Short Communication: Material Behaviour

Features of structural relaxation in diblock copolymers

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ABSTRACT

Time- and temperature-dependent structural relaxation (physical aging) of poly (styrene-b-methyl methacrylate) (PS-b-PMMA) block copolymers was investigated by calorimetry. Our study reveals the interplay of the relaxation responses of the two components of the copolymer in an intermediate temperature regime. That is, when the testing temperature is closely below the glass transition temperatures of PS and PMMA, structural relaxation in these polymer phases takes place concurrently, the corresponding thermogram displays partially superposed dual endothermic peaks as a feature of physical aging in the diblock copolymers. The aging response for each component is identified from a curve fitting method and analyzed by the relaxation of enthalpy. Comparing with the homopolymer analogs, the PS and PMMA in diblock copolymers show enhanced aging rate.

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1. Introduction

Block copolymers usually serve as templates and scaffolds in fabrication of patterned or hierarchical structures down to nanometer scale, so that design and self-assembly of structures from copolymers by phase separation have received vast research interests in last two decades [1—6]. Many procedures to create complicated architectures ranging from uniform ordered planar nanostructures [7] to three-dimensional hierarchical structures [8] have been developed. While the smart design and processing utilizing copolymers have attracted a great deal of attention, the naturally time-dependent instability of the material, including physical aging which affects the physical properties of the chemically immiscible blocks, especially how the properties evolve in the relaxation process, and how they interact each other during aging, remain to be elucidated.

Below the glass transition temperature (T_g), polymeric materials often fall into non-equilibrium state, the conformation of disordered molecules alter with time, toward a lower position in the potential energy landscape. This evolution process is referred to as structural relaxation, or physical aging [9,10]. Many physical properties of polymers such as specific volume, mechanical moduli, gas permeability, and thermal conductivity change concurrently in the process of physical aging.

Physical aging is of highly technological importance, however, to the best of our knowledge, structural relaxation of copolymers has not been systematically investigated, although a lot of research effort exists for homopolymers [9,11—13]. To date the majority of literature related to physical aging of copolymers focuses on particular engineering properties of the material, for instance, a few studies reported the influence of processing on mechanical behavior [14—16] or free volume change [17] in copolymers during aging, and several others examined the physical aging of blends of homopolymer and copolymer, regarding dynamic mechanical response or mechanical strength and elasticity [18,19]. Lack of fundamental understanding and systematic characterization of physical aging of copolymers would bottleneck applications of the material in the aforesaid emerging fields.

Experimentally, due to its high sensitivity and low amount need of materials, thermal analysis is a routine means to characterize aging response from enthalpy recovery, and it has been widely applied to capture aging effect of homopolymers [13]. In contrast, for copolymers, this method has not been adequately exploited to describe structural relaxation of the materials [20].

We systematically investigated the structural relaxation of copolymers using a differential scanning calorimeter (DSC). Here we

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report the features of physical aging of a representative diblock copolymer, *i.e.*, poly (styrene-*b*-methyl methacrylate) (*P*S-*b*-PMMA), which serves as a model system in many studies of block copolymers. The aging features are unique not only in that the aging response of the two blocks deviate from bulk due to nanoscopic confinement induced by phase separation [21], but also because the aging response of the two components were found interacting with each other as PS and PMMA have close T_gs.

2. Experimental

2.1. Materials

The atactic polystyrene-poly (methyl methacrylate) diblock copolymer was purchased from Polymer Source Inc. and used as received. The material has weight-average molecular weight of PS component ($M_{w,PS}$) of 259,000 g/mol and weight-average molecular weight of PMMA component ($M_{w,PMMA}$) of 629,000 g/mol. The component percentage of the material is 29%/71%. In copolymer synthesis process, the molecular weight and polydispersity index (PDI) of polystyrene block was measured by size exclusion chromatography before addition of MMA monomer. The final block copolymer composition was calculated from 1H NMR spectroscopy and PDI of 1.08 was determined by SEC.

The homopolymers PS and PMMA used in control experiments were purchased from Sigma-Aldrich and American Polymer Standards Corporation respectively and used as received. The M_W of homo-PS is 254 kg/mol and PDI is 2.83, and the M_W of homo-PMMA is 620 kg/mol and PDI is 1.05. For better comparison, both of the homopolymers have the same molecular weight with the corresponding polymer blocks in the copolymer sample.

2.2. Testing method

Physical aging measurements were carried out by a Shimadzu DSC-60 plus DSC with nitrogen gas environment. The instrument was calibrated by standard Indium. In aging testing, a 3–5 mg sample was first sealed in an aluminum pan and it was subsequently heated to 180 °C (well above the glass transition temperature of the both polymer components) with a constant ramp rate of 20 °C/min and held for 10 min to remove the residual stress. Then the sample was quenched to a desired aging temperature with constant cooling rate of −30 °C/min and annealed for an aging time (t_a). After that, the sample was quenched to 40 °C (well below the glass transition temperature of PS and PMMA components) with same cooling rate −30 °C/min and then reheated to 180 °C at heating rate of 20 °C/min. The thermogram of the second heating scan was recorded to determine the aging response of the material. The aging testing protocol is represented by Fig. 1.

3. Results and discussion

Fig. 2 depicts representative results of structural relaxation for a *P*S-*b*-PMMA sample (mole fraction of PS block $f_{PS} = 0.29$, $T_{g, Ps-block} = 109$ °C, and $T_{g, PMMA-block} = 127$ °C, determined from the second heating of the DSC trace) at three aging temperatures. As shown in Fig. 2(a), at 89 °C, *i.e.*, 20 °C lower than the $T_{g, Ps-block}$, enthalpy recovery peaks of the PS block were observed growing with increasing aging times, while the aging response of PMMA block was depressed in our experimental timescale due to a large departure of $T_{g, PMMA-block} − T_{aging} = 38$ °C. In contrast, when $T_{aging} = 114$ °C, aging response of PMMA block was clearly captured by the heat capacity curves in Fig. 2(b). As $T_{aging} > T_{g, PS-block}$, the PS block was immediately set at equilibrium in its liquid state after quenching to T_{aging}. Fig. 2(c) illustrates the coupled aging response
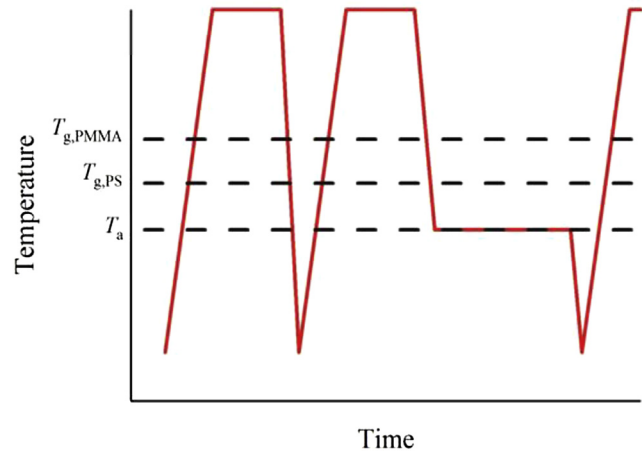

Fig. 1. Temperature protocol of aging experiments.

of PS and PMMA components in the thermogram when $T_{aging} = 99$ °C. Other than this particular representative aging temperature, actually in an intermediate temperature regime closely below $T_{g, Ps-block}$, the structural relaxation response contributed from both PS and PMMA blocks was observed. Owing to the close T_gs of the two components, the overall response of physical aging demonstrated an overlay of DSC traces that correspond to the enthalpy recovery of PS and PMMA blocks, respectively. In our aging times up to 384oo seconds, except that the PS block approached equilibrium, as shown in Fig. 2(c), aging processes of PMMA block kept ongoing during the entire timescale of the testing.

To identify aging response of each component individually, we utilized a curve fitting method on the data sets when the overlapping aging results occurred. Fig. 3(a) shows the aging response when the sample was aged at 99 °C for 38,400 s. As a reference, the unaged curve provides heat capacity data of the PS and PMMA through glass transitions. The grey line is the linear portion of the intermediate state at which the PS phase has transferred into liquid while the PMMA phase remains in glassy state. We hypothesize that the overall aging response in the DSC trace between the T_gs comes from the superposition of the aging response of each component. The curve fitting of the component aging starts from (PMMA phase) or ends upon the grey reference line (PS phase), as shown in Fig. 3(b), according to the thermogram of the baseline. In this figure, the individual heat capacity curve in blue, obtained from Gaussian fit, represents the aging response of PS or PMMA in the copolymer. The summation of these curve fitting results can recover the raw data, as illustrated in Fig. 3(c). As such, the curve fitting separates overlapped aging response in the diblock copolymer, the resultant family of aging curves for each component can be analyzed by the approach established for enthalpy recovery in homopolymers. The aging curves for each component were obtained from curve fitting based on the DSC trace and intermediate state, the accuracy and robustness of the obtained aging response was tested and approved from aging of a homopolymer. That is, we use a part of the aging data (50%) and the baseline to generate the curve fit of aging response, and compare the curve fit with the whole data set and found they match each other very well. The results indicate that given partial availability of the calorimetric peak and baseline in the differential thermogram, the entire aging response could be identified from curve fitting in a relatively narrow temperature regime.

The amount of enthalpy relaxed during aging was evaluated by the discrepancy between integration of thermograms of aged and unaged samples, as expressed by the following equation: