pictures not shown here) to those of 170 °C. Time-resolved light scattering experiments were undertaken to mimic the growth dynamics of the first phase separation process. Figure 3 shows the plots of scattering wavenumber maxima versus heat treatment time for Kraton 1102 as a function of annealing temperatures. The growth dynamic curves for three different temperatures are quite similar except that the onset of phase separation is expedited at higher temperatures. The growth curve is by no means linear, showing a subtle curvature (or a hump, e.g., 150 °C of Figure 3) at an intermediate region. Strictly speaking, the classical temporal scaling law may not be applicable to the entire range of growth in the present macrophase separation. If one approximates the slope in the limited time scale at the late stage, the growth exponent is close to unity, which corresponds to the hydrodynamic regime in systems undergoing thermally induced phase separation.

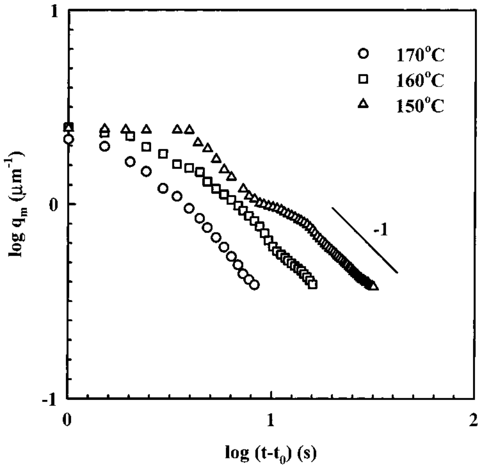

Figure 3. Growth dynamic curves of Kraton 1102 obtained by time-resolved light scattering at indicated temperatures.

A natural question is what kind of phase separation is taking place in Kraton 1102. One can rule out the microscopic phase separation because the microdomain structures in block copolymers are too small to be

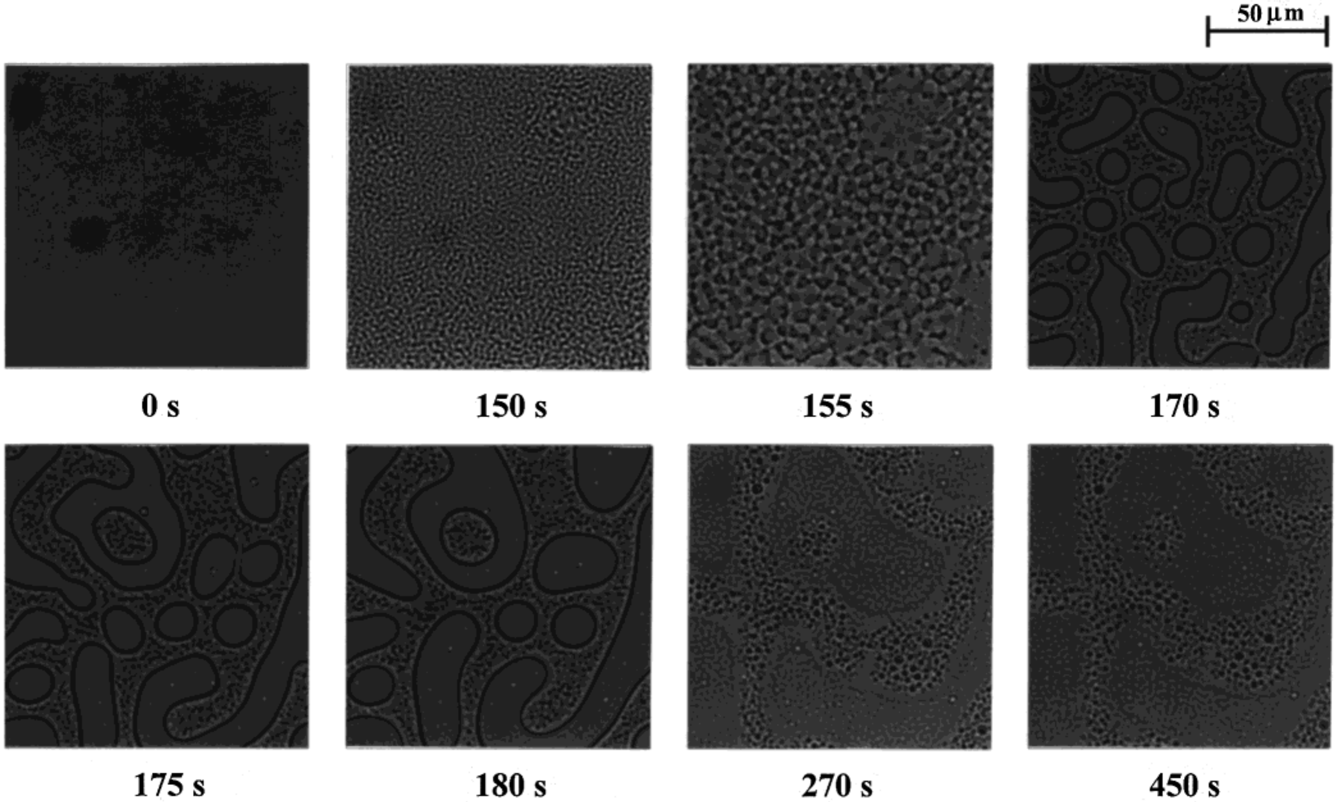

Figure 4. Optical micrographs displaying macroscopic phase separation in as-synthesized SBS triblock copolymer at 170 °C.

detected by light scattering or optical microscopy. Furthermore, the order−disorder transition temperature, T_{ODT}, for Kraton 1102 was reported to be 220 °C,[15] which is significantly higher than the observed phase change at 120 °C. One possible account is that Kraton 1102 is known to be a mixture of SBS triblock and SB diblock copolymers; therefore, the block copolymer mixture could segregate at elevated temperatures. However, the refractive index contrast between the SBS and SB blocks may not be sufficient to cause scattering of light. Another possibility is the thermooxidative chain scission could drive macroscopic phase separation between polybutadiene and butadiene/styrene copolymer segments. To clarify this issue, we conducted similar experiments individually on neat SBS triblock and neat SB diblock copolymers.

Figure 4 shows optical micrographs manifesting macroscopic phase separation in the SBS copolymer at 170 °C. The emergence and growth characteristics of the phase-separated domains of the Kraton 1102 can be reproduced in the neat SBS. That is to say, macrophase separation occurs almost spontaneously, and then the domains grow through coalescence with an essentially similar morphology. The overall similarities in phase-separated structure and growth behavior suggest that macrophase separations in the Kraton 1102 and the as-synthesized neat SBS copolymers probably share the same origin. Since no detectable amount of diblock copolymer is present in the as-synthesized SBS, macrophase separation may be induced by change in chemical structures of the copolymer due to thermal degradation, presumably chain scission.

In a subsequent study on the as-synthesized SB diblock copolymers, the occurrence of macroscopic phase separation can also be confirmed. The emergence of macrophase-separated domains and growth habits in the SB are strikingly similar to those of Kraton 1102 and the as-synthesized SBS block copolymers (pictures are not shown). In addition, the temporal growth curves (scattering wavenumber maximum versus time plots) of the SB and SBS obtained at 170 °C are quite similar (Figure 5) and appear quite consistent with those of Kraton 1102, showing a hump in the growth curves. Despite the fact that the block copolymer types and total molecular weights are different, the same phenomenon occurs in the as-synthesized SBS and SB copolymers. Hence, the possibility of macrophase separation between diblock copolymer and triblock copolymer in Kraton 1102 seems highly unlikely.

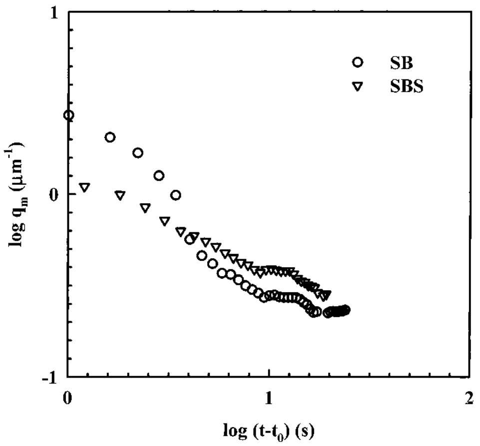

Figure 5. Growth dynamic curves for the as-synthesized SB diblock and SBS triblock copolymers at 170 °C as obtained by time-resolved light scattering.

If thermal degradation were to occur in the block copolymer, an intriguing question that may be raised is why the emerging structures and the growth habits have to be regular and systematic and why phase

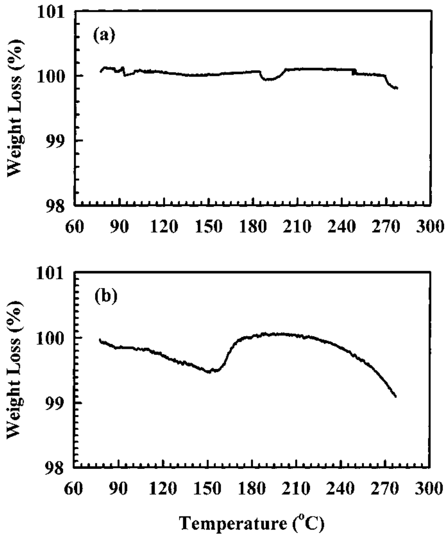

Figure 6. Plots of TGA weight change versus temperature (a) under nitrogen circulation and (b) in open air. The heating rate was 1 °C/min.

separation would occur for a second time. This unusual observation makes us to believe that thermal degradation may be more complex than hitherto reported. In fact, in-chain butene unsaturated double bonds and pendent vinyl double bonds of the butadiene blocks are known to be thermally unstable at elevated temperatures, especially when the copolymer chains are in contact with atmospheric oxygen.[19] The thermooxidative reaction in the butadiene segments causes the block copolymer to break, resulting in macrophase separation. In the nitrogen environment, macrophase separation of the copolymer could not be detected under optical microscopic observation in the temperature range 150−170 °C, which in turn points to the need for active oxygen in the thermooxidative reactions. It is reasonable to infer that the thermooxidation may be the cause of macroscopic phase separation in block copolymers. The same thermooxidative reaction is believed to occur in random SBR, but no macroscopic phase separation could be discerned due to the lack of contrast between the fragmented random SBR copolymers.[18]

To verify the thermooxidative reactions, TGA runs were undertaken on the as-synthesized SB diblock. Parts a and b of Figure 6 represent the plot of weight change versus temperature under nitrogen environment and in open air, respectively. It is seen that under the nitrogen protection the sample weight remains virtually constant up to 200 °C, indicating thermal stability of the copolymer within the temperature range investigated. On the other hand, the sample in open air showed a minor weight reduction from 80 to 150 °C, and then drastic weight gain occurs with continued heating. The initial minor weight loss is probably due to loss of some volatile low molecular weight ingredients. The observed weight gain is known to be due to oxidation which in turn generates radicals. Such oxidative reaction has been well documented as one of the most important steps in polymer degradation. The radicals further attack the unsaturated double bonds, forming hydroxyl, carbonyl, carboxyl, or peroxide groups, thereby resulting in weight gain. It is noticed that the onset temperature of the weight increase is slightly higher than that observed in the light scattering experiment. This minor discrepancy is not surprising in view of the fact that the samples used in TGA experiments were much thicker than the ones used in the light scattering measurement. Since the active oxygen has to permeate from the surface to the bulk, a longer time (or a higher temperature) is required for a thicker film to reach the same oxidation level.

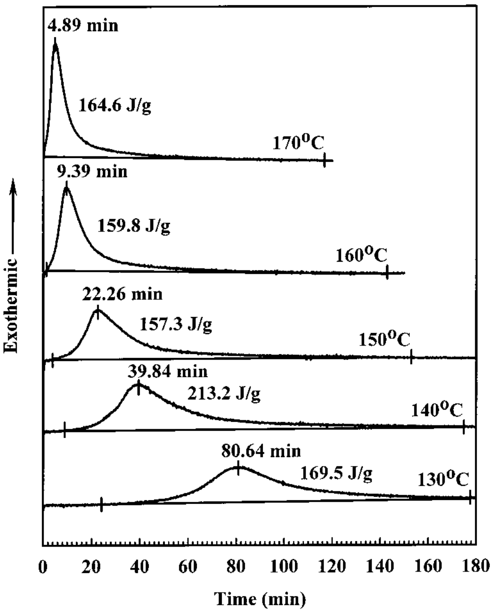

Figure 7. Isothermal DSC scans for the as-synthesized SB diblock as a function of heat treatment time.

The oxidative reaction was further explored in the isothermal DSC experiments on three block copolymers. However, in view of the similarity in phase decomposition behavior among these copolymers, only the DSC isotherms for the SB diblock are shown in Figure 7. In all cases, a single exothermic peak can be discerned, which has been ascribed to oxidative reactions. As expected, the time for the maximum heat release is expedited with increasing isothermal temperature. At 170 °C, the reaction began almost instantly with the exothermic peak being higher and much narrower than those at lower temperatures, which implies a faster reaction rate at higher temperatures. It should be emphasized that the reaction peak can be discerned in the SB copolymer at a lower reaction temperature of 130 °C.

In the literature,[6−9] chain scission and cross-linking have been considered to be the prevalent mechanisms in the oxidative reaction. In order for phase separation to occur between polystyrene-rich copolymer and butadiene segments, chain scission must take place in the block copolymer upon contact with atmospheric oxygen. To determine possible mechanisms of the thermooxidative reaction, GPC experiments were conducted on the SB diblock copolymer by exposing it to 160 °C in open air as a function of exposure time. The heat-treated samples were collected at various time intervals and subsequently dissolved in THF for GPC measurements. The undissolved portion was taken as the gel content.

Figure 8 exhibits the evolution of GPC traces as a function of heating time for the SB diblock. A single peak is discernible at a retention volume of about 17.8 mL for the starting sample. This peak remains stationary for an initial heat treatment of 60 s. The magnitude (or intensity) however reduces noticeably from 120 to 180 s. Concurrently, a broad secondary peak emerges at 120 s (around 19.3 mL) and intensifies while shifting gradually to a higher retention volume with the pro-

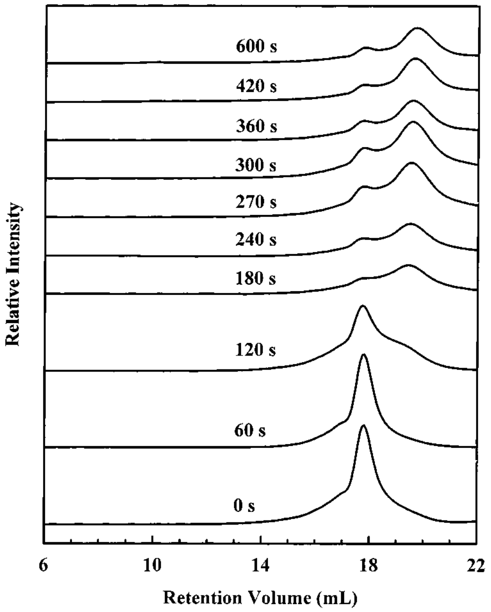

Figure 8. Evolution of GPC traces of the SB diblock as a function of heat treatment time.

gression of heat treatment time. The initial decay of the first peak and the emergence of a second peak suggest the loss of diblock copolymers due to chain scission, resulting in low molar analogues. The dramatic decrease of the first peak indicates that a sizable amount of the original SB diblock has undergone chain scissions. However, the first peak persists all the way to 600 s, implying that a small amount of SB diblock may be left unperturbed. In the thermooxidative chain scission, it takes time for active oxygen (or peroxide radicals) to permeate from the surface to the bulk.

To analyze the change of molecular weight, the peak molecular weight, M_p, was plotted against heat treatment time in Figure 9a. The molecular weight measured here is based on the polystyrene standards, and thus it is higher than the universally corrected values for the as-received copolymers. The initial thermal treatment of the block copolymers inevitably resulted in a broader molecular weight distribution. It can be noticed that the M_p value of the first peak is essentially stationary before and after heat treatment, thereby supporting the aforementioned idea that the first peak is indeed due to the original SB diblock copolymer. However, the emerging second peak corresponding to the PS-rich copolymer is the manifestation of the chain scission in the block copolymer. The gradual decline of M_p from 120 to 600 s is due to the progressive chain scission. When a SB diblock copolymer chain breaks down, it occurs predominantly in the polybutadiene block segments. It is believe that when chain scission continues, more and more butadiene segments are detached from the PS-rich copolymer chains. As evidenced by the sharpening of the second peak, the depletion of butadiene transforms the PS-rich copolymer to the pure PS segment. This scenario may be envisaged as equivalent to chain scission occurring near the chemical junction.

The change of molecular weight of the copolymer is more drastic in the plot of the overall average molecular weight versus time plot (Figure 9b). Both M_w and M_n reduce in a sigmoidal manner, showing a gradual decrease for a short initial period and then dramatically decline with continued heat treatment from 120 to 240 s. Beyond 360 s, both average molecular weights

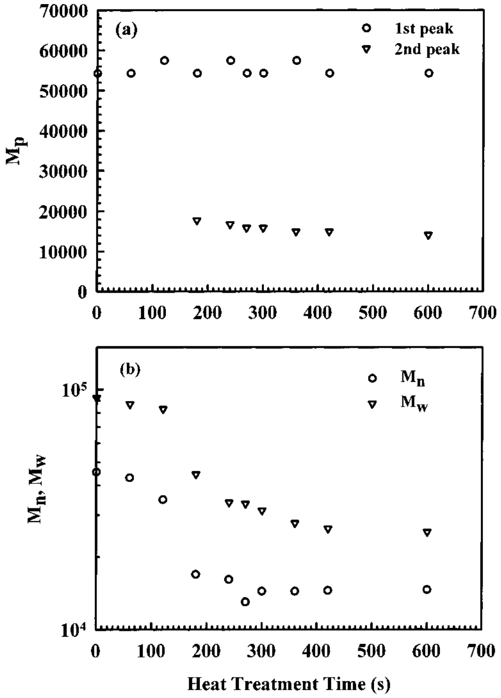

Figure 9. Change of molecular weight of the SB diblock as a function of heat treatment time: (a) peak molecular weight and (b) weight-averaged and number-averaged molecular weight calculated based on the PS standards.

asymptotically level off. Careful examination of the molecular weights suggests that the SB diblock chains break down into polystyrene-rich copolymer, presumably having very short butadiene segments and low molecular weight polybutadiene. Because of the immiscibility between the resulting polystyrene-rich copolymer and polybutadiene chains, macrophase separation is believed to take place.

In thermooxidative reaction of neat polybutadiene and SB copolymers, cross-linking is known to occur in addition to chain scission. Although GPC is useful in probing the change of molecular weight of the dissolved portion of the copolymer, it cannot measure the molecular weight of the undissolved gels (or networks). The progression of the cross-linking reaction has been followed through the measurement of gel content from the undissolved portion in THF for various heat treatment times. The gel content itself may be too rough an estimate for the molecular weight determination, but the relative change of the gel content in time may be useful as a guide as to how the molecular weight increases with the progression of cross-linking. As shown in Figure 10, the gel content is virtually zero in the initial period of 60 s. However, it increases gradually to 5.6% in 240 s, suggesting the onset of cross-linking. Subsequently, the gel content shows a dramatic jump to 28% in the vicinity of 300 s. Comparing with Figure 9b, it appears that the cross-linking reaction starts concurrently with the oxidative chain scission. It is reasonably to infer that the chain scission dominates in the early stage of thermooxidative reaction, but the cross-linking reaction becomes dominant at later times. It is this copolymer chain breakage that has led to macroscopic phase separation between styrene-rich copolymer and polybutadiene segments. The cascading phase separation, showing the emergence of secondary domains, may be attributed to the domination of the cross-linking reaction.

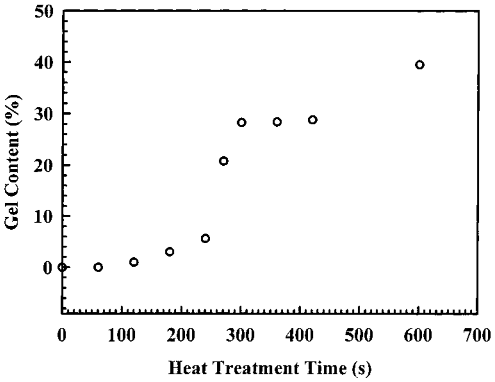

Figure 10. Change of gel content as a function of heat treatment time for the SB diblock.

Conclusions

We have observed macroscopic phase separations in a commercial Kraton 1102, as-synthesized SBS triblock, and as-synthesized SB diblock copolymers upon exposure to air at elevated temperatures, caused by the chain breakup in the SB block copolymers associated with the thermooxidative reaction. Of particular interest is the existence of plateau (hump) of wavenumber maximum with time, as well as the increase of wavenumber maximum in the later stage of phase separations, which may be attributed to the consequence of the competition between chain scission and cross-linking. Another interesting feature is the second phase separation, showing the development of tiny droplets within the preformed domains as well as in the matrix. This secondary phase separation is probably triggered by the cross-linking.

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