Polycaprolactone-Based Block Copolymers. 3. Mechanical Behavior of Diblock Copolymers of Styrene and \( \varepsilon \)-Caprolactone

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ABSTRACT: Polystyrene blocks-\( \varepsilon \)-caprolactone copolymers (PS-PCL) exhibit a two-phase morphology that dictates their mechanical behavior. The dependence of the isochronous torsion modulus on the copolymer composition clearly shows that a phase inversion takes place at ca. 45 wt % PCL. Although the stress-strain curves are governed by the nature of the continuous phase, the minor component influences the values of stress and strain in each deformation region. At least at compositions close to the phase inversion, the minor component appears to act as a rubber phase, as supported by electron microscopy and the appearance of a completely amorphous PS-polyester copolymer comprising 56 wt % polyester. Although brittles at 77 K, a PS-PCL copolymer containing 56 wt % PCL exhibits a ductile fracture when extended by 300%, i.e., when the PCL spherules are transformed into a microfibrillar structure.

Introduction

Ring-opening polymerization of lactones, lactams, and epoxides bestows on the synthesis of polymers, polyamides, and polyesters the advantages of chain reactions. Substituting a living polyaddition of cyclic monomers for the usual step-growth process is the best way to control the introduction of the aforementioned chain blocks in block polymers.1 Living anionic polymerization of styrene and ethylene oxide is the first likely illustration of that opportunity.2 A few years ago, a family of homocyclic \( \varepsilon \)-alkoxides was synthesized as very active anionic coordin- ation-type catalysts in the living polymerization of caprolactone (c-L).3,4 These catalysts have been successfully modified into polymer (FX) bound catalysts able to produce a poly(caprolactone) (PCL) containing block polymers (FX-PCL) with well-defined molecular parameters.5 Among other copolymers, a series of poly(styrene-block-\( \varepsilon \)-caprolactone) (PS-PCL) has been synthesized and characterized. Block polymers of composition near 50 wt % of each component display liquid crystalline structures, at room temperature, in the presence of a selective solvent for the amorphous PS block.6 Phase morphology of bulk copolymers has been investigated by optical and transmission electron microscopy. Monodisperse monocrystals have been prepared by crystallization from highly diluted solutions in a nonvolatile solvent. How PCL blocks crystallize from the melt has been considered in relation to the molecular weight and composition of the copolymers.7-9 The degree of miscibility of PS and PCL, as well as the nature of the continuous phase, has a decisive effect on the crystallization process. A major interest is the potential interfacial activity of PS-PCL copolymers in immiscible PS-PVC blends. Since PS is known to be miscible with PVDC PS-PCL diblocks might behave as compatibilizers or emulsifiers in those polyblend and improve their poor mechanical properties. The main conclusions of this paper will be published in the near future. In this paper we address the mechanical behavior of PS-PCL diblock copolymers. The discussion will emphasize the effects that phase morphology and especially crystallization of PCL blocks have on the mechanical resistance to deformation and ultimate fracture of these materials.

**Experimental Section**

(G-O)-Al(OH)\(_2\)/(diisobutylmethyl)aluminum \( \varepsilon \)-lactone was the initial catalyst, the isopropylene groups of which were replaced by 2- ethylhexyl groups and \( \varepsilon \)-caprolactone (ECL) \( \varepsilon \)-caprolactone (ECL), respectively. The living block polymerization of CL proceeded through the selective anion–oxygen cleavage of the lactone with

![Image](image-url)
Figure 3. Stress-strain curves of PS–PCL diblock copolymers and PCL of 36,000 molecular weight. Samples have been molded at 435 K (52 °C) for PCL into 100-μm-thick films and tested at 300 K at an extension rate of 6 cm min⁻¹.

Figure 4. Optical micrograph of a benzene cast film of PCL and PS–PCL diblock copolymer C4 (see Table II).

Table II. Mechanical Properties of the Poly(styrene-block-ε-caprolactone) Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>E(MPa)</th>
<th>τₚ (MPa)</th>
<th>τₚ₀ (MPa)</th>
<th>τₚ₁ (MPa)</th>
<th>τₚ₀ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>3300</td>
<td>40</td>
<td>3</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>C₁</td>
<td>1550</td>
<td>24.5</td>
<td>3.5</td>
<td>24</td>
<td>20</td>
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<tr>
<td>C₂</td>
<td>4400</td>
<td>12.5</td>
<td>1.4</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>C₃</td>
<td>300</td>
<td>16.0</td>
<td>1.4</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>C₄</td>
<td>20</td>
<td>10.0</td>
<td>0.8</td>
<td>10.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Values reported for a specimen (M₂; 10,000) molded according to AIST 412-D. \( M_2: \text{100,000} \).

Figure 5. Transmission electron micrograph of the PS–PS diblock copolymer containing 64 wt % PCL and cast from butane (sample C₂; see Table I). PCL is observed as dark phases, and the mean size of the PS domains is about 300 nm.

Figure 6. Scanning electron micrograph of the fracture surface of the PS–PCL diblock copolymer containing 56 wt % PCL. Sample C₅ molded according to AIST 412-D and fractured at 77 K. Observed at a higher magnification on Figure 6C (denoted C). Area E on Figure 6B is the region of the greater crack speed (hackle) characterized by surface roughness on a scale upwards of a few microns. After an extension by 300%, the diblock copolymer no longer behaves in a brittle manner in contrast to most polymers fractured at low temperature (below Tₖ). A fibrillar structure is now obvious in the direction of the applied stress (Figure 7). The failure has also promoted the formation of stairs, the front of which shows a randomly sized honeycomb region which could have resulted from stress-induced fissures. Fissures should be interpreted as if each fissure is a void, which separates two separate faces. Comparison of Figures 6 and 7 supports the claim that the extension of the diblock copolymer C₅ beyond the yield point (300%) induces a dramatic reorganization of the intact structure and accounts for the ductility observed. Ductility still persists at 77 K as supported by the presence of the voids in the sample opposite to fracture when surfaces to be observed by SEM are prepared.

Discussion of the stress-strain results relies on the presence of semicrystalline phases formed by the minor component. Although the view is already supported by transmission electron microscopy (Figure 5), another evidence can be found in the load-extension curve of a PS-ε-caprolactone diblock copolymer. It has been reported elsewhere that the random copolymerization of \( \varepsilon \)-caprolactone (c-CL) and (β-dimethyl-ε-caprolactone (mixed isomers, XCL) leads to an amorphous polymer which provides the weight percentage of the method derivative is higher than 6%. This is the reason for preparing a completely amorphous PS–polyester diblock copolymer in which the polyester block is a random copolymer of c-CL.
Introduction. Finally, it is obvious that the mechanical behavior of the PS–PCL diblock copolymers changes dramatically when the phase inversion occurs, i.e., when the nature of the component blocks is reversed. Nevertheless, the minor component does not form systematically dispersed microdomains, especially at compositions close to the phase inversion composition, in the minor component forms semicontinuous phases intermingled within the matrix of the major block; there is evidence of a strong dependence of the stress-strain curves on the two-phase morphology.

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Registry No. (Si–CL) block copolymer, 106107-55-5.

References and Notes


Block Copolymers near the Microphase Separation Transition. 4. Dielectric Spectroscopy

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ABSTRACT: In this paper, we report evidence of local concentration fluctuations in thermodynamically homogeneous diblock copolymers near the microphase separation transition (MST). Dielectric spectroscopy has been used to probe the local structure of a series of 1,4-polybutadiene/1,2-polybutadiene diblock copolymers with morphologies that ranged from well-ordered to disordered. Four transitions, corresponding to the primary (glass) and secondary transitions of each block, are observed in the dielectric loss spectrum of each copolymer studied. Observation of a primary transition for each block provides evidence of local concentration heterogeneity. At the MST, the glassy block exhibits an apparent glass transition, even in samples that are homogeneous on the molecular length scales probed by small-angle neutron-scattering and rheological measurements. To characterize these heterogeneities, the dielectric loss data have been fit with four discrete transitions, representing each of the glass and secondary transitions. Model fits indicate that the disordered block copolymers are characterized by large-amplitude concentration fluctuations which diminish in magnitude with decreasing x, where x is the segment–segment interaction parameter and x' is the degree of polymerization. These results are consistent with recent fluctuation corrections by Fredrickson and Helfand to Leibler's mean-field theory for diblock copolymers near the MST.

Introduction. Most of the thermodynamic properties characterizing polymer mixtures are determined by local (segment–segment) interactions. In general, these nature of the short-range interactions, which occur over length scales around the size of a polymer repeat unit, are inferred from experiments that probe length scales larger than the radius of gyration (Rg) of the polymer coils. Techniques such as differential scanning calorimetry (DSC), cloud-point measurements, dynamic mechanical spectroscopy, or zero-angle scattering using light, X-rays, or neutrons have been used to determine the phase diagrams of polymer mixtures from which x, the Flory-Huggins segment–segment interaction parameter, can be obtained. The success of these macroscopic measurements in establishing x derives from the mean-field nature of polymer–polymer phase behavior, which breaks down only very near the critical point where fluctuation effects are manifested.1 Diblock copolymers represent an alternative class of materials that may be used to study segment–segment interactions. The local interactions in block copolymers are, in principle, indistinguishable from those of binary polymer blends when one considers the homogeneous state. Whereas mean-field theories predict that polymer–polymer mixtures can macroscopically phase separate when the parameter x exceeds 2 (ref 2), x is the degree of polymerization.