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Collaborative studies of thermo-oxidative degradation of styrene–isoprene diblock copolymer

Scott Meng[a], S.I. Kuchanov[b], Jingli Xu[a], Thein Kyu[a,*]

[a]Department of Polymer Engineering, The University of Akron, Akron, OH 44325, USA
[b]Keldysh Institute of Applied Mathematics, Russian Academy of Science, Moscow, Russia

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Abstract

Mechanisms and dynamics of thermo-oxidative degradation of styrene-*co*-isoprene (SI) diblock at a temperature above the order–disorder transition temperature, T_{odt}, have been investigated both experimentally and theoretically. The structural development of SI during degradation was monitored by optical microscopy, and the reduction of molecular weight and molecular weight distribution during the degradation was determined by gel permeation chromatography (GPC). The degradation process was modeled in the framework of a kinetic model based on the framework of the Flory principle. The theoretical predictions were compared with the GPC results. Fourier transformed infrared spectroscopy (FTIR) experiment was conducted in situ during the thermo-oxidative degradation of the SI copolymers, to gain further insight into the chemical modification mechanisms, the reduction of unsaturated double bonds and the formation of carbonyl and hydroxyl groups.

Keywords: Gel permeation chromatography; Thermo-oxidative degradation; Styrene–isoprene diblock

1. Introduction

In the past decades, numerous efforts have been directed to the elucidation of thermodynamics of block copolymer and dynamics of microphase separation and pattern formation of microdomains [1–8]. One of the most intriguing characteristics of block copolymer is that, on account of the repulsive forces between the chemically joint block, it tends to micro-phase separate upon temperature quenching and self-assemble to ordered structures such as spherical, cylindrical, lamellar, and gyroid domains, in a manner dependent on chemical structure, block ratio, and molecular weight of the block copolymer [9–12]. Block copolymer can be classified as AB diblock, ABA triblock, and ABC triblock etc. in accordance with the configurations of the building blocks. The critical temperature for such a transition to take place is termed as the 'order–disorder transition' temperature (T_{odt}). Such segregated domains are normally within the length scale from tens to a few hundred nanometers. Aimed to take advantage of the self-assembly nature of block-copolymers for a variety of applications, numerous designs and development have come feasible [13–18].

While the aforementioned microstructures of the block copolymers are well investigated, the problem such as thermo-oxidative degradation encountered in the utilization of these copolymers is not fully understood, although its practical significance has been well recognized. In particular, the rubbery constituents of styrene–butadiene and styrene–isoprene block copolymers are susceptible to the attack of oxygen, especially at elevated temperatures [19–22]. Such effect is especially pronounced in the block copolymer containing unsaturated bonds (i.e. C=C double bonds) in the backbone.

The degradation of block copolymers in turn drives macroscopic phase separation between the styrene–degraded isoprene copolymer and isoprene segments due to chain scission of the copolymers and concurrent chemical

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* Corresponding author. Tel.: +1 330 9726672; fax: +1 330 2582339.
E-mail address: tkyu@uakron.edu (T. Kyu).

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modifications of the building blocks, giving rise to the thermodynamic immiscibility between the chemically modified isoprene chains and the detached segments, i.e. a byproduct from degradation reactions. The interplay between the degradation reaction kinetics and chemical modification makes the whole scenario of macroscopic phase separation extremely complicated.

Fan and Kyu carried out an extensive study on macroscopic phase separation in a commercial styrene-*block*-isoprene–*block*-styrene (SIS) triblock (containing 20% of styrene-*block*-isoprene (SI) residual diblock) subjected to thermo-oxidative degradation [23]. It was demonstrated experimentally that chemical modification of both the SIS backbone and the isoprene units occurred together with chain scission throughout the degradation process. The trend of temporal evolution of the molecular weight of polyisoprene and molecular weight distribution was elaborated by gel permeation chromatography. In a similar study [24], Fan and Kyu observed that, unlike SI or SIS copolymer, styrene-*block*-butadiene (SB) diblock and styrene-*block*-butadiene-*block*-styrene (SBS) triblock undergo cross-linking reaction as well as chain scission during the thermo-oxidative degradation. In a theoretical attempt [25], the cross-linking reaction in competition with the chain scission reaction for SB and SBS was incorporated in a coarse grain phase separation model coupled with the reaction kinetic model.

To gain an in-depth understanding as to how the molecular weight and molecular weight distribution evolve during the thermo-oxidative degradation, theoretical modeling is essential. Kok and co-workers developed a quantitative theory, allowing one to calculate molecular inhomogeneity of the degraded products formed during the course of the degradation of a diblock copolymer as well as to find conditions, where transition from a stable state to an unstable state took place [26]. The validity of the aforementioned model has yet to be tested because the experimental data were not available at the time. This is one of the motivations of the present collaborative work between the US team and the Russian counter part, which combines the experimental investigations and theoretical modeling to elucidate reduction of the molecular weight of isoprene leading to polydispersity or molecular weight distribution, which is one of the most significant features during degradation of SI diblock copolymer.

In our previous work [23], the complex nature of thermo-oxidative degradation of the commercial SIS triblock copolymer containing some level of SI block has presented a very difficult task for the establishment of theoretical modeling. In this work, we have made use of a pure SI diblock copolymer synthesized in the lab scale to put the theory to test. In order to make our joint-study as simple as possible, a degradation temperature has been chosen to be above the order–disorder transition temperature of diblock copolymer, thereby ruling out any contribution from the microscopic phase separation.

2. Experimental section

The material used in the experiment is a 50/50 styrene-*block*-isoprene diblock copolymer synthesized in the lab of Professor C.D. Han, having the T_{odt} of 146 °C. The samples were first prepared by dissolving the SI diblock in toluene to obtain a solution of 5 wt% of the copolymer. Then, thin films were cast on the glass slides to obtain an average film thickness around 50 μm. Subsequently, the slides were dried inside a vacuum oven for 180 h at 50 °C to remove any residual solvent.

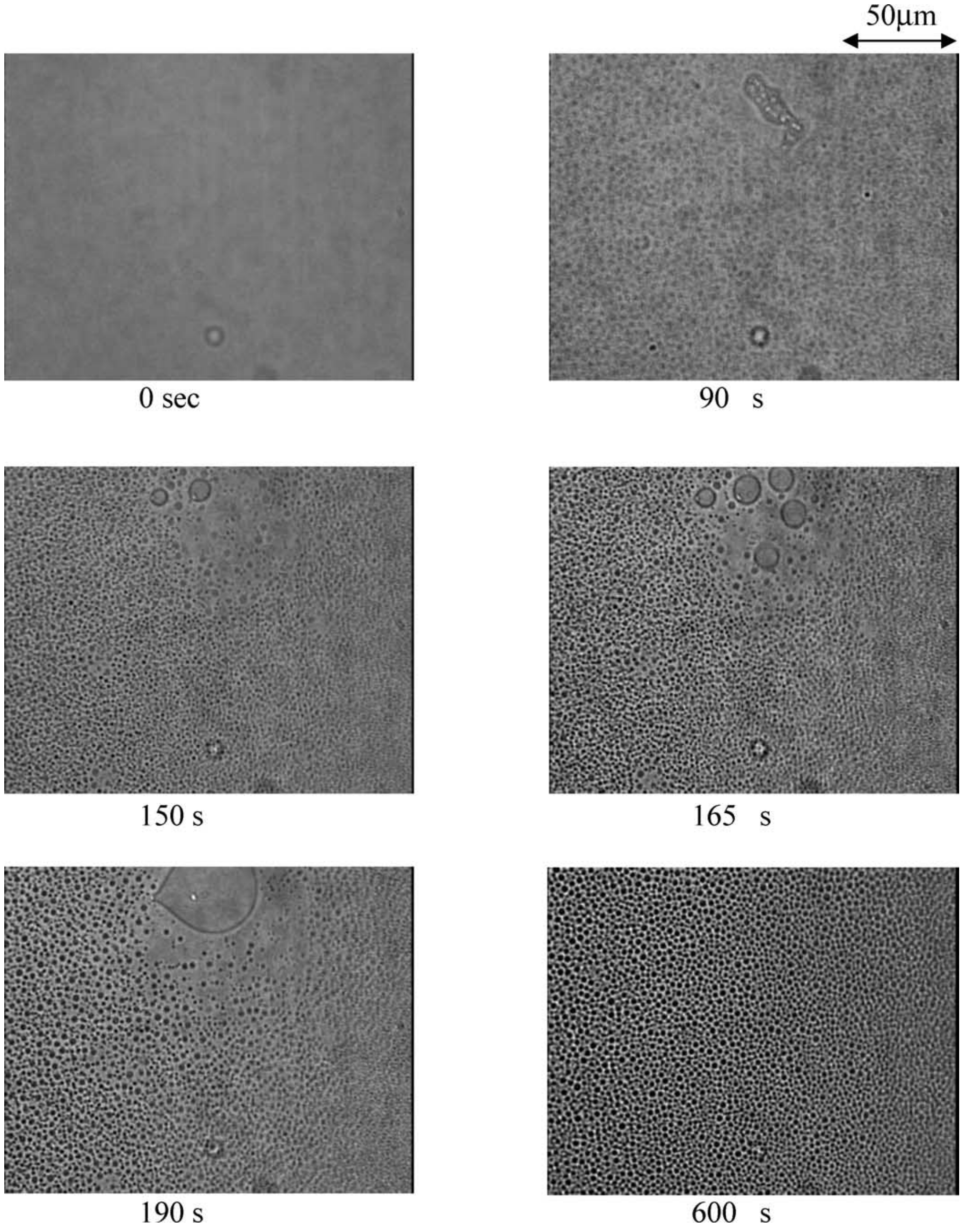
The sample glass slides were placed inside the optical microscope hot stage controlled at 155 °C for in situ morphology observation. Regarding the study on temporal change of the molecular weight during degradation, the samples were kept in the hot stage under various exposure times at 155 °C. The degraded samples at different times were dissolved in tetrahydrofuran (THF) solvent. The solutions that received different exposure times were injected to gel permeation chromatography (GPC) for the determination of time dependent molecular weights and polydispersity. The GPC instrument (Waters) was equipped with a high-pressure liquid chromatography pump (model 510) and a differential refractometer (model 410).

In the morphological characterization, an optical microscope (model BX60) from Olympus Corporation was utilized. Attached to the microscope was a hot stage from Linkam Scientific Corporation (Model LTS353) that allows a precise temperature control within ±0.1 °C. Fourier Transformed Infrared spectroscopy (FTIR) (Excalibur series, Model FTS 3000, Digilab) was employed using a heated cell (Thermo Spectra-Tech) together with a temperature controller (OMEGA). The in-situ FTIR experiment on the thermo-oxidative reaction of the SI diblock films was performed in the open air environment.

3. Results and discussion

Fig. 1 represents the snap-shots of the optical micrographs of the SI diblock, showing the emergence of the phase separated structures driven by thermo-oxidative degradation during the exposure to open air 155 °C. The structural development seems to be reminiscent of spinodal decomposition, though it is by no means a proof. It appears that, upon heating the SI diblock above T_{odt}, chain scission starts to take place first, leading to macroscopic phase separation between the degraded SI diblock having short isoprene segments and the degraded pure isoprene units. There was no discernible amount of gel formation which suggests that the cross-linking reaction, if any, may be insignificant.

To probe the molecular weight change during the thermo-oxidative degradation, a GPC measurement was performed on the samples that received various exposure times in atmospheric oxygen at 155 °C. In Fig. 2, is shown



0 sec 90 s

150 s 165 s

190 s 600 s

Fig. 1. Optical micrographs of structure development in SI undergoing oxidative thermal degradation at 155 °C.

the primary peak shifting to a higher retention time, indicating that the molecular weight of SI diblock declines due to the catastrophic chain scission of the SI backbone. The same trend can be witnessed in the fragmented neat isoprene undergoing degradation, as evidenced in the emergence of a broad new peak that also moves to a higher retention time during the course of degradation. Deconvolution of the primary and secondary peaks on the GPC curves, in turn, gave the molecular weight variation as a function of exposure time. The reductions of the weight-average and number-average molecular weight (M_w and M_n) of the SI and isoprene segments were plotted in Fig. 3(a) and (b), respectively. For the quantitative comparison with theory, the values of M_w and M_n of SI and isoprene unit during degradation were tabulated in Tables 1 and 2.

3.1. Comparison with theory

A quantitative theory of degradation of a diblock copolymer melt has been elaborated in the context of the simplest kinetic model [26], based on the framework of the Flory principle [27]. This means that the cleavages of chemical bonds occur randomly, which may be described by the constants k_1 and k_2 of elementary reactions of the

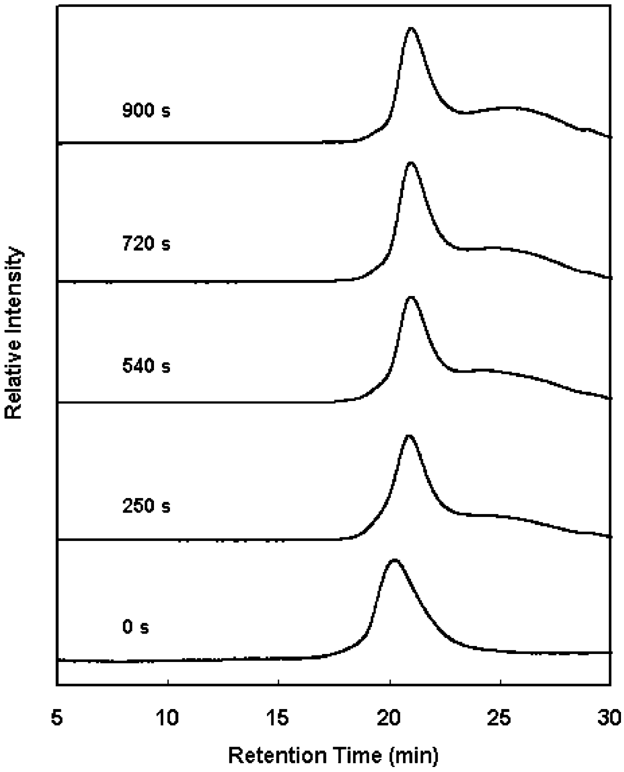


Fig. 2. Evolution of GPC traces of SI diblock polymer as a function of exposure time at 155 °C.

degradation of bonds in the blocks of each type of monomeric units. For the system in hand, the reactivity k_1 vanishes, because under the experimental conditions, the blocks of styrene units remain virtually stable without undergoing degradation. In this case, among the degradation products are the diblock copolymer molecules containing identical styrene block whose length l_1 differs from that of isoprene block l_2. The rate constant of the degradation of such molecules is, evidently, equal to $k_2 l_2$ for the model employed. Other products of the degradation of the initial diblock copolymer are isoprene molecules of different lengths. The evolution of their molecular weight distribution during the course of the degradation as well as that of the distribution of diblock copolymer molecules for their chemical size and composition may be readily calculated by formulas derived earlier [26]. Here, we shall restrict our calculation to the first and the second order statistical moments of these distributions since, just these statistical characteristics of the chemical structure enter into the expression for the number average M_n and weight average M_w values of the molecular weights of the degradation products.

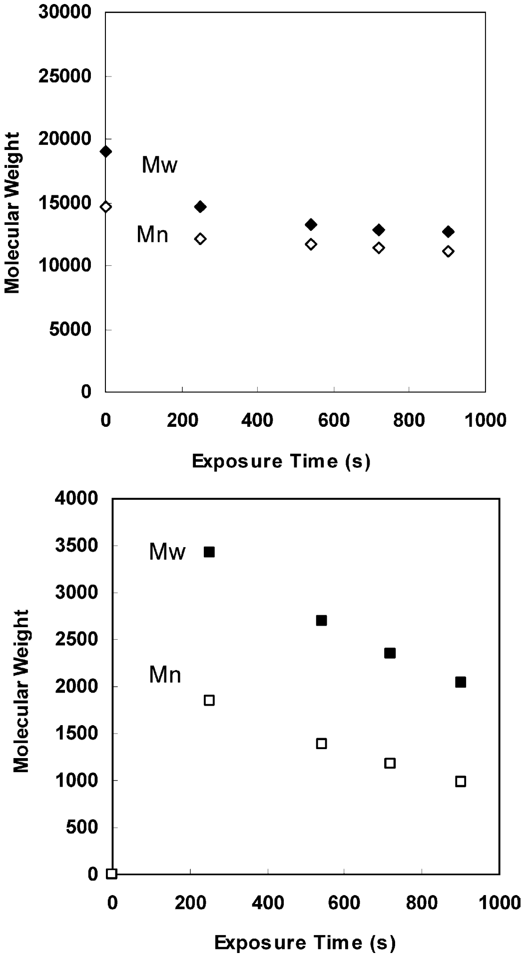


Fig. 3. (a) Plot of molecular weight of SI unit degradation as a function of exposure time at 155 °C. (b) Plot of molecular weight of isoprene unit degradation as a function of exposure time at 155 °C.

Neglecting the polydispersity of the initial diblock copolymer for the sake of simplicity, let us consider it as consisting of identical molecules whose molecular weight is 19×10^3. The molecular weights of the constituent blocks of styrene and isoprene are 11×10^3 and 8×10^3, respectively. This implies that the degrees of polymerization of these blocks are $N_1=107$ and $N_2=118$. The molecular weight of a block copolymer molecule randomly chosen, $W=w_1 l_1+w_2 l_2$, is a stochastic variable. For the system of interest, the molecular weights of the monomers are $w_1=103$ and $w_2=68$, whereas the value $l_1=N_1$. However, the

Table 1
Theoretical and experimental dependencies on exposure time of isoprene oligomers undergoing oxidative thermal degradation at 155 °C

t (s)	M_w exp.	M_w calc.	M_n exp.	M_n calc.	K exp. (PDI)	K calc. (PDI)
250	3431	3834	1846	2285	1.86	1.68
540	2690	2690	1394	1440	1.93	1.87
720	2343	2224	1168	1158	2.01	1.92
900	2033	1881	983	965	2.06	1.95

Table 2
Theoretical and experimental dependencies on exposure time of SI diblock copolymer undergoing oxidative thermal degradation at 155 °C

t (s)	M_w exp.	M_w calc.	M_n exp.	M_n calc.	K exp. (PDI)	K calc. (PDI)
250	14,644	14,963	12,175	14,474	1.2	1.03
540	13,218	13,077	11,741	12,838	1.13	1.02
720	12,858	12,545	11,349	12,393	1.13	1.01
900	12,659	12,220	11,127	12,117	1.14	1.01

length of isoprene block l_2 is a random variable whose average value $\bar{l}_2$ and mean square value $\bar{l}_2^2$ change with time of the degradation t as follows [26]

$$\bar{l}_2 = \frac{N_2}{\theta_2}[1 - \exp(\theta_2)] \quad \text{and}$$
$$\bar{l}_2^2 = 2\left(\frac{N_2}{\theta_2}\right)^2[1-(1+\theta_2)\exp(\theta_2)] \tag{1}$$

where $\theta_2 = N_2k_2t$. Proceeding from these expressions, it is straight forward to calculate the evolution of average molecular weights of a diblock copolymer.

$$M_n = w_1N_1 + w_2\bar{l}_2, \quad M_w = \bar{W}^2/\bar{W},$$
$$\bar{W}^2 = w_1^2N_1^2 + 2w_1w_2N_1\bar{l}_2 + w_2^2\bar{l}_2^2 \tag{2}$$

The same statistical characteristics for isoprene homopolymer molecules are found by formulas [26]

$$M_n^h = w_2P_n^h = w_2\frac{N_2}{\theta_2^2}[\theta_2 - 1 + \exp(-\theta_2)],$$
$$M_w^h = w_2P_w^h = w_2\frac{2N_2[\theta_2(1+\exp(-\theta_2)) - 2(1-\exp(-\theta_2))]}{\theta_2[\theta_2 - 1 + \exp(-\theta_2)]} \tag{3}$$

Eqs. (2) and (3) comprise the only unknown parameter whose value, $k_2 = 6.75\times10^{-5}\ \mathrm{s}^{-1}$, were determined by equating the theoretical and experimental values of the weight average molecular weight of polyisoprene molecules involved in the reaction system within 540 s after the beginning of the block copolymer degradation. Having found the constant k_2 of this reaction, we managed to calculate molecular weights M_n and M_w of respective homopolymers and of diblock copolymers at four different values of the exposure time.

The comparison between the results of the aforementioned calculation with the experimental data is presented in Tables 1 and 2. Taking into consideration the uncertainty in accuracy inherent in the chromatographic method the average molecular weights of the degradation products should be rounded in the interpretation the proposed kinetic model may be regarded as plausible description of macromolecular reactions in hand.

The theory developed in the previous paper [26] enables one not only to describe the evolution of the statistical characteristics of the chemical structure of the products of degradation of any diblock copolymer, but also to predict the possibility of the kinetically induced spinodal decomposition of the homogeneous state of the melt consisting of these products. The necessary condition of such a de-mixing is that the system should fall in the spinodal region of the system due to the change of its molecular structure characteristics. This happens if a reaction system, during the course of its evolution, crosses the spinodal line, where the homogeneous state becomes thermodynamically unstable with respect to the fluctuations of the composition of styrene and isoprene monomeric units. Depending on the spatial length scale of these fluctuations, that may be either macroscopic or mesoscopic, trivial and non-trivial spinodal branches may be differentiated, respectively.

As a point of interest when reactivity k_1 vanishes, the theoretical consideration leads to the following conclusions. The qualitative picture of the thermodynamic behavior of a reaction system is governed exclusively by the ratio of the lengths N_1 and N_2 of styrene and isoprene blocks in the initial block copolymer, i.e. by its composition $X_1 = 1 - X_2 = N_1/(N_1 + N_2)$. If the styrene block is longer than the isoprene unit ($N_1 > N_2$), a reaction system will never reach the spinodal region during the degradation process. When the inverse inequality holds ($N_1 < N_2$), there is a temperature interval (ΔT_{sp}) where the system does fall into this spinodal region. It may proceed in either way, depending on which particular branch of the spinodal the system crosses at the instance of the loss of its thermodynamic stability. This branch will certainly be a non-trivial one, provided that a copolymer composition lies in the region $0.327 < X_1 < 1/2$ when the lengths of blocks N_1 and N_2 differ just slightly. Within the region of compositions $0 < X_1 < 0.327$, where the above distinction is far more pronounced, the interval ΔT_{sp} consists of two intervals, $\Delta T'_{sp}$ and $\Delta T''_{sp}$. A system during the course of its evolution crosses either non-trivial or trivial branch of the spinodal when the temperature T, at which a copolymer degradation occurs, falls within the first or the second of the aforementioned intervals, respectively. Theoretical calculations [26] revealed that the intervals $\Delta T'_{sp}$r and $\Delta T''_{sp}$ were rather narrow and that the first of them was in the region of the lower temperature as compared to the second one.

In the initial copolymer whose blocks are of lengths $N_1 = 107$ and $N_2 = 118$, the mole fraction of the styrene units $X_1 = 0.475$. Thus, the melt of the products of its degradation can lose its thermodynamic stability with respect to the fluctuations of the composition of the monomeric units in the mesoscopic scale only. Our calculations carried out based on the formulae derived earlier [26] show that such a stability loss should happen in the system at hand at $t^*=60$ s after the beginning of the degradation. This value is rather close to that, $t^*\approx 80$–90 s, when we experimentally observed the phase separation in the reaction system.

To determine theoretically the boundaries of the interval ΔT_{sp}, we resorted to empirical dependence $\chi=7.85\times 10^{-3}+17.6/T$ of the Flory–Huggins parameter χ of the styrene and isoprene units interaction on temperature T [28]. Using this formula as well as the relationships disclosed in the previous paper [26] which describes the change of the spinodal value χ_{sp} of parameter χ during degradation, it is possible to calculate interval ΔT_{sp}. These calculations permitted us to establish the boundaries $T=451.2$ and 452 K which differ from the temperature of the experiment approximately by 5%. The most controversial issue from the viewpoint of the adequacy of this simplest model for the description of real systems is the undoubtedly lowered value of the width of interval ΔT_{sp}. This may be due to various factors, which we have neglected in the theoretical treatment. First, is the disregard of the polydispersity of the initial block-copolymer molecules. Other factors have to do with the fact that the isoprene blocks comprise, generally speaking, monomeric units of two types being formed as a result of (1–4) and (3–4) addition of the monomer to growing macro-radicals. That is why our assumption concerning the possibility of the description of a reaction system in terms of one kinetic parameter k_2 and one thermodynamic parameter χ may prove to be rather rough when calculating some thermodynamic characteristics of such a system. Despite this deficiency, the model chosen enables a number of important qualitative predictions regarding the thermodynamic behavior of the melt composed of the products of degradation of monodisperse styrene–isoprene diblock copolymer under varying lengths N_1 and N_2 of its blocks.

At fixed overall length N with the ratio N_2/N_2 decreasing from unity, the boundary temperatures of interval ΔT_{sp} grow, the larger of which increases more rapidly than the smaller counterpart. This leads to the broadening of the interval ΔT_{sp}. Both boundary temperatures of the ΔT_{sp} gap as well as the rate of its widening under the alteration of the initial copolymer composition will be the higher, the larger is the overall length of its molecules.

An intriguing question arises, if the SI and isoprene units keep declining as indicated in Tables 1 and 2, from a thermodynamic point of view, the decreasing molecular weight due to chain scission of SI and isoprene is supposed to favor the phase dissolution if the coexistence curve falls below the reaction temperature so that it should come to a point that the phase-separated structures start to dissolve. However, as shown in Fig. 1, no phase dissolution was observed after phase separation, which implies that the coexistence curve may be approaching the reaction temperature so that the supercooling, i.e. the difference between the coexistence point and the reaction temperature, gets smaller with elapsed time. Since, the average length scale of the phase separated domains is inversely proportional to the supercooling, the phase separated domains continue to grow as evidenced in Fig. 1. However, this mechanism alone is inadequate to explain the macroscopic phase separation because the continued chain scission eventually pushes the coexistence point to fall below the reaction temperature which eventually should drive the phase dissolution.

We suspect that there must be an additional mechanism that prevents the cross-linking reaction of the radicals. To gain further insight into the intriguing degradation phenomena, an in-situ FTIR experiment was conducted by exposing the sample to the open air at an elevated temperature above T_{odt}, say at 155 °C. The real-time evolution of some characteristic IR bands of the block was monitored during degradation. The initial and final spectra of the SI sample are depicted in Fig. 4. We paid attention to certain bands of interest such as 840, 1717, and 3437 cm^{-1} which have been assigned to C=C double bond stretching from the 1,4-trans microstructure of the isoprene segment, carbonyl group, and hydroxyl group, respectively [29,30]. For the purpose of comparison, the absorbance was normalized according to $A=A_t/A_{t0}$, where A_t refers to the absorbance of the band of interest at time t and A_{t0} denotes the initial absorbance of that same band at the onset time. The temporal evolution of these bands is displayed in Fig. 5. Of particular interest was the reduction of IR absorption peaks of the C=C double bonds, in contrast to the increase of the peaks of carbonyl and hydroxyl groups. This suggested a correlation between the loss of C=C bonds and the formation of the carbonyl and hydroxyl groups. According to the existing degradation mechanism of SI block in the literature (see the scheme

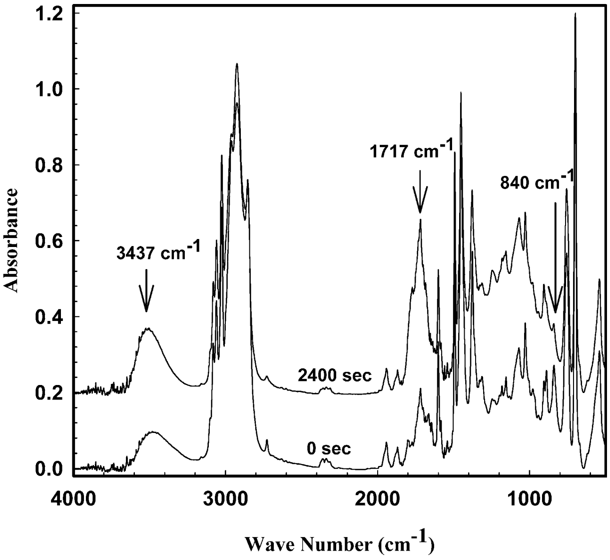


Fig. 4. FTIR spectra of SI block copolymer sample before oxidation (lower curve), and after 40 min of oxidation (upper curve).

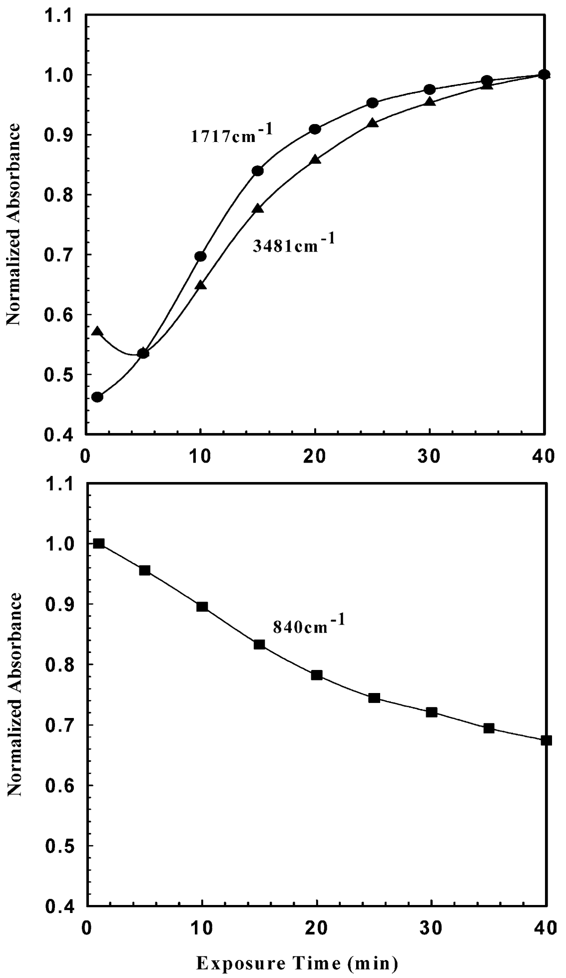
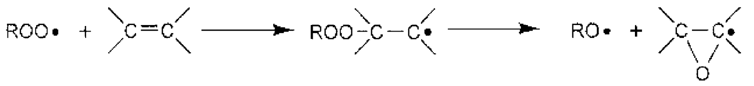
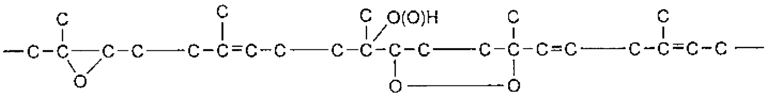


Fig. 5. Plots of development of carbonyl (1717 cm^{-1}) and hydroxyl (3437 cm^{-1}) groups vs. time (upper figure), and C=C double bond (840 cm^{-1}) vs. time (lower figure) of the SI sample undergoing oxidative thermal degradation with different exposure time.

below), carbonyl and hydroxyl groups are the products from the oxidative degradation reactions once C=C bonds are attacked by peroxy radicals [31].



Possible structures formed are shown in schemes I and II [31].



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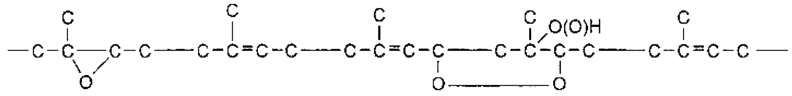

II

Therefore, during the course of degradation, the chemical modification occurs in the SI and isoprene unit while the chain scission is taking place. As demonstrated, the time-evolution curves of carbonyl and hydroxyl groups actually reveal the kinetics of chemical modification. Comparing the plots in Fig. 2 and the curves in Fig. 5, it is reasonable to infer that the chemical modification takes place during the chain scission. It is noteworthy that although the time span of Fig. 4 is three times longer than the results in Figs. 1 and 2, the asymptotic trends in Figs. 1, 2, and 4 are seemingly the same. Chemical modification certainly accounts for the lack of phase dissolution in the SI diblock and SIS triblock as opposed to the SB or SBS block copolymers [24,25].

It can be anticipated that if thermo-oxidative degradation were undertaken below the T_{odt}, a more complex phenomenon may occur; involving phase separation competed by the phase dissolution and the subsequent secondary phase separation between the chemically modified SI backbone and isoprene segments. Another important point is that the interaction parameter χ is strongly correlated with the chemical modification in a manner dependent upon the type of structures possibly formed. This fact has not been taken into account in the present simplest theory, since it is not feasible to determine experimentally the interaction parameter $\chi(t)$ due to the complex degradation chemistry that evolves during the course of chemical modification.

4. Summary

The mechanism of thermo-oxidative degradation in SI diblock was studied with a combined experimental and theoretical approach. It was uncovered that the catastrophic chain scission took place, which was the main cause for the observed phase separation between the fragmented isoprene segment and styrene–short isoprene copolymers. The kinetic theory presented here was able to capture the essence of chain scission, and a good accordance was found between the theoretical predictions and experimental findings. Moreover, the chemical modification was believed to be a very important factor controlling phase decomposition that occurred concurrently with the chain scission. Contrary to the SB and SBS systems, the cross-linking reaction was virtually absent in the SI and SIS which might be due to the dominant role of the chemical modification of the SI backbone and detached isoprene units over the radical reaction.

Acknowledgements

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