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Reaction Kinetics of Thermooxidative Degradation in a Styrene-*b*-butadiene Diblock Copolymer

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ABSTRACT: Reaction kinetics of thermooxidative degradations in a styrene-*block*-butadiene diblock (SB) copolymer has been investigated by taking into consideration oxidative chain scission and cross-linking reactions. The gel permeation chromatography (GPC) study revealed that the chain scission not only lowers the overall molecular weight of the copolymer but also drives macrophase separation between polystyrene-rich copolymer and polybutadiene segments. As evidenced in the gel content determination, the molecular weight increases rapidly when the cross-linking reaction becomes dominant. To describe the thermooxidative reaction in the SB copolymer, we propose a simplified reaction scheme in which macrophase separation occurs between polystyrene and polybutadiene segments. Numerical calculations showed that our kinetic model indeed captures the experimental trends such as initial reduction and subsequent increase in molecular weight. The location of concave minimum in the molecular weight vs time curve was found to depend on the competition between the rates of chain scission and of cross-linking reactions. The effect of kinetic parameters on the variation of molecular weight of the diblock has been demonstrated.

Introduction

Thermooxidative degradation in polymers during melt processing and/or service environments has been known to be one of the most crucial processes that profoundly affects mechanical and physical properties of the materials.[1−7] Even though thermooxidative reactions in homopolymers appear fundamentally complicated, the most significant effects are well documented that involve changes in chemical structure, molecular weight, and its distribution. Often new functional groups are formed at chain ends during the thermooxidative reaction. Such chemical and physical changes in the block copolymers exert profound influence not only on the structure-forming aspects and growth dynamics pertaining to macroscopic phase separation between the constituent copolymer segments but also on physical and mechanical properties of the resulting materials.

In principle, a polymer could degrade at elevated temperatures even without exposing to air. However, degradation is always faster in the presence of oxygen. Oxidation of hydrocarbons is normally an autoaccelerating reaction in which the rate is negligibly slow initially, but it gradually expedites before reaching asymptotically a constant value. The rate of oxidation is largely determined by the diffusion rate of active oxygen into the bulk and subsequent cross-linking reaction,[1,2] and thus sample thickness plays a crucial role in thermooxidative degradation. In thick samples, it takes a longer time for the reaction to propagate from the polymer surface to the bulk interior. At a low oxygen pressure, alkyl radicals could couple among themselves and/or with peroxide radicals, forming chemical cross-links. In unsaturated polymers, epoxide would appear as more significant products, making chain scission and cross-linking to be of secondary importance as oxidation proceeds.

Degradation kinetics has been studied for over a half century; however, most works have focused on either chain scission or cross-linking reaction in homopolymers[1−6] and to a lesser extent in copolymers.[7] For polybutadiene, it has been shown that the thermooxidative degradation occurs through chain scission and cross-linking;[1] however, there is little or no report on the kinetics of the aforementioned two competing processes. In a recent work on the kinetics of thermooxidative degradation of styrene-*block*-butadiene-*block*-styrene (SBS) triblock copolymer, the degradation process was treated in the context of a macro-kinetic model.[7,8] In fact, such a macro-kinetic model has been widely employed to describe cross-linking or condensation reaction; therefore, the chain scission has been largely neglected in the literature.

In a previous paper,[9] we reported the experimental observation of macroscopic phase decomposition in styrene−butadiene (SB) block copolymers, including a commercial copolymer (Kraton 1102), as-synthesized SBS triblock, and as-synthesized SB diblock copolymers subjected to atmospheric oxygen at elevated temperatures. It has been demonstrated that thermooxidative reaction is the origin of the macrophase separations between polystyrene-rich copolymers and polybutadiene segments. More specifically, the thermooxidative degradation involves chain scission and cross-linking reactions in which the chain scission prevails in the early stage of phase separation, but cross-linking becomes dominant at a later time.[9]

In the present paper, we focused our attention on modeling of the reaction kinetic equation pertaining to thermooxidative degradation of SB diblock copolymer. Emphasis has been placed on the elucidation of the competing mechanisms of chain scission and cross-linking reactions that reflects the overall behavior of the average molecular weight change with respect to time. The effects of kinetic parameters on the reaction kinetics and the change of molecular weight have been demonstrated. Of particular importance is that the numerical calculation based on our kinetic model for the thermooxidative reaction shows qualitative agreement with the experimental observations.

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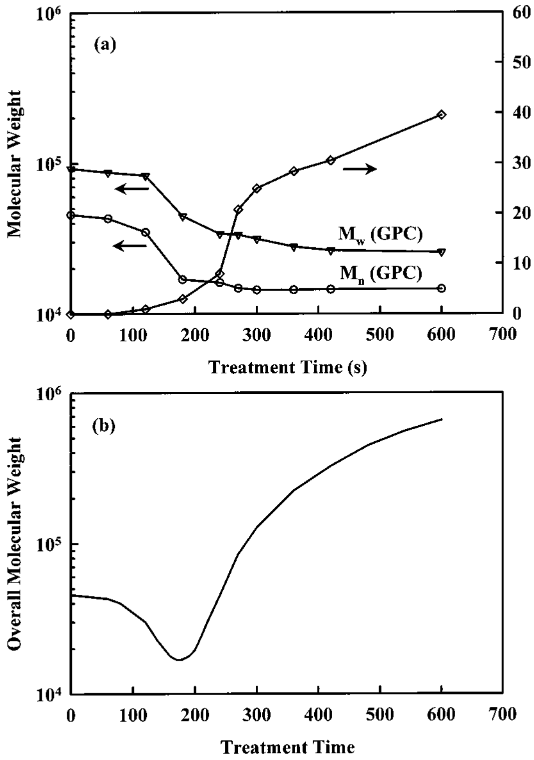

Figure 1. Variation of molecular weight and gel contents of a SB diblock copolymer as a function of heat treatment time. The heat treatment was undertaken at 160 °C.

Results and Discussion

In Figure 1a is shown the temporal change of weight-average (M_w) and number-average (M_n) molecular weights of the as-synthesized SB diblock copolymer and the gel contents. Initially, there is little or no change in the molecular weight of SB up to heat treatment time of 100 s at 160 °C. When the chain scission reaction starts, the molecular weight decreases drastically (100−180 s); i.e., the M_n drops to almost $^1/_3$ of its original value at 180 s. The rapid rise of the gel contents can be discerned around 180−300 s, and then the value levels off asymptotically. It is reasonable to infer that chain scission was the primary process at the initial stage of decomposition, whereas cross-linking dominated in the intermediate to late stages. The combined temporal change of the GPC molecular weight and the gel contents, as represented schematically by the overall molecular weight, show an initial decrease and subsequent increase with time, exhibiting a concave shape as depicted in Figure 1b. Physically, the concave minimum in the overall molecular weight vs time curve is a direct consequence of the competition between the chain scission and the cross-linking reactions controlled by the kinetic parameters of thermooxidative reactions.

Initially, the majority of SB diblock copolymer underwent chain scission, which in turn drives macroscopic phase separation between polystyrene-rich copolymer and pure polybutadiene. When chain scission continues, more and more butadiene segments are believed to detach from the PS-rich copolymer chains. The depletion of butadiene eventually transforms the PS-rich copolymer to the pure PS segment, which may be envisaged as equivalent to chain scission occurring near the chemical junction.

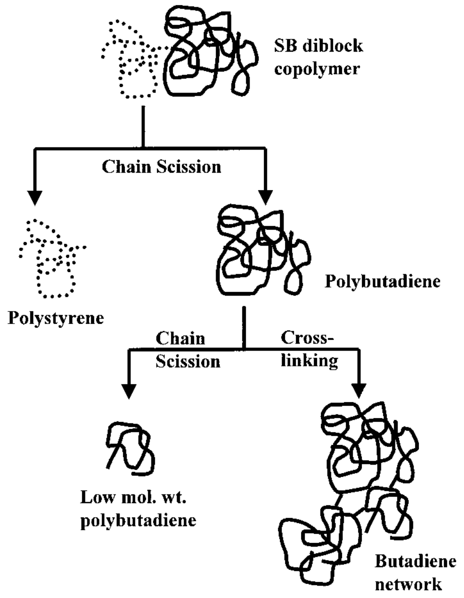

Figure 2. A simplified reaction scheme, showing chain scission and cross-linking reaction in a SB diblock.

Simplified Reaction Scheme

The process of thermooxidative degradation-induced phase separations in SB diblock copolymer is undoubtedly complex. It is assumed that the sample under consideration is sufficiently thin, and the initial chain scission occurs primarily at the chemical junctions; i.e., any residual butadiene segments continue to detach from the polystyrene chains with progressive chain scission such that all diblock copolymer chains are segregated macroscopically to pure polystyrene and polybutadiene segments. With the progression of the reaction, polystyrene chains are assumed to remain nonreactive, but polybutadiene chains undergo further chain scission and/or cross-linking. Again, the cross-linking reaction is expected to be dominant in the later stages, resulting in rapid increase in the average molecular weight of polybutadiene. Such a simplified reaction scheme is represented in Figure 2.

To model the aforementioned simplified reaction, let us consider an average degree of polymerization of butadiene chains, N_B. The rate of temporal change of N_B may be split into two parts, viz., chain scission and cross-linking reactions as follows:

$$\frac{\mathrm{d}N_B}{\mathrm{d}t} = \left.\frac{\mathrm{d}N_B}{\mathrm{d}t}\right|_{CS} + \left.\frac{\mathrm{d}N_B}{\mathrm{d}t}\right|_{CL} \tag{3}$$

where the subscript CS stands for the chain scission whereas CL represents the cross-linking.

For the chain scission, as realized for highly oxidizable hydrocarbons at low oxygen pressure, the following equation holds:[1]

$$-\frac{\mathrm{d}[O_2]}{\mathrm{d}t} = k_i[O_2] \tag{4}$$

where k_i is a kinetic constant and $[O_2]$ denotes the concentration of active oxygen. On the other hand, considering only the random chain scission induced by a pure thermal process, the rate of change of weak links in polybutadiene segments in time is given by[10]

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = k_\mathrm{n} n \tag{5}$$

where n represents the concentration of weak links (or reactive sites for oxygen to attack), which is proportional to the average degree of polymerization, N_B. In the thermooxidative reaction, the reaction rate is determined by the effective collisions between the active oxygen and the weak links; thus, the concentration of active oxygen needs to be factorized into the kinetic equation for the thermooxidative chain scission of polybutadiene chains as follows:

$$\left.\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t}\right|_\mathrm{CS} = -k_\mathrm{s}[\mathrm{O}_2]N_\mathrm{B} \tag{6}$$

where k_s is the kinetic constant for the thermooxidative chain scission.

Now let us consider the cross-linking reaction. To the best of our knowledge, there is no theoretical model that relates the degree of conversion to the average molecular weight of a cross-linked polymer. The overall molecular weight is often taken as infinity after gelation even though it should be finite in practice. In this work, the following expression has been adopted to correlate the degree of conversion, p, to the average degree of polymerization during cross-linking reaction,[10]

$$p = 1 - \frac{1}{N_\mathrm{B}} \tag{7}$$

Note that eq 7 is actually valid only for a typical radical polymerization at low conversions. In the cross-linking reaction, the increase of molecular weight should be much faster than what eq 7 predicts. Although eq 7 appears to be a rough approximation, it should be adequate to describe a qualitative trend. From eq 7, one can easily deduce that

$$\left.\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t}\right|_\mathrm{CL} = {N_\mathrm{B}}^2\frac{\mathrm{d}p}{\mathrm{d}t} \tag{8}$$

In the context of the macro-kinetic approach,[7,8] the rate of conversion for the cross-linking reaction is generally expressed as

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k_p p^m (1-p)^n \tag{9}$$

Note that k_p is the kinetic constant for cross-linking reaction; m and n are reaction exponents. Combining eqs 8 and 9, one obtains the reaction rate equation for the cross-linking part as

$$\left.\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t}\right|_\mathrm{CL} = k_p{N_\mathrm{B}}^2\left(1-\frac{1}{N_\mathrm{B}}\right)^m\left(\frac{1}{N_\mathrm{B}}\right)^n \tag{10}$$

Combining eqs 6 and 10, we obtain the following kinetic equation for the simplified reaction scheme:

$$\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t} = -k_\mathrm{s}[\mathrm{O}_2]N_\mathrm{B} + k_p{N_\mathrm{B}}^2\left(1-\frac{1}{N_\mathrm{B}}\right)^m\left(\frac{1}{N_\mathrm{B}}\right)^n \tag{11}$$

The average degree of polymerization of polybutadiene chains can be calculated based on eqs 4 and 11. It appears that an exact solution of eq 11 may not exist; thus, a numerical solution has been employed using the Runge–Kutta method of order 4 with a volumetric oxygen concentration that is the same as in air, viz., 0.21. When the rate of chain scission is larger than the rate of cross-linking, N_B decreases accordingly, and vice versa, N_B is expected to increase with time. The relative contribution between the first term on the right-hand side of eq 11 representing the chain scission and the second term representing the cross-linking determines the temporal change of the average molecular weight of polybutadiene chains during thermooxidative degradation.

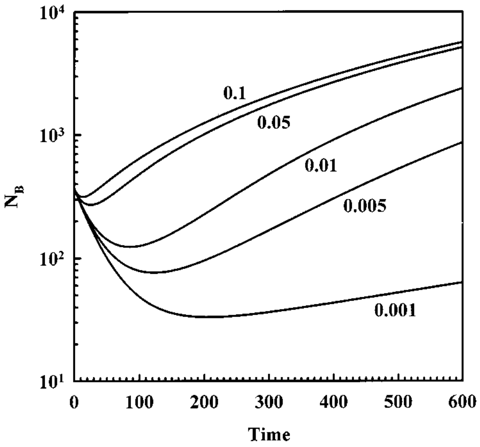

Figure 3. Influence of the rate constant of the peroxide formation, k_i, on temporal dependence of N_B. Individual curves are labeled with the k_i values utilized along with other parameters: $k_\mathrm{s} = 0.2$, $p = 1$, $k_p = 0.2$, $m = 0.5$, $n = 1.5$, and $N_{\mathrm{B}0} = 370$.

Numerical Calculations

As expected, the competition of chain scission and cross-linking can be seen for various kinetic parameters. To better understand the role of kinetic parameters in the thermooxidative degradation of the SB diblock copolymer, we have computed the influence of individual kinetic parameters on the change of the average degree of polymerization of polybutadiene, N_B. Figure 3 shows the influence of the rate constant k_i, which relates to the formation of peroxide radicals, on N_B. It is seen that for small k_i values N_B decreases drastically in the initial stage of chain scission. After reaching the concave minimum in the molecular weight vs time curve, N_B shows an upward turn in the late stage in accordance with the cross-linking. The minimum in the temporal change of k_i curve shifts to a shorter time with increasing k_i. These observations are not surprising because a large k_i value represents a rapid decay of active oxygen concentration. It is envisaged that the excess free radicals expedite the cross-linking reaction. However, when the k_i reaches a certain value (say 0.05), there is no significant change in the kinetic behavior. In practice, k_i may be a time variable due to the changing chemical composition undergoing chain scission and network formation.

Next, we shall examine the effect of kinetic constant of chain scission reaction, k_s, on N_B. As shown in Figure 4, the molecular weight first decreases due to the chain scission, and then after reaching a minimum it increases as cross-linking begins. Since k_s is the rate of chain scission, it is natural that a larger k_s drives N_B to decline much faster. Note that if k_s were too small, e.g. 0.01, then the chain scission is negligibly slow as compared to the cross-linking; thus, no initial reduction in N_B could be discerned.

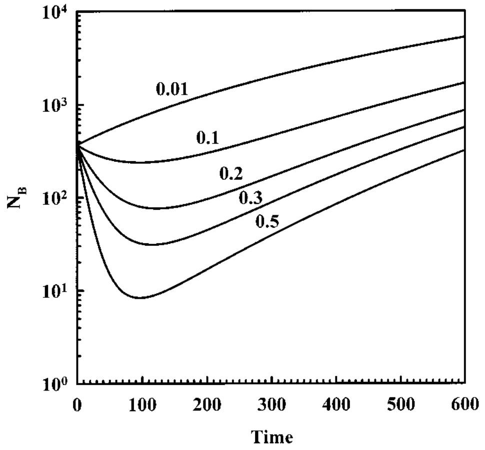

Figure 4. Effect of the rate constant of chain scission reaction, k_s, on temporal dependence of N_B. Individual curves are labeled with the k_s values utilized. All other parameters were the same as in Figure 3 with $k_i = 0.005$.

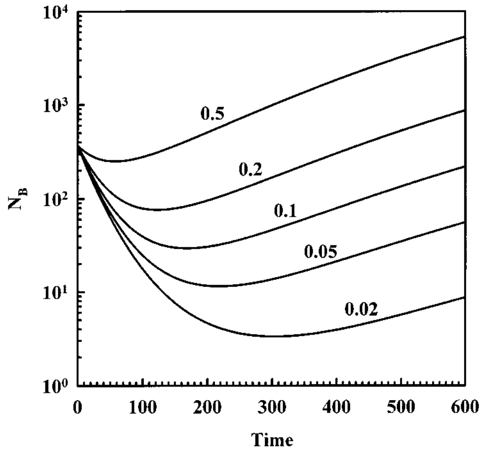

Figure 5. Effect of the rate constant of cross-linking reaction, k_p, on temporal dependence of N_B. Individual curves are labeled with the k_p values utilized. All other parameters were the same as in Figure 3 with $k_i = 0.005$.

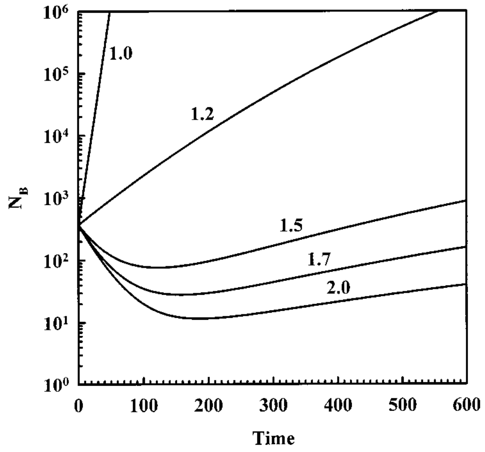

Figure 6. Effect of reaction exponent, n, on temporal dependence of N_B. Individual curves are labeled with the n values utilized. All other parameters were the same as in Figure 3 with $k_i = 0.005$.

Figure 5 exhibits the effect of kinetic constant of cross-linking reaction, k_p, on N_B. Since increasing k_p is analogous to reducing k_s, the observed trend is complementary to that of the k_s (see Figure 4). The larger k_p indicates the faster cross-linking reaction; thus, the average degree of polymerization of polybutadiene increases more rapidly. It is noticed that the five curves are more or less parallel beyond the minimum N_B value. This finding is reasonable because the chain scission reaction in polybutadiene becomes less and less important in the cross-linking dominant region. The chain scission term (the first term) in eq 11 is negligibly small relative to the cross-linking term (the second term); therefore, the rate of change of N_B is then proportional to that of conversion, p.

A careful examination of eq 11 reveals that since N_B is usually much larger than unity, the term $(1 - 1/N_B)$ is close to 1, which in turn suggests that m exerts essentially little or no effect on the behavior of molecular weight change. Our numerical calculation confirmed the above inference that different m values exhibit no significant influence on the average molecular weight, N_B. One can therefore envisage that the n value would play a crucial role in the temporal change of molecular weight in polybutadiene chains (Figure 6). From eq 11, it is seen that the change of N_B in the cross-linking reaction is of the order $2 - n$. Therefore, the smaller the n value, the faster the cross-linking reaction; thus, the molecular weight increases sharply. Interestingly, when $n < 1.5$ there is a sudden change in the curvature from concave to linear. According to the kinetic study of thermooxidative degradation of SBS by Holjevac and Rek,[8] the m and n values were found to be 0.37 and 1.43 at 160 °C, respectively. These exponents may be slightly underestimated since the thermooxidative degradation was treated as a cross-linking reaction alone in their work. Hence, the choice of $m = 0.5$ and $n = 1.5$ in our numerical computations is within the reported experimental range.

The calculated curves for various n values in Figure 6 show the trends of molecular weight variation with heat treatment time for the fast ($n = 1$) and slow cross-linking ($n = 2$). The calculated curves with $k_i = 0.005$ (Figure 3), $k_s = 0.2$ (Figure 4), $k_p = 0.2$ (Figure 5), and $n = 1.5$ (Figure 6) qualitatively resemble the observed experimental trend depicted in Figure 1. Despite the simplification of our kinetic model, it captures the physical essence such as initial reduction and subsequent increase in molecular weight of the butadiene segments of the block copolymer caused by the thermooxidative reactions involving chain scission and cross-linking.

Another important finding in the chain scission of the SB block copolymers is the macrophase separation between the constituent polystyrene and butadiene segments.[8] In the literature,[11,12] it has been known that blends of neat PS and neat PB exhibit an upper critical solution temperature (UCST) with a critical point that depends on molecular weight of the constituent polymers and the intermolecular interaction parameter. To determine a snapshot of the UCST coexistence curve of a binary polymer blend at a given reaction time, the Flory−Huggins free energy density of mixing, F, may be employed,

$$F = \frac{f}{nk_BT} = \frac{\phi_B}{N_B}\ln\phi_B + \frac{\phi_S}{N_S}\ln\phi_S + \chi\phi_B\phi_S \quad (12)$$

where k_B is the Boltzmann constant and T the absolute temperature. N_B and N_S represent the degree of polymerization (or numbers of statistical chains) of PB and PS molecules. ϕ_B and ϕ_S, representing the volume fractions of PB and PS, respectively, may be given by

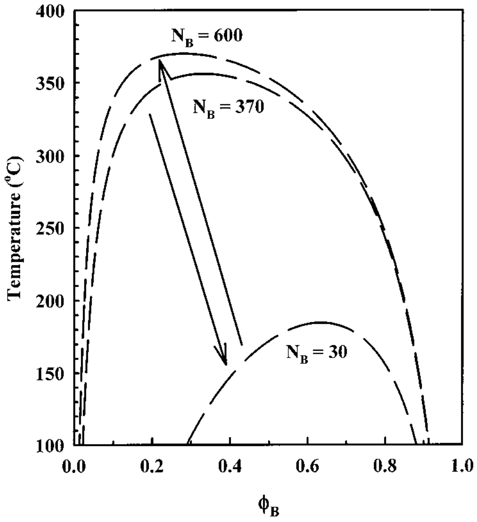

Figure 7. Snapshots of the UCST phase diagram of a PS/PB blend showing the suppression of T_c upon chain scission and elevation of T_c with increasing degree of polymerization of polybutadiene segments, N_B, due to cross-linking.

$\phi_B = n_B N_B/n$ and $\phi_S = n_S N_S/n$, and $n = n_B N_B + n_S N_S$. n_B and n_S are the numbers of PB and PS chains, respectively. χ represents the Flory−Huggins interaction parameter which is generally assumed to be a function of reciprocal absolute temperature, viz., $\chi = \alpha + \beta/T$, where α and β are constants. Furthermore, the χ interaction parameter is directly related to the critical temperature, T_c, through the temperature dependence of χ, i.e., $\chi = \alpha + (\chi_c - \alpha)T_c/T$, where χ_c is the critical interaction parameter at the critical point.

To calculate the critical temperature, we used the polymer−polymer interaction energy density of PS/PB pair obtained by Lin and Roe:[13] $\Lambda = 1.573 - 0.0021T$ (cal/cm^3). χ_c is related to Λ in the form of $\chi = \Lambda V_{ref}/RT$, where R is a universal gas constant (1.98 cal deg^{-1}) and V_{ref} is the reference volume of 61.45 cm^3, taking the molar volume of butadiene monomer as the reference volume. That gives the interaction parameter at 160 °C to be 0.0475, which is very close to the experimental value of 0.048 reported by Nealy et al.[14]

Figure 7 shows the snapshot of the temporal evolution of the UCST phase diagram calculated according to the FH theory described in eq 12. Upon chain scission the degree of polymerization of polybutadiene segments, N_B, is lowered, which in turn suppresses T_c of the PS/PB blend. Assuming the PS chains are thermally stable in the temperature range investigated, the N_B of PB would be 370 after the breakage of diblock copolymers; therefore, the χ_c is estimated to be 0.0124, which in turn gives $T_c = 356$ °C. Hence, the PS/PB blend at the reaction temperature of 160 °C is certainly in the unstable region where spinodal decomposition would take place. This explains why spinodal-like interconnected structure was observed experimentally in the macroscopic phase separation in the diblock copolymer driven by thermooxidative reaction.[9]

The continued decrease of PB chains suppresses the UCST, but the reaction temperature (160 °C) still remains in the unstable region which makes the phase-separated domains grow further through coalescence. In principle, it is possible that the further decline of molecular weight could suppress the UCST below the reaction temperature such that the phase-separated domains could disappear completely. When the cross-linking reaction starts to dominate over the chain scission, the UCST curve shifts asymmetrically to a higher temperature as depicted in Figure 7.

There is no doubt that the change of chemical structure due to the oxidative reaction involving the attachments of carboxyl, carbonyl, or peroxide groups to the PB segments would certainly influence the χ interaction parameter of the system. However, it may not be the direct cause for the up-and-down movement of the UCST, leading to macrophase separation, phase dissolution, and subsequent phase separation. It is believed that the change of molecular weight of PB driven by the chain scission and cross-linking is the major contributor that makes the UCST move down or up during chain scission and cross-linking.

Concluding Remarks

In this paper we have deduced a kinetic equation for thermooxidative degradation of a SB diblock copolymer based on a simplified kinetic scheme by taking into consideration the competition of chain scission and cross-linking reactions. It was shown that the phase diagram was suppressed initially due to the reduction of average molecular weight driven by the chain scission, and subsequently it shifted to a higher temperature due to the drastic increase in molecular weight caused by cross-linking. The k_s and k_p have opposite effects on the temporal change of molecular weight, e.g., the k_p, representing a faster cross-linking reaction, drives the minimum of the temporal variation of the molecular weight to move to a shorter time, and vice versa. Despite the simplification in our kinetic model for the thermooxidative reactions, our calculation captures the experimental trends such as initial reduction and subsequent increase in molecular weight of the SB block copolymer.

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