



Synthesis and properties of a new high-temperature liquid crystalline thermoplastic elastomer based on mesogen-jacketed liquid crystalline polymer



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ABSTRACT

In order to obtain high-temperature resistant thermoplastic elastomers (TPEs), we designed and synthesized a new kind of ABA triblock copolymer containing a mesogen-jacketed liquid crystalline polymer, poly(4'-(methoxy)-2-vinylbiphenyl-4-methyl ether) (PMVBP), as the hard blocks and polybutadiene (PB) as the soft block. PB was synthesized by ring-opening metathesis polymerization in the presence of a chain transfer agent, and PMVBP was synthesized by nitroxide-mediated radical polymerization. The glass transition temperature of the PMVBP block is 186–211 °C, which is much higher than that of polystyrene. More importantly, PMVBP can maintain its liquid crystallinity even when the temperature is as high as 270 °C, which can enhance the mechanical properties of TPEs based on PMVBP, especially at high temperatures. All the resulting PMVBP-PB-PMVBP triblock copolymer samples form lamellar microphase-separated structures after combined treatment of solvent annealing and thermal annealing. They are good candidates for TPEs with a high operating temperature of more than 200 °C.

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1. Introduction

Thermoplastic elastomers (TPEs) are usually composed of two resin segments (hard segments) and a rubber segment (soft segment) of triblock copolymers [1–3]. The hard segments in the triblock copolymers form physical crosslinking points, while the soft segment is highly elastic and contributes flexibility. The physical crosslinking points can reversibly break or form with the change of temperature, leading to the plastic processing properties of TPEs. Because TPEs have many unique physical and mechanical properties, they are known as the “third-generation synthetic rubbers” [4]. In the past decades, TPEs have experienced extremely rapid development and have been widely used in almost all areas of rubber products, such as building materials, medical equipment, and communications materials [5].

There are many kinds of TPEs, among which the most common products are polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and its corresponding hydrogenated derivatives [6–9]. SBS has many advantages, such as good tensile strength, elasticity, abrasion resistance, fatigue resistance, easiness for dyeing, and relatively low cost. However, the hard segment, polystyrene (PS), of SBS is easy to soften at high temperatures, which limits the high-temperature applications of SBS [10,11].

With the development of polymerization technology, how to obtain high-temperature resistant TPEs is a research focus in the field in recent years. The application of metal-catalyzed ring-opening metathesis polymerization (ROMP) brings new development of polyolefins [12–14]. Bifunctional polyolefins such as polybutadiene (PB) can be facilely synthesized by ROMP in the presence of symmetric acyclic olefin chain transfer agents (CTAs). This gives significant opportunities for the development of PB, polyisoprene (PI), and their corresponding TPEs [15–17].

Many studies have focused on the relationship between the chain structure and the phase structure in TPEs [10,18–22]. With the variation of the chain structure, the phase structure generally

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also changes, which is an effective way to improve the performance of TPEs. Introducing liquid crystalline (LC) polymers to TPEs to obtain liquid crystalline thermoplastic elastomers (LCTPEs) has become another strategy in obtaining high-temperature resistant TPEs [23–26]. The relationship among the liquid crystallinity, the microphase-separated structures, and the mechanical properties of these LCTPEs has been explored. The presence of liquid crystallinity in the hard segment renders high glass transition temperatures (T_g 's) and extra physical networks, which can increase the high service temperature and improve the mechanical properties of TPEs.

Mesogen-jacketed LC polymers (MJLCPs) are semi-rigid LC polymers, which have relatively large side groups laterally attached to the main chain through a very short spacer or just a C-C bond [27–29]. From the chemical viewpoint, MJLCPs are side-chain polymers, which can be readily synthesized by chain polymerization. However, from the physical viewpoint, the properties of MJLCPs are similar to those of main-chain LC polymers. MJLCPs usually are rigid or semi-rigid, with high T_g values and high LC-to-isotropic transition temperatures. Generally, the liquid crystallinity of MJLCPs is dependent on their molecular weights (MWs) [30–32]. Compared with PS, most MJLCPs with a PS main chain have higher mechanical strengths and higher T_g 's.

Yi et al. synthesized LCTPEs containing a typical MJLCP, poly{2,5-bis[4-methoxyphenyl]oxycarbonyl}styrene (PMPCS), as the hard segments and poly-*n*-butyl (P*n*BA) as the soft block [33]. Because the chemical properties of these two blocks are different, microphase separation occurs in bulk. The introduction of the MJLCP as the hard segments leads to stable physical networks, which are still stable above the T_g of PMPCS. The sample has a high melt viscosity, a high elongation at break, and a low tensile modulus. However, only when the MW of PMPCS is above 10×10^3 g/mol, can columnar LC phases form, which limits the synthesis and application of PMPCS-based LCTPEs [30,31]. In addition, because the elasticity of the soft segment P*n*BA is poor, the mechanical properties of this kind of LCTPEs are unsatisfactory. Liu et al. introduced an MJLCP as the soft segment and poly(4-vinylpyridine) as the hard segment to obtain an MJLCP-based TPE [34]. However, the T_g of the soft segment was too high to afford elasticity, and the position and the quantity of the metal coordination in the hard segment were not controllable. In addition, the mechanical properties of the TPE were not superior. In our recent work [35], we prepared new LCTPEs with PMPCS as hard blocks and PB as the soft block, and the materials showed relatively good mechanical properties. However, the service temperatures of these TPEs were not very high. In our previous work [32], we synthesized a new MJLCP, poly[4'-(methoxy)-2-vinylbiphenyl-4-methyl ether] (PMVBP), which has a relatively high T_g of 173–208 °C. And a hexagonal columnar (Col_h) LC phase forms when the number-averaged MW (M_n) of PMVBP is only above 5.3×10^3 g/mol, which is a low threshold MW for the LC formation for MJLCPs.

In this work, we combined ROMP chain transfer (ROMP-CT) with nitroxide-mediated radical polymerization (NMRP) to synthesize an ABA triblock copolymer containing the MJLCP, PMVBP, as the hard segments and PB as the soft segment. We investigated the relationship between the mechanical properties and the compositions of the resultant TPEs. The chemical structure of the target triblock copolymer, PMVBP-*b*-PB-*b*-PMVBP (V-B-V), is shown in Chart 1.

2. Materials and methods

2.1. Materials

cis-2-Butene-1,4-diol (J&K, 97%), 2-bromo-2-methylpropionyl

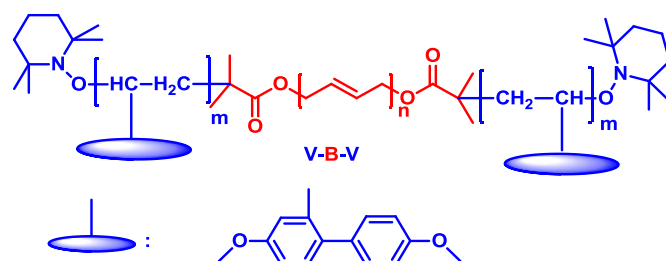


Chart 1. Chemical structure of V-B-V.

bromide (J&K, 98%), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), borane-tetrahydrofuran complex (J&K, 1.0 M solution in tetrahydrofuran, THF), Grubbs' catalyst (second generation, Sigma-Aldrich, 98%), and *N,N,N',N',N''*-pentamethyl diethylenetriamine (PMDETA, 98%, TCI) were used without further purification. The cyclic olefin monomer 1,5-cyclooctadiene (COD, J&K, 98.5%) was pretreated by borane-THF complex (1.0 M solution in THF), and then distilled under a reduced pressure. Triethylamine (TEA) was distilled from potassium hydroxide (KOH). Dichloromethane (DCM), THF, and chlorobenzene (PhCl) were purified by the M. Braun solvent purification system. All other reagents were commercially available and used as received.

2.2. Measurements

The chemical structures of the intermediates, the chain transfer agent, the monomer, and the polymers were characterized by ¹H/¹³C NMR, high-resolution mass spectrometry (HR-MS), and elemental analysis (EA). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained with a Bruker ARX400 spectrometer using deuterated chloroform as the solvent and tetramethylsilane as the internal standard at ambient temperature. HR-MS spectra were recorded on a Bruker Apex IV Fourier-transform ion cyclotron resonance mass spectrometer by electrospray ionization (ESI). EA was carried out with an Elementar Vario EL instrument. Other characterization methods, such as gel permeation chromatographic (GPC) measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light microscopy (PLM), one-dimensional wide-angle X-ray scattering (1D WAXS), small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), and tensile measurements were performed according to the procedures previously described [33,34].

2.3. Synthetic procedures

The synthetic route of V-B-V is shown in Scheme 1. The synthetic details are described below.

2.3.1. Synthesis of chain transfer agent 1,2-Bis(2,2,6,6-Tetramethylpiperidinoxyisobutyryloxy)-2-butene, CTA-NMRP

The synthetic route of the chain transfer agent is shown in Scheme 2. The method of synthesizing 1,2-bis(bromoisobutyryloxy)-2-butene has been reported in our previous work [35]. A mixture of 1,2-bis(bromoisobutyryloxy)-2-butene (2.00 g, 5.30 mmol), TEMPO (1.85 g, 11.7 mmol), PMDETA (56.0 μL, 0.260 mmol), and DMF (30.0 mL) were added into a polymerization tube. After the air in the tube was removed by three freeze-pump-thaw cycles, Cu (1.00 g, 15.6 mmol) and CuBr (37.4 mg, 0.260 mmol) were added into the tube under freezing conditions. After another three freeze-pump-thaw cycles, the tube was sealed under vacuum. Then the mixture was thawed, and the polymerization was conducted at ambient

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