High Temperature Thermoplastic Elastomers Synthesized by Living Anionic Polymerization in Hydrocarbon Solvent at Room Temperature

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ABSTRACT: We present the synthesis and characterization of a new class of high temperature thermoplastic elastomers composed of polybenzofulvene−polyisoprene−polybenzofulvene (FIF) triblock copolymers. All copolymers were prepared by living anionic polymerization in benzene at room temperature. Homopolymerization and effects of additives on the glass transition temperature (Tg) of polybenzofulvene (PBF) were also investigated. Among all triblock copolymers studied, FIF with 14 vol % of PBF exhibited a maximum stress of 14.3 ± 1.3 MPa and strain at break of 1390 ± 66% from tensile tests. The stress−strain curves of FIF-10 and 14 were analyzed by a statistical molecular approach using a nonaffine tube model to estimate the thermoplastic elastomer behavior. Dynamic mechanical analysis showed that the softening temperature of PBF in FIF was 145 °C, much higher than that of thermoplastic elastomers with polystyrene hard blocks. Microphase separation of FIF triblock copolymers was observed by small-angle X-ray scattering, even though long-range order was not achieved under the annealing conditions employed. In addition, the microphase separation of the resulting triblock copolymers was examined by atomic force microscopy.

INTRODUCTION

Since its discovery and after thriving for 60 years, living anionic polymerization1 has played a critical role in academic and industrial fields of polymer research because well-defined polymers with predictable molecular weight, narrow molecular weight distributions, and linear to complex macromolecular architectures can be prepared by this technique.2,3 Additionally, living anionic polymerization can produce polymers with negligible impurities in quantitative yields and with short production times under industrially relevant conditions. Therefore, anionic polymerization remains more favorable for commercialization as compared to other controlled polymerization techniques.4,5

Styrenic thermoplastic elastomers (STPEs), prepared by living anionic polymerization in hydrocarbon solvents at mild temperatures, are largely used in the fields of paving, roofing, footwear, and medical tubing.6 Such materials are A−B−A type triblock copolymers consisting of 1,4-polyisoprene (Tg ~ −56 °C) or 1,4-polybutadiene (Tg ~ −90 °C) as the rubbery B block which is physically cross-linked by glassy A blocks of polystyrene (PS, Tg ~ 100 °C) on both ends. Triblock copolymers of polystyrene-b-polysisoprene-b-polystyrene (SIS), designed first by Milkoivich and Holden,7 were targeted to improve the green strength and hot tear properties of polyeisoprene for production of synthetic rubber tires in large volume. However, this application failed, and other advanced consumptions of STPEs are still largely limited by the glass transition temperature of PS.8 When the service temperature approaches 100 °C, softening of the PS domains weakens the
physical cross-linking, leading to a sharp drop in tensile strength.

In order to improve the upper service temperature (UST) of TPEs, incorporating a glassy block with glass transition temperature higher than 100 °C is important. High Tg polymers such as poly(α-methylstyrene) (Tg ~ 173 °C) or poly(α-methyl-p-methylstyrene) (Tg ~ 183 °C) could be used as an alternative glassy block to replace PS. However, the bulkiness introduced by the methyl group at the α position leads to low ceiling temperatures (<60 °C), requiring low polymerization temperatures (~78 °C) in polar solvents such as tetrahydrofuran (THF) in order to achieve quantitative yields. Use of PS derivatives with bulky pendant group at the para position, such as poly(α-methylstyrene) (Tg ~ 173 °C) or poly(α-methyl-p-methylstyrene) (Tg ~ 183 °C) could also increase the UST of TPEs. However, the liphophilic nature introduced by these pendent groups causes phase separation between polydienes and reduces tensile strength. Catalytic hydrogenation to fully saturate PS into poly(vinylcyclohexane) (PVCH, Tg ~ 147 °C) produces TPEs with higher UST and better thermal stabilities, but these conditions will hydrogenate polydienes at the same time. The additional cost as well as the complete hydrogenation has limited the development of this approach, especially in applications where unsaturated polydienes are required.

As another approach, anionic polymerization of methyl methacrylate and other methacrylates in THF at ~78 °C was performed by initiating methacrylate monomer from a difunctional polydiene anion. Since polymerization of butadiene or isoprene in polar solvents will form less of the desired 1,4 microstructure, and thus dramatically increase the Tg of the difunctional polydiene anion needs to be synthesized in a hydrocarbon solvent. Because of the low polymerization temperature and high cost, this approach is not suitable for large scale industrial application. The various TPEs synthesized by other living-controlled polymerization techniques have also shown limited industrial applications. The use of cationic polymerization to produce high Tg polymers suffers from the same limitation due to the polymerization temperature. On the other hand, high service temperature TPEs prepared by controlled radical polymerization such as atom transfer radical polymerization require longer reaction times and pretermination to control the polymerization and generally contain metal catalyst.

Benzofulvene (BF) is a conjugated diene hydrocarbon monomer that undergoes polymerization by anionic, cationic, and radical mechanisms. As a derivative of fulvene, BF displays living anionic polymerization behavior in both THF as a polar solvent and benzene as a hydrocarbon solvent. The microstructure of the resulting polybenzofulvene (PB) depends on the polymerization solvents, temperatures, additives, and initiators. Regardless of the microstructure, for PB with a molecular weight above 10 kg/mol, the glass transition temperature is higher than 140 °C. The high glass transition temperature along with the capacity to undergo living anionic polymerization in hydrocarbon solvents makes BF an ideal candidate as the glassy building block for developing thermoplastic elastomers with higher upper service temperatures.

In this study, we present the synthesis and characterization of A-B-A triblock copolymer type thermoplastic elastomers, with polyisoprene as the elastic B block and PB as the glassy A block, via anionic polymerization. FIF triblock copolymers with four different compositions were prepared by living anionic polymerization in benzene at room temperature. The tensile testing of FIF samples was carried out to obtain stress-strain curves, and their mechanical properties are compared with those of Kraton D1112P SIS. Based on tensile testing, the optimal chemical composition of FIF for use as a TPE was investigated. Small-angle X-ray scattering (SAXS) were used to confirm the microphase separation between PI and PB. Atomic force microscopy (AFM) was employed to examine the morphology of FIF copolymer. The effect of polar additives on the Tg of PB is also presented.

<table>
<thead>
<tr>
<th>Table 1. Anionic Polymerization of BF in Benzene in the Absence of Additives</th>
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<td>8</td>
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</table>

*Mw*(calc) = (MW monomer) × [BF]/[initiator]. *Mw*(obsd) was characterized by SEC equipped with triple detectors: refractive index (RI), light scattering (LS) and viscometer detectors. *PDI* was calculated by SEC with polystyrene standard in THF. Tg was measured by DSC on the second heating scans. "Bimodal."
(1,3-phenylene)bis(3-methyl-1-phenylpentylidene) dilithium initiator in benzene were prepared according to reported procedure and diluted into desired concentration. Generally, the solution of DLI in benzene was prepared by addition of 2.2 equiv of sec-BuLi (27.06 mmol) into 1,3-bis(1-phenylvinyl)benzene (123.3 mmol, 3.47 g) in hexane (300 mL). Since DLI is insoluble in hexane, as the reaction proceeded DLI was precipitated inside the reactor. After removing hexane by filtration, the resulting red solid was diluted with benzene and calibrated by conducting a polymerization with isoprene and measuring the molecular weight of the resulting polymer. BF monomer was synthesized based on the literature, diluted with anhydrous benzene (0.3−0.5 M), and ampulized under high vacuum condition. All ampules of monomer, initiator, and additives were stored at −30 °C.

Anionic Polymerization of BF Monomer. All anionic polymerizations were carried out under high vacuum condition (10−6 Torr) with purified all glass apparatus equipped with break-seals. In a typical polymerization, the solution of BF (7.03 mmol, 0.900 g) in benzene was introduced into the solution of sec-BuLi (0.0235 mmol) in hexane, and the solution of polymer was quenched with degassed methanol after 1 h. All polymers were precipitated into large excess of methanol with 0.5% BHT, filtered, and dried. The characterization of PBF was performed by 1H NMR, size exclusion chromatography (SEC), and differential scanning calorimetry (DSC). The yield of PBF was quantitative (42.3 kg/mol, yield = 100%, molecular weight distribution PDI = 1.08, Tg = 152.2 °C, Table 1, run 5).

Anionic Polymerization of BF Monomer in the Presence of Additives. The solution of DME (0.121 mmol) in benzene was introduced into the solution of n-BuLi (0.0121 mmol) in hexane at 0 °C using an ice bath and kept at 5 °C. The solution of BF (1.54 mmol, 0.197 g) in benzene was added to the initiation system. After complete polymerization, the solution of polymer was quenched with degassed methanol, and the purification was performed as described above. The yield of PBF was 99% (16.3 kg/mol, PDI = 1.10, Tg = 191.5 °C, Table 2, run 9). For anionic polymerizations of BF monomer in the presence of other additives, similar addition and purification procedures were employed. When sec-BuOLi was used as the additive, the polymerization was carried out at room temperature.

Triblock Copolymerization of Isoprene and BF. In a typical polymerization procedure, DLI and sec-BuOLi were first mixed in benzene followed by addition of isoprene. After complete consumption of isoprene, as monitored by SEC over 5 days, BF monomer (5.75 mmol, 0.737 g) was introduced into the solution of living polysisoprene (0.0614 mmol, 4.36 g) in benzene, and the resulting solution of this triblock copolymer was terminated with degassed methanol after 8 h. All FIF triblock copolymers were precipitated into large excess of methanol with 0.5 wt % of IRGANOX B 225 as the long-term thermal stabilizer. Precipitates were filtered and dried in vacuum oven for 48 h.

Preparation of Samples. For tensile tests, a solution of 2 g of polymer in 80 mL of toluene was stirred overnight at room temperature and casted into a glass bowl with inner diameter of about 90 mm and evaporated slowly over 7 days. Upon removing residual solvent from the films, all samples were annealed at 70 °C under vacuum (10−1 Torr) and stamped into dog bone shaped specimens (type SA, ISO 527/2) with film thickness around 0.2−0.3 mm. For dynamic mechanical analysis, polymer solutions were cast into smaller PTFE dishes, resulting in film thicknesses of 0.5−0.6 mm. For the measurement of small-angle X-ray scattering, we first attempted to anneal solvent cast samples at 170 °C for 24 h under N2 in order to achieve a thermodynamically equilibrated morphology. However, all samples of PI and PBF were thermally cross-linked as evidenced by SEC traces. Thus, all samples were annealed at 155 °C for 12 h under dynamic vacuum. No noticeable cross-linked polymers with very high molecular weights were detected by SEC. For atomic force microscopy, mold pressed polymer sheet was trimmed and microtomed at −120 °C using a diamond knife into ultrathin section with thickness around 100 nm.

Table 2. Anionic Polymerization of BF in Benzene in the Presence of Additives

<table>
<thead>
<tr>
<th>run</th>
<th>sample ID</th>
<th>BF (mmol)</th>
<th>initiator (mmol)</th>
<th>[additive]/[initiator]</th>
<th>Mw (kg/mol)</th>
<th>PDI</th>
<th>yield (%)</th>
<th>Tg (°C)</th>
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<tr>
<td>9</td>
<td>PBF_DME_16</td>
<td>1.54</td>
<td>0.0121</td>
<td>10</td>
<td>16.3</td>
<td>15.9</td>
<td>1.10</td>
<td>191.5</td>
</tr>
<tr>
<td>10</td>
<td>PBF_DME_40</td>
<td>3.08</td>
<td>0.0099</td>
<td>10</td>
<td>40.0</td>
<td>39.0</td>
<td>1.12</td>
<td>198.7</td>
</tr>
<tr>
<td>11</td>
<td>PBF_DABCO_20</td>
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<td>0.0201</td>
<td>3</td>
<td>20.3</td>
<td>28.5</td>
<td>1.86</td>
<td>187.0</td>
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<tr>
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<td>PBF_TMEDA_20</td>
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<td>0.0220</td>
<td>1</td>
<td>19.8</td>
<td>12.2</td>
<td>2.35</td>
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<td>0.0554</td>
<td>10</td>
<td>7.3</td>
<td>6.9</td>
<td>1.16</td>
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</tr>
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<td>PBF_sec-BuOLi_23</td>
<td>4.05</td>
<td>0.0228</td>
<td>10</td>
<td>22.7</td>
<td>23.1</td>
<td>1.10</td>
<td>153.1</td>
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Mw (calcd) = (MW monomer) × [BF]/[initiator]. Mw (obsd) was characterized by SEC equipped with triple detectors: refractive index (RI), light scattering (LS), and viscometer detectors; dn/dc of PBF was 0.227. PDI was calculated by SEC with polystyrene standard in THF. Tg was measured by DSC on the second heating scans. Multimodal. Initiator: n-BuLi (runs 9,10) and sec-BuLi (runs 11−14).
Modeling of Tensile Data. To understand the deformation behavior of block copolymers on molecular scale, the nonaffine and non-Gaussian tube model was adapted and applied to the stress–strain data of FIF copolymers. The model quantifies the amount of the...
Table 3. Composition of FIF Triblock Copolymers

<table>
<thead>
<tr>
<th>run</th>
<th>sample ID</th>
<th>PI (kg/mol)</th>
<th>M_n&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;a&lt;/sup&gt;</th>
<th>FIF (kg/mol)</th>
<th>M_n&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PBF (kg/mol)</th>
<th>M_n&lt;sup&gt;b&lt;/sup&gt;</th>
<th>NMR (%)</th>
<th>SEC (%)</th>
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<tr>
<td>15</td>
<td>FIF-10</td>
<td>76.7</td>
<td>1.08</td>
<td>87.8</td>
<td>1.08</td>
<td>5.6</td>
<td>9.5</td>
<td>10.1</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>16</td>
<td>FIF-22</td>
<td>76.7</td>
<td>1.08</td>
<td>98.2</td>
<td>1.10</td>
<td>10.7</td>
<td>22.0</td>
<td>19.1</td>
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<tr>
<td>17</td>
<td>FIF-31</td>
<td>76.7</td>
<td>1.08</td>
<td>106.0</td>
<td>1.09</td>
<td>20.0</td>
<td>30.9</td>
<td>30.1</td>
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<tr>
<td>18</td>
<td>FIF-14</td>
<td>87.6</td>
<td>1.11</td>
<td>110.6</td>
<td>1.14</td>
<td>11.5</td>
<td>13.6</td>
<td>12.8</td>
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<sup>a</sup>M<sub>n</sub> of PI and FIF was characterized by SEC equipped with triple detectors: refractive index (RI), light scattering (LS), and viscometer detectors. PDI was calculated from SEC with polystyrene standard in THF.

"chemical" (G<sub>c</sub>) and the "physical" (entanglements, G<sub>e</sub>) part of the overall modulus. Further, information is obtained on the average number of statistical segments between two successively trapped entanglements. In contrast to chemically cross-linked elastomers, the application of a rubber elasticity model requires additional explanations when used for tensile data of TPEs. In TPEs, the glassy region, where G<sub>c</sub> becomes most obvious in the Gaussian region, where G<sub>c</sub> corresponds to the slope. Changes in G<sub>c</sub> result in a vertical shift.

Equation 2 holds for uniaxial deformation taking into account an incompressible elastomer matrix. It contains three parameters: the chemical and the physical cross-link modulus (G<sub>c</sub>, G<sub>e</sub>) and the parameter n = n<sub>e</sub>/T<sub>e</sub>. The latter represents the number of statistical segments between two successively trapped entanglements with the trapping factor T<sub>e</sub>. The model curve of eq 2 can be subdivide into three regions: the neo-Hookean, the Gaussian region (approximately constant slope), and the upturn region. While n controls the upturn region, the impact of G<sub>c</sub> and G<sub>e</sub> becomes most obvious in the Gaussian region, where G<sub>e</sub> corresponds to the slope. Changes in G<sub>c</sub> result in a vertical shift.

Figure 4. SEC curves of FIF triblock copolymers.

Anionic Polymerization of BF in Benzene at Room Temperature without Polar Additive. Previously, Ishizone examined the anionic polymerization of BF in benzene at 0, 40, and 55 °C. The molecular weight was targeted from 2.8 to 29 kg/mol. In order to fully examine the anionic polymerization behavior of BF, especially at room temperature, we first polymerized benzofulvene in benzene with sec-BuLi as initiator with targeted molecular weight ranging from 4.5 to 200 kg/mol (Table 1). Controlled molecular weights and narrow polydispersity indexes (PDI < 1.16) were achieved when the target molecular weight was lower than 86.4 kg/mol (Table 1, runs 1–7; see Figure S1 for SEC curves in Supporting Information). All polymers were recovered in quantitative yield.

However, the polymerization of BF targeting 200 kg/mol, as shown in Table 1, run 8, was uncontrolled and exhibited a bimodal distribution with a M<sub>n</sub> of 175 kg/mol lower than calculation. The glass transition temperature of PBF increased from 127 to 153 °C as the M<sub>n</sub> was increased from 4.5 to 86.4 kg/mol (black squares in Figure 1). Slightly change of T<sub>g</sub> was observed after the molecular weight was above 18.9 kg/mol. Quantitative 13C NMR analysis indicated 22%–28% of 1,2-microstructure was presented in PBF synthesized with sec-BuLi.
without polar additive. This observation is consistent with previously reported data where the molecular weight was targeted from 2.8 to 29 kg/mol.28

**Effects of Additives on Glass Transition Temperature.** One feature of anionic polymerization of diene monomers is that different polar additives can change the reactivity of the propagating anion and lead to polymers with different microstructures, i.e., tunable 1,2- and 1,4-addition.36 Different from "conventional additives" which are small molecules added to compound during processing, the terminology “additives” as
used in this paper indicates chemicals added during the polymerization to change the microstructure of resulting polymers. Generally, glass transition temperatures \( (T_g) \) of polydienes such as polybutadiene and polysoprene increase as the percentage of 1,2-addition in the polymer chain. Ishizone studied anionic polymerization of BHV and polyisoprene increased as the percentage of 1,2-addition relative to that of 1,4-addition in the polymer chain. 

Attempts to tailor the microstructure of PBF by using polar additives in hydrocarbon solvent was not reported in their work. Thus, it is of our interest to investigate the effects of polar additives on the microstructure and the glass transition temperature of PBF.

Different from isoprene or butadiene, BF is a relative bulky monomer similar to 1,3-cyclohexadiene (CHD). For the anionic polymerization of CHD, controlled polymerization behavior was observed when additives such as 1,4-diazabicyclo[2.2.2]octane (DABCO), dimethoxyethane (DME), and \( N,N,N',N' \)-tetramethylethylenediamine (TEMDA) were used during the polymerization in benzene or cyclohexane. The percentage of 1,2-addition in the resulting poly(1,3-cyclohexadiene) (PCHD) was 7%, 28%, and 45% with respect to these three additives. The glass transition temperature increased as the percentage of 1,2-addition increased. Thus, the same initiation systems used in tailing microstructure of PCHD were employed in this research.

Surprisingly, when DME was used as the additive, the resulting polymers displayed glass transition temperatures above 190 \( ^\circ \)C (red cycle in Figure 1a). The PBF_DME_40 (Table 2, run 10) with \( M_n \) of 39.0 kg/mol exhibited higher \( T_g \) of 198.7 \( ^\circ \)C than 191.5 \( ^\circ \)C of PBF_DME_16 (Table 2, run 9) with \( M_n \) of 15.9 kg/mol. Both polymerizations yielded polymers having predicted \( M_n \), narrow polydispersity indexes (PDI < 1.12) and with quantitative yield. \( ^{13} \)C NMR spectra showed that PBF_DME_16 has about 99% of 1,2-addition microstructure. The high \( T_g \) feature of PBF_DME is attributed to the high percentage of 1,2-microstructure in the polymer chain. It is worth noting that polymerizations with DME as the additive were performed at 5 \( ^\circ \)C with \( n \)-BuLi as the initiator. In hydrocarbon solvent, lower polymerization temperature of diene monomer leads to higher percentage of 1,2-addition. 

Unlike controlled polymerization of CHD, polymerizations of BF using either 1,4-diazabicyclo[2.2.2]octane (DABCO) or \( N,N,N',N' \)-tetramethylethylenediamine (TEMDA) as additives were uncontrolled, where broad MWDs and multimodal curves were observed in SEC. 12% and 86% yields were obtained using the TEMDA and DABCO initiation systems, respectively. The PBF_DABCO_20 (Table 2, run 11) synthesized with DABCO as additive showed high \( T_g \) of 187 \( ^\circ \)C (green square in Figure 1a), however, with a yield of 86%. It has been observed that the living polymer anion has relatively low stability in the presence of DABCO after the the consumption of monomers. This might be the reason we observed low yields and uncontrolled polymerization of benzofulvene with DABCO as the additive.

Polymerization of BF with TEMDA was also uncontrolled with a yield of only 12% (PBF_TEMDA_20, run 12, Table 2). The low yield and uncontrolled polymerization are likely due to lithiation between benzene and the sec-BuOLi/TEMDA complex. Generally cyclohexane is employed as the hydrocarbon solvent when TEMDA is used as the additive during anionic polymerization. However, PBF has very limited solubility in cyclohexane. Thus, we proceeded to carry out the polymerization in benzene in order to evaluate the glass transition temperature of the polymer. The resulting polymer PBF_TEMDA_20 showed a \( T_g \) of 155.2 \( ^\circ \)C (pink triangle in Figure 1a), similar to the \( T_g \) of PBF synthesized without additive.

Additional to the three aforementioned additives, we also evaluated the polymerization behavior of benzofulvene with sec-BuOLi (lithium sec-butoxide) as the additive since this additive is critical to preparation and use of the difunctional living polyisoprene anion. PBF prepared by using sec-BuOLi showed lower \( T_g \) of 142.3 and 153.1 \( ^\circ \)C (blue triangle in Figure 1a) with 22% and 28% of 1,2-addition, respectively (runs 13 and 14 in Table 2), which is similar to polymerization without any additives. Both polymerizations produced polymers with predicted \( M_n \), narrow PDI and quantitative yield. For the anionic polymerization of isoprene and butadiene, it has been observed that sec-BuOLi has little effect on polydiene microstructure and \( T_g \) giving products comparable to those obtained without any additives.

Finally, we plot \( T_g \) versus percentage of 1,2-addition where molecular weight is sufficiently high that \( T_g \) does not depend on \( M_n \) (Figure 1b). The data we used are PBF-40 (black square in Figure 1b, \( M_n = 38.3 \) kg/mol, \( T_g = 152 ^\circ C \) with 24% of 1,2-microstructure), PBF_DME-40 (red cycle in Figure 1b, \( M_n = 40.0 \) kg/mol, \( T_g = 199 ^\circ C \) with 98% of 1,2-microstructure), and PBF_THF-16 (blue star in Figure 1b). The glass transition temperature \( (T_g \) = 162 \( ^\circ \)C) and molecular weight \( (M_n = 16 \) kg/mol) of PBF_THF-16 were reported in a previous publication.
by Ishizone (Table 1, run 3). As the percentage of 1,2-addition increased from 24 to 41 to 98%, the glass transition temperature increased linearly from 152 to 162 to 199 °C.

Microstructure Analysis of PBF Synthesized without Additive and with DME as the Additive. In order to analyze the microstructure of PBF, we tracked chemical shifts of three different carbons: C_α for quaternary carbon in 1,2-addition, C_m for methylene carbon in between 1,2- and 1,4-addition, and C_t for tertiary carbon of 1,4-addition. According to previous reports, there are four possible dimers in polybenzofulvene if stereoregularity is not taken into consideration: h-1,4–1,4-t; h-1,4–1,2-t; h-1,2–1,4-t, and h-1,2–1,2-t. Here, h means head and t means tail in the structure (Figure 2). In Figure 3, the signal at 57 ppm was assigned to C_m in both PBF-10 and PBF-DME-16 since this signal was only observed in $^1^3^C$ NMR spectra. Signals at 46 and 48 ppm for PBF-10 (spectra a and b in Figure 3) were assigned to C_t since these signals were observed in both $^1^3^C$ NMR spectra and positive phase in DEPT-135. Integration from quantitative $^1^3^C$ NMR spectra of C_m and C_t showed 28% of 1,2-addition in PBF-10. Surprisingly, the C_m signal was not observed in PBF-DME-16 and only C_t signal was observed from 25 to 50 ppm. Thus, the microstructure in PBF-DME-16 was dominated by 1,2-addition. Signals in $^1^H$ NMR spectra in Figure S2 (see Supporting Information) were rather broad and could not be used to analyze the microstructure.

Triblock Copolymerization of BF with Isoprene. There are three possible methods to prepare polybenzofulvene–polyisoprene–polybenzofulvene (FIF) triblock copolymers by living anionic polymerization. The first method is to sequentially initiate BF, isoprene, and BF monomer after complete consumption of the previous monomer (sequential anionic polymerization). The second method is to couple living polybenzofulvene–polyisoprene diblock copolymer by the polyisoprene chain end anion using a difunctional linking agent such as dichlorodimethylsilane or α,α′-dibromo-p-xylene (anion coupling reaction). The third method is to initiate BF polymerization using a diblock functional isoprene anion prepared by a difunctional lithium initiator (difunctional initiator method). Since isoprene cannot be initiated by polybenzofulvene anion, neither sequential anionic polymerization using BF monomer as first monomer nor anion coupling reaction using polybenzofulvene–polyisoprenyllithium anion could be used to prepare polybenzofulvene-b-polyisoprene-b-polybenzofulvene (FIF) triblock copolymers. To synthesize FIF triblock copolymers with four different compositions (Scheme 1), the third approach involving the use of a difunctional lithium initiator (DLI) with BuOLi (molar ratio = 10), prepared in benzene at room temperature, was employed. FIF with 9.5 vol % (FIF-10), 13.6 vol % (FIF-14), 22.0 vol % (FIF-22), and 30.9 vol % (FIF-31) PBF were prepared by the DLI approach (Table 3). In FIF-10, -22, and -31 (runs 15–17), the M_n of PI is 76.6 kg/mol, whereas FIF-14 (run 18) has 87.6 kg/mol of PI M_n. All resulting triblock copolymers have narrow PDI’s and predicted molecular weight, which were confirmed by SEC (Figure 4) and $^1^H$ NMR (Figure 5). As shown in Figure 5, signals of 6.75–7.60 ppm, 4.95–5.25 ppm, and 4.55–4.80 ppm in the $^1^H$ NMR spectra correspond to aromatic proton (H_a) in PBF block, 1,4-addition proton (H_b) in PI block, and 3,4-addition proton (H_c) in PI block, respectively. According to the analysis of $^1^H$ NMR spectra, we confirmed that PI block in FIF triblock copolymers has 93% 1,4-addition. The volume percentage of PBF presented in FIF was calculated based on integration $^1^H$ NMR with the density of PBF homopolymers of 1.146 g/cm³ as well as on SEC as listed in Table 3. The thermal properties of FIF were evaluated using DSC and TGA as shown in Figures S3 and S4 (see Supporting Information).

Dynamic Mechanical Analysis (DMA). The relaxation behavior of the triblock copolymers FIF-14, -22, and -31 was investigated by dynamic shear measurements. Temperature sweeps measured in the range from −100 to 200 °C at a frequency of 10 rad/s are shown in Figure 6. A low temperature relaxation process was observed at −54 °C corresponding to the glass-to-rubber transition (α_g) of the PI phase indicated by a stepwise decrease in G’(T) and a peak in G″(T). The observed softening temperature was close to the thermal glass temperature T_g = −56.7 °C of PI as taken from DSC scans with a rate of 10 °C/min (Figure S3). During further heating the storage modulus G’(T) showed another pronounced drop when the temperature approaches 140 °C. This drop in G’(T) can be related to the glass-to-rubber transition of the PBF hard phase (α_pBF) and was accompanied by a broad peak in the loss modulus G″(T). The measured softening temperatures were consistent with the T_g values of the PBF end block reported in Table 1. The storage modulus G’(T) in the temperature range between the α_p and α_pBF processes increased systematically as the volume fraction of PBF was increased. Low G’ values of a few MPa were obtained in this temperature range for FIF-14 similar to the situation in classical TPEs, and filled elastomers while much larger storage moduli (30 MPa < G’ < 300 MPa) were found for FIF-22 and FIF-31. This indicates a transition from isolated PBF domains in FIF-14 to a percolated PBF phase in FIF-22 and FIF-31. Note that a certain temperature-dependent decrease in G’ occurs for all samples in the range between the α relaxations of both phases, α_p and α_pBF.
accompanied by relatively large absolute values of the loss modulus \( G''(T) \). Both findings can be interpreted as an indication for the occurrence of interfacial material with intermediate softening temperatures containing isoprene and BF units. The fraction of interfacial material increased obviously with increasing PBF content as indicated by larger \( G'' \) contributions. Interestingly, an additional very broad, smeared relaxation process with a maximum near 30 °C was indicated for samples with higher PBF contents (FIF-22, FIF-31). This finding may be related to the existence of a relative uniform interphase with given isoprene-BF contents apart from the pure PI and PBF phases.

**Stress–Strain Behavior of FIF Triblock Copolymers.**

After studying the softening behavior, the tensile strength of FIF triblock copolymers was tested. It was found that the Young’s modulus \( (E) \), tensile stress \( (\sigma) \), and strain at break \( (\epsilon_B) \) could be tuned based on the volume fraction of PBF (Table 4).

The rather low Young’s modulus for FIF-10 and FIF-14 gave indications for a noncontinuous hard phase in the rubbery matrix. Specifically, FIF-14 displayed highest strain at break of 1394 ± 66% and the best tensile strength of 14.3 ± 1.3 MPa (Figure 7) among all samples. These tensile properties were competitive with Kraton D1112P, a commercial SIS triblock among all samples. These tensile properties were competitive with Kraton D1112P, a commercial SIS triblock copolymer used in sealants, coating, adhesives, and other applications. Interestingly, an additional very broad, smeared relaxation process with a maximum near 30 °C was indicated for samples with higher PBF contents (FIF-22, FIF-31). This finding may be related to the existence of a relative uniform interphase with given isoprene-BF contents apart from the pure PI and PBF phases.

**Microphase Separation Behavior.**

The microphase separation behavior between PBF and PI in FIF triblock copolymers was investigated by SAXS. In the SAXS measurements (Figure 9a), microphase separation without long-range order was observed between PBF and PI in all FIF samples. A broad secondary peak was observed approximately at 3.3q* after the maximum primary peak q*. However, none of the reflection pattern \( (q/q^*) \) of FIF-10, -14, -22, and -31 matched with Bragg reflection for the morphology of any A-B-A type block copolymer. The broad, rounded peaks separated by cusp-like minima in the SAX data are characteristic of form factor scattering resulting from the shape of the microphase separated domains. The absence of Bragg peaks indicates that these domains are not ordered on a lattice, but rather are randomly distributed. Both spherical and cylinder form factor can be used to fit SAXS data of FIF-10 and FIF-14 (Figure 9b). This indicates a morphology of disordered, worm-like, microphase-separated spheres and cylinders in FIF-10 and FIF-14. For FIF-22 and FIF-31 SAXS data can be fit to cylindrical form factors with radii ranging from 9 to 16 nm for the various samples. This indicates a morphology of disordered, worm-like, microphase-separated cylinders for FIF-22 and FIF-31. Since all samples were annealed at 155 °C for 12 h in order to prevent thermo-cross-linking of unsaturated carbon–carbon double bond in FIFs, this annealing condition might be insufficient for glassy PBF domains to reorganize into an ordered lattice.

The average PBF–PI domain distance \( (d_{AV,PBF–PI}) \) of all four FIF samples were calculated from \( d_{AV,PBF–PI} = 2\pi/q^* \) and summarized in Table 5. As the volume fraction of PBF (\( \phi_{PBF} \)) increased from 9.5% to 30.9%, the average PBF–PI domain distance increased from 35.3 to 57.1 nm. Assuming PBF in FIF-10 and FIF-14 formed spherical assemblies, the average diameter of the PBF spheres, \( d_{AV,PBF,sph} \) can be calculated by eq 3:

\[
d_{AV,PBF,sph} = d_{AV,PBF–PI} \sqrt{\frac{3}{\pi}} \phi_{PBF}
\]

Lastly, bulk morphology of FIF-10 was examined by atomic force microscopy using tapping-mode in the air on a cryo-microtomed cross section (Figure 10). Disordered worm-like domains were observed in the phase image (Figure 10b), since the observed contrast in the phase images mostly reflects differences in elastic and adhesive properties between PI and PBF blocks. The length scales and periodicities from AFM measurement were consistent with those from SAXS.

**CONCLUSIONS**

In summary, FIF triblock copolymers with four different compositions were synthesized by living anionic polymerization in benzene at room temperature. Dynamic mechanical analysis indicated that the softening temperature of PBF in FIF copolymers was around 145 °C. Tensile testing of sample FIF-14 (with 14 vol % of PBF) displayed a maximum stress of
Among the additives studied, the initiation system of DME/PrBuLi produced PBF with the highest T_g above 190 °C.

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**REFERENCES**


