



Bulk physical aging behavior of cross-linked polystyrene compared to its linear precursor: Effects of cross-linking and aging temperature



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ABSTRACT

The bulk physical aging behavior of cross-linked polystyrene (PS) is directly compared to that of its linear precursor polystyrene-co-vinylbenzocyclobutene (PS-VBCB) with 8.5 or 12.5 mol% VBCB content. The VBCB units incorporated into a linear PS precursor cross-link with one another upon annealing at 250 °C. Physical aging rates of bulk PS-VBCB films before and after cross-linking are characterized using ellipsometry by monitoring the decrease in thickness during isothermal annealing at a specific aging temperature (T_a) below the glass transition temperature (T_g). Physical aging rates show strong dependences on T_a values, with neat PS, linear PS-VBCB precursors with 8.5 or 12.5 mol% VBCB, and cross-linked PS with 8.5 mol% VBCB exhibiting maxima at $T_a - T_g = -40$ to -30 °C. In contrast, cross-linked PS with 12.5 mol% VBCB exhibits a maximum aging rate at $T_a - T_g = -65$ to -45 °C. The distribution of T_a -dependent aging rates broadens in cross-linked PS samples compared to linear precursors, which is correlated with increased T_g breadth or heterogeneity after cross-linking. Comparisons of aging rates of cross-linked PS with linear precursors demonstrate that cross-linking can lead to an increased, decreased, or unchanged aging rate depending on the values of T_a and $T_a - T_g$: e.g., when $T_a - T_g > -60$ °C, both cross-linked PS samples have a lower aging rate compared to their linear precursors at the same $T_a - T_g$ whereas the cross-linked PS exhibits a similar or even greater aging rate compared to the linear precursor when $T_a - T_g < -60$ °C. These results help to reconcile previous seemingly contradictory observations regarding effects of cross-linking on physical aging rates. To the best of our knowledge, cross-linking induced enhancement of physical aging rates of cross-linked polymers relative to their linear precursors at the same $T_a - T_g$ value is being reported for the first time here.

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1. Introduction

When a bulk glass-forming liquid (e.g., a polymer) is cooled, the system undergoes a dramatic slowing down in cooperative segmental dynamics near the glass transition temperature (T_g). Below T_g , the segments cannot rearrange structurally into thermodynamic equilibrium within the time scale of cooling, resulting in a non-equilibrium glass [1–5]. When annealed at a specific aging temperature (T_a) below T_g , the glass undergoes structural relaxation from non-equilibrium conformations toward an overall equilibrium state in a relaxation process termed physical aging [2,4,6–8]. In the case of a polymer, the physical aging process leads to time-dependent material properties including increases in density and modulus and decreases in specific enthalpy, permeability, impact

strength, and ultimate elongation [2,6,9–11]. Understanding the physical aging behavior of polymers is both scientifically and technologically important. For example, for polymeric materials used in the aerospace industry (cross-linked epoxy resin composites are commonly used materials), which often serve under harsh environmental conditions for extended periods of time, the aging induced changes of material properties need to be suppressed to guarantee structural integrity over the use lifetime [10]. Physical aging of glassy polymers and the ensuing instability of permeation properties over time have also been major obstacles to the commercialization of such polymeric materials for some membrane applications [4,6,11].

Research on physical aging behavior of polymers has involved various polymeric systems, including linear polymers [12–32], cross-linked polymer networks [9,10,33–46], physically associating polymer networks [47], star polymers [48,49], polymer blends [50–53], and polymer nanocomposites [8,54–60]. (Many

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techniques including volume relaxation by dilatometry [19,22,51] or ellipsometry [12–14,28,32,48,49], enthalpy relaxation by differential scanning calorimetry [9,23,24,34–38,58], and fluorescence [15–17,29,30,33,54,55,60], among others [21,22,26,27,39,50], have been used in this research.) Physical aging behavior has been shown to be affected by molecular structures of the polymers as well as the incorporation of blend components into the polymer matrix [8–10,33–47,54–60]. Noteworthy for our investigation is the fact that some previous studies on physical aging behavior of cross-linked polymers have reported that at a constant $T_a - T_g$ the relaxation rate decreases or the time required to reach structural equilibrium increases with increasing cross-link density [9,34–36,38]. Such results were explained by that fact that cross-linking can introduce topological constraints to molecular reorganization that is required to achieve structural relaxations [9,34–36,38]. However, other studies [44–46,61] have reported that cross-linking has nearly no effect on the physical aging behavior of polymeric systems. For example, Cook et al. [46] compared the physical aging behavior at the same $T_a - T_g$ for both linear and cross-linked epoxies with similar chemical structures, and they reported that the aging rates were essentially the same. They argued that at a certain degree of undercooling, or constant $T_a - T_g$, the relaxation time and hence the rate of molecular mobility should be constant as predicted by the William-Landel-Ferry (WLF) equation [62]. (We note that WLF equation is generally used to capture the temperature dependence of segmental relaxation times above T_g for a wide range of polymers in the rubbery state but is not valid in the glassy state [62].) They then suggested that the rate of structural relaxation, which relies on molecular mobility, should be the same at the same degree of undercooling for these systems before and after cross-linking.

These substantially different and, in some cases, seemingly contradictory results regarding the effects of cross-linking on physical aging rates from previous studies [9,34–36,38,44–46,61] suggest the need for a direct comparison of the physical aging behavior of cross-linked polymers to that of direct linear precursor polymers. In order to make such a comparison, we chose to study the linear precursor polystyrene-co-vinylbenzocyclobutene (PS-VBCB) at low VBCB content, which can undergo quantitative cross-linking to form cross-linked polystyrene (PS) by thermal annealing at a relatively high temperature, e.g., 250 °C, for a sufficient amount of time [63–66] (In Ref. [63], we demonstrated that cross-linking exhibits a major impact on the T_g -confinement effect in polymer films.). This system was selected for the following reasons: first, the cross-linking process of the linear PS-VBCB precursor only requires simple thermal annealing without addition of any small molecules that may introduce additive/plasticizer effects and thereby complicate the physical aging process [67–69]; second, the linear PS-VBCB copolymer precursor is structurally similar to neat PS and can serve as a model system for studying the effects of cross-linking on physical aging behavior. We note that previous studies on physical aging behavior of cross-linked polymers have often focused on epoxy-based networks, which are usually structurally complex due to significant effects from hydrogen bonding. (Hydrogen bonding is known to affect physical aging behavior [18].)

Here, physical aging rates of bulk PS-VBCB films before and after cross-linking are characterized using ellipsometry by continuously monitoring the decrease in thickness during isothermal aging at a specific T_a below T_g . Using a streamlined procedure developed by Roth and coworkers [12], we show that physical aging rates of both linear PS-VBCB precursors and cross-linked PS samples exhibit strong dependences on T_a values and exhibit a maximum at particular values of $T_a - T_g$. We also find that the distribution of T_a -dependent physical aging rates broadens in cross-linked PS samples compared to linear precursors, which we correlate with

increased T_g breadth or heterogeneity after cross-linking. We further compare the physical aging rates of cross-linked PS samples to those of linear precursors at the same T_a and $T_a - T_g$ values and demonstrate that cross-linking can lead to an increased, decreased, or unchanged aging rate depending on the values of T_a and $T_a - T_g$. In particular, when $T_a - T_g > -60$ °C, both cross-linked PS samples exhibit a lower aging rate compared to their linear precursors at the same $T_a - T_g$ whereas the cross-linked PS shows a similar or even greater aging rate compared to the linear precursor when $T_a - T_g < -60$ °C.

2. Experimental

4-Vinylbenzocyclobutene (VBCB) (Aldrich, 97%) and benzoyl peroxide (BPO) (Aldrich, $\geq 98\%$) were used as received. Styrene (Aldrich, $\geq 99\%$) was deinhibited with inhibitor remover (Aldrich) and dried over CaH₂ overnight. Neat linear PS homopolymer ($M_n = 280$ kg/mol) and linear PS-VBCB copolymers with 8.5 ($M_n = 276$ kg/mol) and 12.5 mol% VBCB units ($M_n = 281$ kg/mol) were synthesized by free radical polymerization at 60 °C with low BPO concentration (0.2 mg BPO/mL monomer) as described in Ref. [63] (See Ref. [63] for more details of synthesis and characterization of the linear PS-VBCB copolymers.).

Single-layer films (with thicknesses well above 450 nm) of neat linear PS and linear PS-VBCB copolymer precursors were prepared for ellipsometry characterization by dissolving them in toluene and then spin coating [70] the solution onto Si wafers with native oxide layer (WaferNet). After spin coating, films were annealed at $T_{g,bulk} + \sim 20$ °C in a vacuum oven for at least 12 h to remove any residual solvent and to ensure uniform sample history. Cross-linked PS films were achieved by thermally annealing linear PS-VBCB films at 250 °C for 90 min under dry nitrogen. A glass chamber was mounted on the heating stage to ensure the nitrogen atmosphere during the cross-linking process. (A control study was performed with neat, linear PS using the same heating protocol.) At 250 °C, the VBCB cyclobutene ring will open and is able to couple with neighboring VBCB (usually on adjacent polymer chains), resulting in a cross-linked PS network [63–66]. As demonstrated in Ref. [63], PS-VBCB samples have reached “complete cross-linking” or as much cross-linking as possible after annealing at 250 °C for 90 min, and cross-link density, or degree of cross-linking, of the resulting cross-linked PS increases with increasing VBCB content in the linear PS-VBCB precursor (i.e., cross-linked PS with 12.5 mol% VBCB has a greater cross-link density than that with and 8.5 mol% VBCB). As measured at the respective T_g of each polymer, a very small difference was observed in thickness before and after cross-linking for a given film [63]. (See Supplemental Information.) Values of T_g for the linear and cross-linked PS samples are those determined by ellipsometry in Ref. [63] on the same samples used in this study; see Table 1.

The sub- T_g isothermal physical aging behavior of cross-linked PS and its linear precursor PS-VBCB were characterized using ellipsometry [12–14] to measure the decrease in film thickness (h) associated with the densification of the material during structural relaxation [2,4,6,7,12,19,71] with increasing aging time, t . Spectroscopic ellipsometry (M-2000D, J.A. Woollam Co.) was used to measure ellipsometric angles (ψ and Δ), which were fitted to h using a Cauchy layer model [12–14,53,72]. Prior to physical aging measurements, both linear PS-VBCB and cross-linked PS films were annealed at $T_{g,bulk} + 40$ °C for 30 min; these films were then quenched at a controlled cooling rate of -50 °C min⁻¹ (identical to that used in Ref. [13] for supported PS and polysulfone films) to a chosen T_a and maintained there for 360 min for structural relaxations to occur. (Quenching rate is known to affect the physical aging behavior of glassy polymers [13].)

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