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Thermoplastic elastomers of alloocimene and isobutylene triblock copolymers

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ABSTRACT

A novel triblock copolymer, having a center block of high molecular weight polyisobutylene (PIB) and alloocimene (allo) end-blocks, was synthesized and the mechanical properties characterized. The phase-separated morphology consists of tethered PIB, with the glassy allo domains functioning as reinforcing filler. Thus, at ambient temperature the dynamic modulus is larger than that of PIB homopolymer by about 40%, and there is pronounced reinforcement from the glassy domains. The triblock polymer exhibits thermoplastic elastomer behavior, consistent with the structure. For temperatures above the allo glass transition (71 °C), the material undergoes an order–disorder transition, which causes substantial softening; however, this lability of the mechanical response is largely reversible. Since the repeat units of polyisobutylene cannot be crosslinked, this new material offers a route to processible, PIB based networks.

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1. Introduction

PIB is an unusual polymer, having distinctive characteristics such as (i) very low permeability [1] due to slow diffusion of dissolved gases; (ii) a propensity for strain-induced crystallization [2,3] despite slow thermal crystallization; (iii) high mechanical damping and energy dissipation [4,5]; and (iv) anomalous segmental relaxation dynamics [6,7] that includes a spectacular breakdown of time-temperature superpositioning [8]. These properties have led to many applications [9]. PIB is also resistant to crosslinking, either free radical initiated or by sulfur vulcanization, and consequently commercial PIB ("butyl rubber") is usually a copolymer with isoprene to provide reactive sites. However, only 2–5 mol% isoprene can be incorporated; thus, butyl rubber cures very slowly and only to a limited degree. Various isobutylene block copolymers [10–16] have been synthesized, and thermoplastic PIB elastomers are particularly intriguing for their commercial potential [17–21].

Recently the controlled/living emulsion copolymerization of isobutylene with 2,6-dimethyl-2,4,6-octatriene (alloocimene or "allo") was reported, yielding block copolymers with allo-rich sequences coupled to polyisobutylene (PIB) [22,23]. A detailed description of the triblock synthesis will be published [24]. The diblock polymers exhibit thermoplastic elastomer properties, with allo-rich domains serving as physical crosslinks. Preliminary characterization of the triblock PIB-allo copolymers indicated significant tensile strength (~12 MPa) and elongation (600%) [22]. The conjugated diene side chains of the allo units also provide the possibility for chemical modification. Due to the high allo content, these thermoplastic elastomers cure very efficiently and much faster than butyl rubber. In this work we characterize the mechanical properties and their relation to structure in a poly(allo)-*b*-PIB-*b*-poly(allo) triblock copolymer.

2. Experimental

Isobutylene and alloocimene were sequentially reacted to form the triblock, with details of the synthesis found elsewhere [24]. The polymer studied herein had a number average molecular weight of 260 kg/mol (polydispersity = 1.6). The respective block molecular weights were in the ratio 0.21:1:0.13, with the allo content from ^{1}H NMR equal to 25.5% by weight. Dynamic mechanical experiments were carried out on an Anton Paar MCR 502 using a parallel plate geometry at low strains, and with a cone and plate geometry to quantify the strain dependence. The surface of a spin-coated

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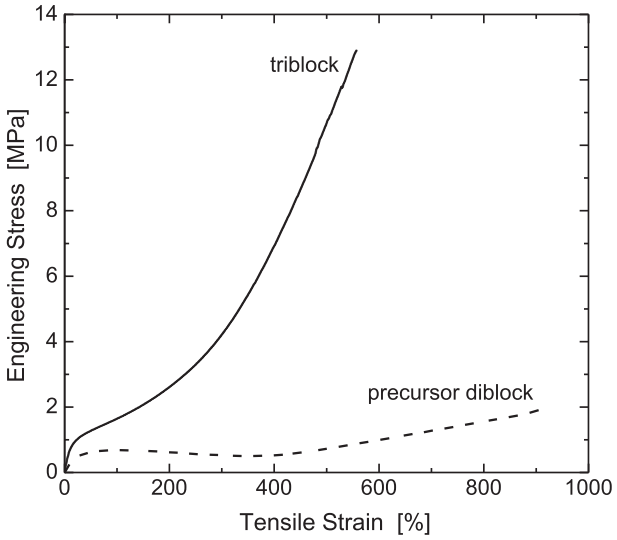

Fig. 1. Stress – strain response measured in extension of the precursor diblock (dashed line: M_n = 254 kg/mol; M_w/M_n = 1.47; 15.9 wt. % allo), and of the triblock obtained after addition of the second allo block (solid line: M_n = 244 kg/mol; M_w/M_n = 1.63; 25.5 wt. % allo).

(2000 rpm) film was imaged by atomic force microscopy (Cypher ES AFM, Asylum Research, CA) under nitrogen at various temperatures from RT to 90 °C; that is, through the allo softening point. The substrate temperature was controlled by the heating stage of instrument, with a thermocouple integrated with the sample stage, and the AFM probe cell sealed from the environment to minimize heat loss. Temperature was increased at 0.1C/s, with ~15 min equilibration at each measurement temperature. Transmission electron microscopy (TEM) was performed on 50 nm thick, cryomicrotomed films, with OsO_4 staining used to enhance the contrast.

3. Results and discussion

Fig. 1 compares the stress–strain response of the triblock and the precursor diblock, measured in tension at a nominal strain rate of 0.1 s^{-1}. The tethering the PIB chains at both ends increases the stress at failure by about a factor of 6. The tensile strength of the triblock, 13 MPa, is substantial for a rubbery polymer lacking covalent crosslinks. The failure strain is ~600%, consistent with thermoplastic elastomer behavior.

The triblock has a phase-separated morphology, as evidenced indirectly by its thermoplastic elastomeric behavior (Fig. 1), and directly with AFM and TEM images shown in Fig. 2. The dark regions in the TEM micrograph represent the stained allo phases, and the continuous light phase represents the PIB. The phase

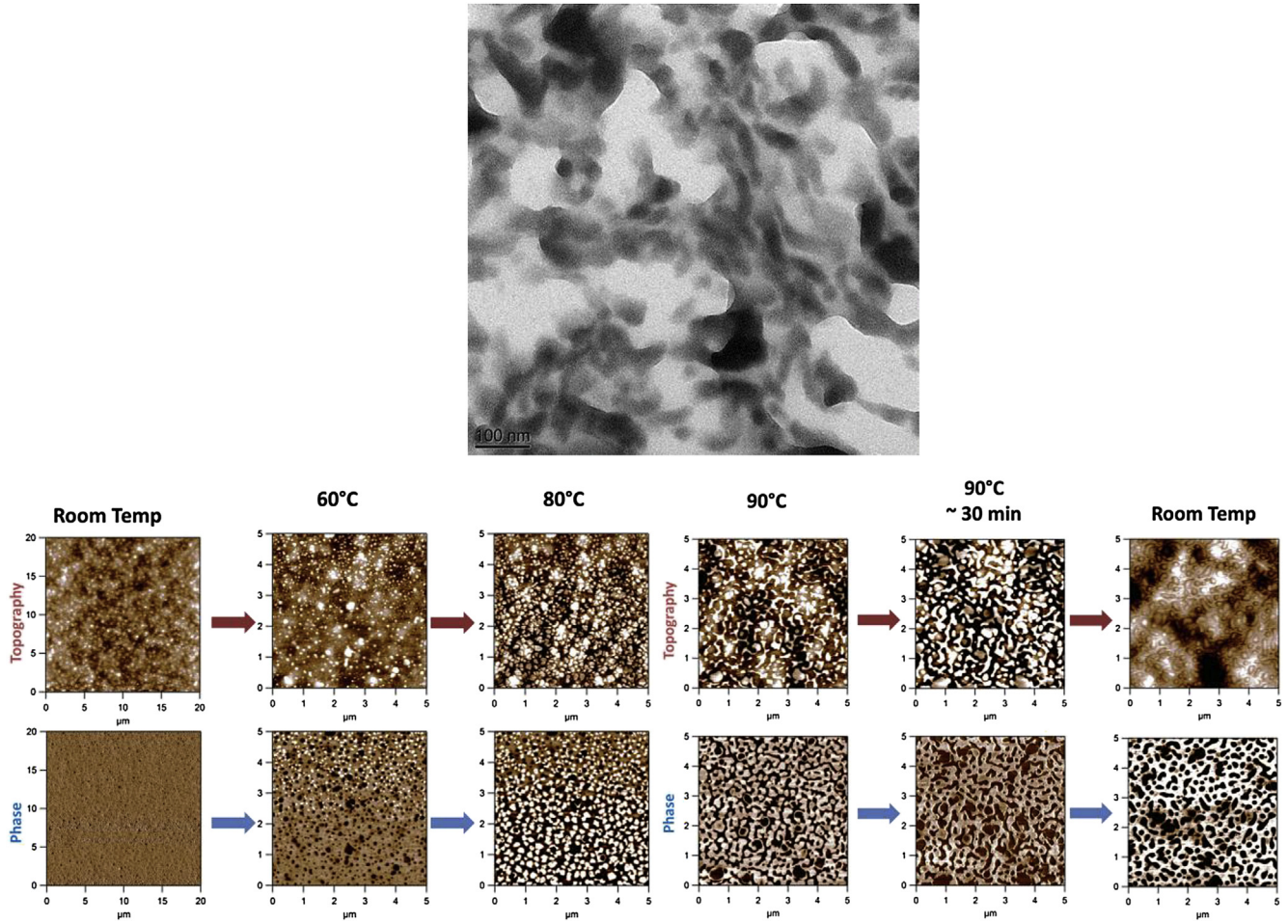

Fig. 2. (upper) TEM of the triblock at RT. (lower) AFM images of the topography and phase images of the spun-cast triblock copolymer at various temperatures through the softening point of the allo domains. The AFM image was obtained with hard tapping; brighter spots in phase image indicate a softer surface relative to the darker areas.