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Polycaprolactone-Based Block Copolymers. 3. Mechanical Behavior of Diblock Copolymers of Styrene and ε-Caprolactone

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ABSTRACT: Poly(styrene-*block*-ε-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 forms semicontinuous phases as supported by electron microscopy and by the mechanical hysteresis of a completely amorphous PS–polyester copolymer comprising 55 wt % polyester. Although brittle at 77 K, a PS–PCL copolymer containing 56 wt % PCL exhibits a ductile fracture when extended by 300%, i.e., when the PCL spherulites are transformed into a microfibrillar structure.

Introduction

Ring-opening polymerization of lactones, lactams, and epoxides bestows on the synthesis of polyesters, polyamides, and polyethers 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 chains in block polymers.[1] Living anionic block polymerization of styrene and ethylene oxide is the first likely illustration of that opportunity.[2] A few years ago, a family of bimetallic μ-oxo alkoxides was synthesized as very active anionic coordination-type catalysts in the living polymerization of ε-caprolactone (ε-CL).[3,4] These catalysts have been successfully modified into polymer (PX) bound catalysts able to produce poly(ε-caprolactone) (PCL) containing block polymers (PX-PCL) with well-defined molecular parameters.[5] Among other copolymers, a series of poly(styrene-*block*-ε-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. Monolamellar monocrystals have been prepared by crystallization from highly dilute solutions in a nonsolvent of PCL.[7] How PCL blocks crystallize from the melt has been considered in relation to the molecular weight and composition of the copolymers.[7] 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 PCL is known to be miscible with PVC,[8] PS–PCL diblocks might behave as compatibilizers or emulsifiers in these polyblends and improve their poor mechanical properties. The main conclusions of this will be published in the near future. In this paper we address the question of 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.

Table I
Molecular Parameters of the Investigated Poly(styrene-*block*-ε-caprolactone) Copolymers

sample	$\bar{M}_n$ PS	$\bar{M}_n$ PCL	PCL, wt %
C1	70 000	35 000	33
C2	70 000	55 000	44
C3	70 000	90 000	56
C4	40 000	100 000	70
Al[a]	90 000	110 000	55

[a] Al comprises a random copolyester block of ε-CL and β,δ-dimethyl-ε-caprolactone (60%).

Experimental Section

(μ-Oxo)bis[bis(1-methylethoxy)aluminum]zinc was the initial catalyst, the isopropyloxy groups of which were replaced by 2-ethylhexanoate and hydroxy-terminated polystyrene (PS), respectively. The living block polymerization of ε-CL proceeded through the selective acyl–oxygen cleavage of the lactone with

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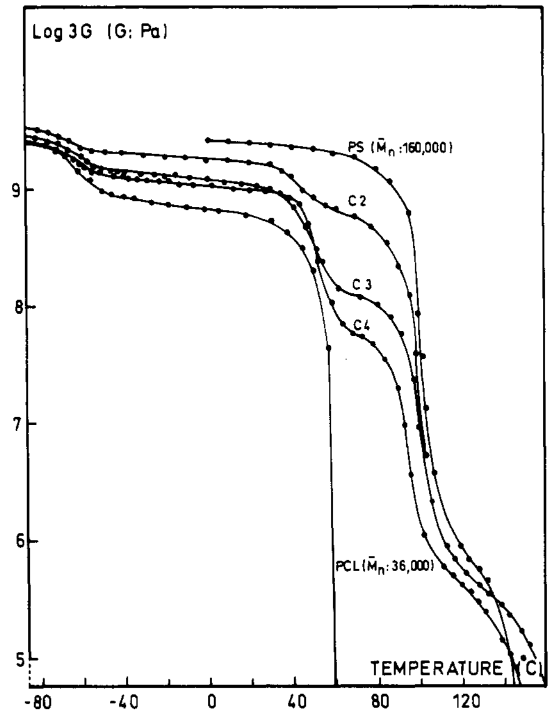


Figure 1. Isochronous (10-s) torsion modulus versus temperature curve of PS–PCL diblock copolymers in comparison with the related homopolymers.

insertion into the Al–OPS bond of the polymer-bound catalyst, all the Al-2-ethylhexanoate bonds being inactive. Copolymerizations were carried out under argon atmosphere in a previously dried glass reactor. The synthesis of the catalyst and the copolymerization procedure were extensively described elsewhere.[5] The absolute molecular weight of the first block (PS) and the final block copolymer were determined by osmometry and/or size exclusion chromatography using the universal calibration method.[5] The copolymer composition was calculated from ^{1}H NMR spectra recorded on a Varian HA-100 spectrometer. Table I summarizes the main molecular features of the diblock copolymers investigated in this study.

Films were cast from highly dilute copolymer solution in benzene (0.1%) and examined by transmission electron microscopy (TEM) in a JEOL Model JEM 100 U microscope and by optical microscopy under polarized light. They were previously dried at 333 K, for 24 h, under reduced pressure. The fracture surfaces of samples molded at 433 K for 3 min were examined by scanning electron microscopy (Stereoscan Cambridge). A Gehman-type torsion pendulum and an Instron Model 1026 were used for mechanical testing of samples molded according to ASTM 412 D (433 K for 3 min) and films of about 100 μm thickness (dried at 333 K for 24 h), respectively.

Results and Discussion

Figure 1 illustrates the thermal dependence of the torsion modulus for PS–PCL copolymers of increasing PCL content in comparison with the related homopolymers. The glass transition temperature (T_g) of each block as well as melting temperature (T_m) of PCL is clearly observed, which supports an extended phase separation. The two-phase morphology of PS–PCL copolymers has been extensively discussed in relation to the molecular weight of each block in a previous paper.[7] The modulus of the plateau observed between melting of PCL and T_g of PS decreases in the expected way as the PS content decreases. It is worth noting that copolymers containing more than 50 wt % PS are brittle, as supported by the failure of the testing sample at T_g of PS. In contrast, when PCL is the major component, copolymers exhibit a rubbery plateau above T_g of PS. This plateau extends over twice the temperature range than that observed for PS. The viscous flow is delayed. Copolymer C3 has a larger rubbery plateau than C4 as a consequence of the longer PS block it contains in spite of a smaller PCL content.

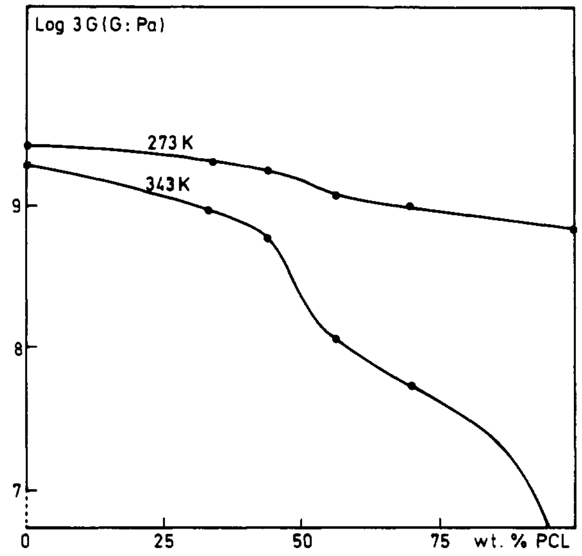


Figure 2. Dependence of the isochronous (10-s) torsion modulus on the composition of PS–PCL diblock copolymers, at 273 and 343 K, respectively.

Figure 2 shows the torsion modulus at 273 K (a temperature below both the T_g of PS and the T_m of PCL) as a function of copolymer composition. The modulus decreases slowly but continuously with a small inflection point at 45 wt % PCL. At 343 K (a temperature between T_m of PCL and T_g of PS), an S-shaped curve is reported with a much stronger inflection point. The torsion modulus is of the same order of magnitude as that of PS, when PS is the major component (≥55 wt %). Beyond that composition, the torsion modulus drops off, and its value is consistent with a multiphase material in which PCL forms the continuous phase. These data indicate that a phase inversion occurs at 45 wt % PCL, and this is in a good agreement with previous observations by transmission electron microscopy.[7] This agreement between mechanical and microscopic measurements taken on samples prepared in a different way has to be outlined. It might indicate that the experimental results reflect a phase behavior at least close to equilibrium. Thus, a straightforward relation emerges between phase morphology and mechanical behavior of PS–PCL copolymers. The origin of the brittleness of the PS-rich copolymers is found in the continuous but fragile matrix formed by the rather low molecular weight (40–70000) PS. For this polymer, the average molecular weight between entangelements is expected to be about 20000.[9] When PCL is the major component as in C3 and C4, the melting of the PCL does not cause a dramatic drop in the modulus as is observed in the homopolyester in Figure 1. This is commonly observed for block copolymer systems in which the block elements are incompatible and exist as separated domains. Below T_g of PS, the PCL blocks are inhibited from viscous motion because of the glassy PS domains. Above the T_g of PS, the melt viscosity seems higher, perhaps an indication that the two-phase morphology persists even at temperatures above the T_g of PS. Similar observations have been reported for multiphase polystyrene–polybutadiene,[10] polystyrene–poly(ethylene oxide),[11] and polybutadiene–nylon 6[12] copolymers.

The stress–strain behavior of PS–PCL copolymers has been investigated using ca. 100-μm-thick films. Copolymers containing less than 44 wt % PCL were too

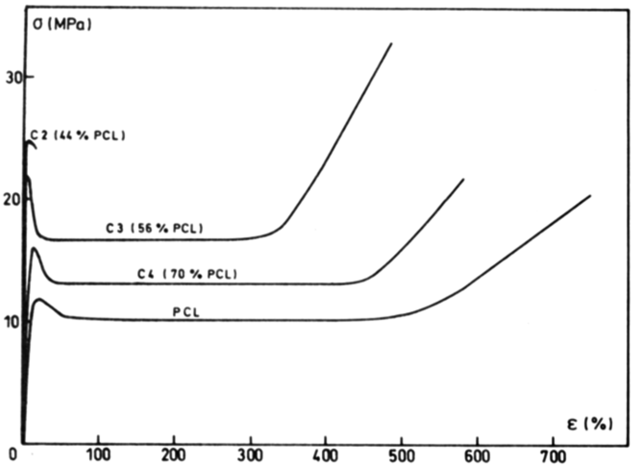


Figure 3. Stress–strain curves of PS–PCL diblock copolymers and PCL of 36000 molecular weight. Samples have been molded at 433 K (373 K for PCL) into 100-μm-thick films and tested at 300 K at an extension rate of 6 cm min^{-1}.

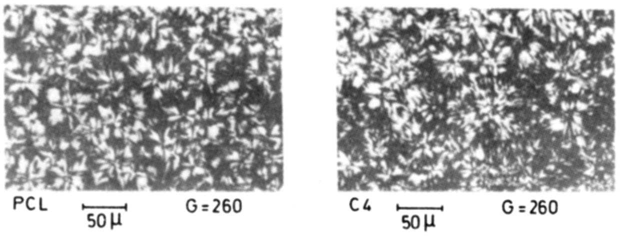


Figure 4. Optical micrograph of a benzene cast film of PCL and PS–PCL diblock copolymer C4 (see Table I).

Table II
Mechanical Properties of the Poly(styrene-*block*-ε-caprolactone) Copolymers[a]

sample	E, MPa	σ_y, MPa	ϵ_y, %	σ_D, MPa	σ_B, MPa	ϵ_B, %
PS[b]	3350				40	3
C_2	1550	24.5	3.5		24	20
C_3	700	21.5	6	16	32.5	480
C_4	300	16.0	14	12.5	21.5	575
PCL[c]	170	12.0	19	10	20	750

[a] 100-μm films molded at 433 K, except for PCL (373 K). [b] Values reported for a specimen ($\bar{M}_n$: 160000) molded according to ASTM 412 D. [c] $\bar{M}_n$: 120000.

brittle to be characterized. Figure 3 compares PCL and block copolymers containing 70, 56, and 44 wt % PCL, respectively. The homopolyester exhibits the typical behavior of a semicrystalline polymer tested at a temperature intermediate between T_g and T_m.[13] Although deformed at a rather high rate (600% min^{-1}), the PCL chains have enough mobility to relieve the applied stress by rearrangement of the internal structure of the polyester sample. As shown in Figure 4, a benzene cast film of PCL is spherulitic and the spherulites are undeformed and expectedly interconnected to each other. In the initial step of the deformation process, there is a sharp rise in load with increasing extension. In this strain-softening region, some plastic deformation already occurs, which is not very obvious on Figure 3, due to the poorly extended scale of the extension axis and the high deformation rate. According to a general pattern valid for any semicrystalline polymer, shear forces within the spherulites predominate at the yield point and promote the slippage of the crystal lamellae.[13] Necking occurs beyond the yield point as shown by a decrease in stress, after which the stress remains constant with increasing strain over a broad range of strain. During this deformation step, lamellae present in the original spherulites are transformed into microfibrils by slip, separation, and orientation parallel to the extension direction. Finally when the fully microfibrillar structure has been developed, a fiberlike deformation region is reached, referred to as strain hardening. Plastic deformation requires now ever increasing stress in order to promote slippage of the fibrils past one another and to overcome frictional forces and unfolding of lamellae on the fibril surfaces.

During the whole loading process, the amorphous regions of PCL are being deformed simultaneously to the deformation of spherulites into a microfibrillar structure. Thus, the final anisotropic structure of the polymer and the features of the stress–strain curve result from the concomitant deformation of both crystalline and amorphous regions and from their mutual interaction. This complexity is still more pronounced when the PS–PCL diblock copolymers are concerned, since phases of semicrystalline PCL are now intimately associated with glassy phases of PS. Actually, the two types of phases are anchored to each other through covalent bonds, resulting in a strong interfacial adhesion and an efficient transfer of stress between the phases. Of course, how the amorphous PS domains are deformed is an open question. Only dichroism measurements (unavailable to the authors) could indicate whether the PS domains remain unaligned after deformation of the PCL spherulites. Figure 3 shows that, when the PCL percentage is larger than ca. 50 wt %, diblock copolymers exhibit a stress–strain pattern with the same characteristic features as PCL. A dramatic change occurs, however, for copolymers containing less than 50 wt % PCL. A much more fragile behavior, reminiscent of PS, is indeed observed instead of the ductile behavior of PCL. This observation is quite consistent with Figure 2 which supports a phase inversion taking place in a composition range intermediate to that of copolymers C2 (44 wt % PCL) and C3 (56 wt % PCL). It is thus reasonable that the stress–strain behavior be dominated by the polymer present in the continuous phase. Nevertheless, since they are intimately intermingled within the matrix formed by the major component, phases of the second partner should influence the main characteristics of the stress–strain curve. Such an effect can be found in Table II which summarizes the values of the initial modulus (E), the stress (σ), and strain (ϵ) at yield point (σ_y, ϵ_y) and at break (σ_B, ϵ_B), respectively, as well as the constant stress (σ_D) beyond the yield point.

Going from pure PCL to copolymers containing 56 wt % PCL, a general increase in stiffness is observed, and values of Table II support that the dispersed PS phases have a reinforcing effect in each deformation region. The initial modulus increases 4 times, while a 2-fold increase in the yield stress is observed in connection to a substantial decrease in the yield strain. It ensues that, although PCL is the major component, elasticity and ultimate failure of PS microdomains control the strain-softening region. As discussed later, extra data support that the PS phases are semicontinuous. It is therefore questionable whether PS is a filler or its phase morphology contributes to the PCL stiffening. Moreover, the necking becomes more pronounced and sharper; i.e., the decrease in stress is greater and extends over a decreasing elongation range. It appears that necking would be initiated in the more brittle PS microdomains whereas the neck would "consume" the whole specimen in the same way as in the semicrystalline polyester but at a higher stress. Thermal analysis shows that drawing copolymer C3 has no significant effect on the degree of crystallinity of PCL phases (45%) but promotes a substantial increase in the melting point, i.e., from 55°

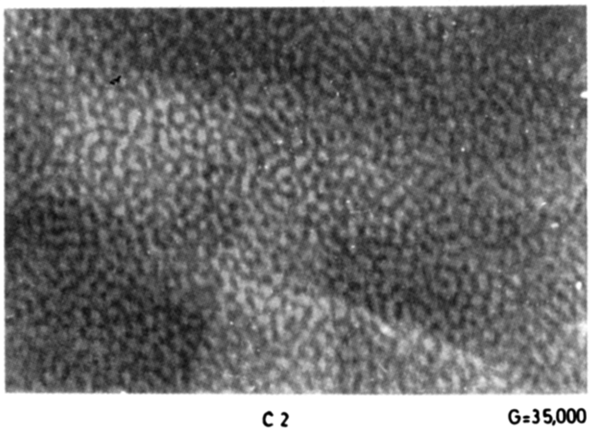
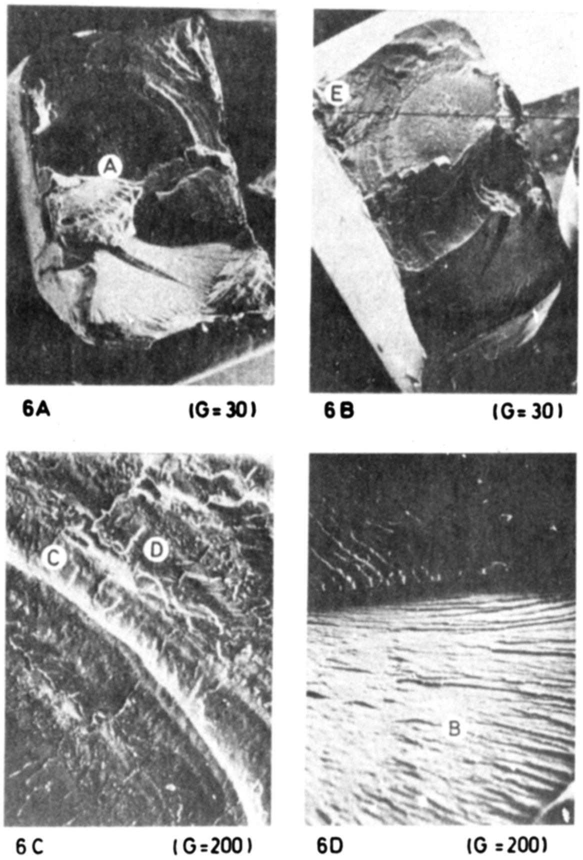


Figure 5. Transmission electron micrograph of the PS–PCL diblock copolymer containing 44 wt % PCL and cast from benzene (sample C2, see Table I). PCL is observed as dark phases,[7] and the mean size of the microdomains is 400 Å.

to 63 °C and a narrowing of the melting temperature range. Quite clearly, at room temperature, i.e., approximately 30 °C lower than the melting point, deformation of the crystalline structure not only gives rise to alignment of crystalline lamellae parallel to the drawing direction but also allows removal of crystal defects and/or growth in the size of PCL crystal domains. The partial restoration of crystal perfection should reduce the strength of the fibrous material caused by the disappearance of tie molecules. This effect can, however, be overcome by the presence of PS microdomains. It might also be suggested that PCL spherulites are greatly hindered as they propagate through a melt containing dispersed and incompatible PS domains. The drawing process could accordingly initiate the further growth of these small PCL crystal domains. Finally, the stress-hardening region occurs earlier and the stress rises more rapidly as the PCL content decreases. This effect supports that the glassy PS microdomains to which PCL blocks are chemically bonded connect more strongly adjacent fibrils of PCL and restrict their longitudinal displacement.

In the same way as PS dictates the main features of the stress–strain curve of PCL when PS is the minor component, the mechanical behavior of PS should be affected by PCL present at a content smaller than 50 wt %. Indeed, copolymer C2 is less brittle than PS. Yielding and initiation of necking are observed, resulting in an elongation at break of 20% instead of a few percent for PS (Table II). When the film is observed after failure, it is obvious that it has crazed in tension. Undoubtedly, the ductile PCL microdomains, which are at least partly interconnected to each other (Figure 5), are efficient in delaying the ultimate rupture.



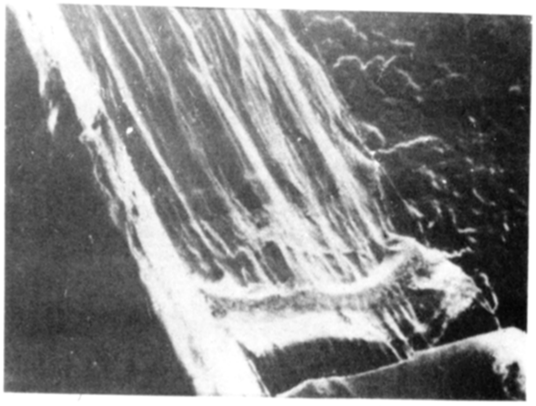
6A (G=30) 6B (G=30)

6C (G=200) 6D (G=200)

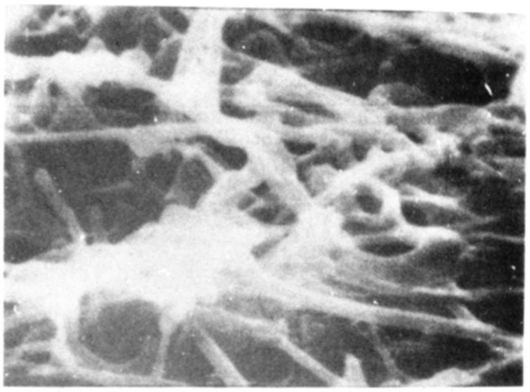
Figure 6. Scanning electron micrograph of the fracture surface of the PS–PCL diblock copolymer containing 56 wt % PCL. Sample C3 molded according to ASTM 412 D and fracturated at 77 K.

In order to ascertain that the lamellae present in the original spherulitic PCL phases are destroyed during drawing in favor of microfibrils, copolymer C3 has been molded according to ASTM 412 D. The molded sample has been fracturated at low temperature (77 K) before any previous deformation and after an extension of 300%. The fracture surfaces have been observed by scanning electron microscopy (SEM). Before extension, the copolymer behaves as a glassy amorphous polymer.[14,15] Figure 6 shows indeed the main features of a brittle fracture. The fracture surfaces, as shown in parts A and B of Figure 6, are mainly perpendicular to the length of the specimen, and their upper part allows us to observe a central initiation point surrounded by the three typical regions: mirror area, mist area, and hackle area. Figure 6D gives some details of the mirror region (noted B), while the mist area has been observed at a higher magnification on Figure 6C (denoted C). Area E on Figure 6B is the region of the greatest 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 fracturated at low temperature (below T_g). 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-face 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 enclosed on two separate faces. Comparison of Figures 6 and 7 supports that the extension of the diblock copolymer C3 beyond the yield point (300%) induces a dramatic reorganization of the intimate structure and accounts for the ductility observed. Ductility still persists at 77 K as supported by the resistance that the sample opposes to fracture when surfaces to be observed by SEM are prepared.

Discussion of the stress–strain results relies on the presence of semicontinuous phases formed by the minor component. Although that view is already supported by transmission electron microscopy (Figure 8), another evidence can be found in the load-extension curve of a (PS–amorphous polyester) diblock copolymer. It has been reported elsewhere that the random copolymerization of ϵ-caprolactone (ϵ-CL) and β,δ-dimethyl-ϵ-caprolactone (mixed isomers, XCL) leads to an amorphous polyester provided the weight percentage of the methyl derivative is higher than ca. 40%.[16] It is thus possible to prepare a completely amorphous PS–polyester diblock copolymer in which the polyester block is a random copolymer of ϵ-CL

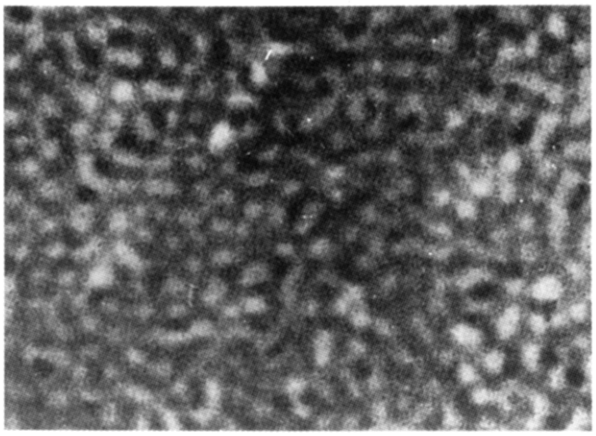


7A (G = 40)



7 B (G = 40,000)

Figure 7. Scanning electron micrograph of the fracture surface of the PS–PCL diblock copolymer containing 56 wt % PCL. Sample C3 molded according to ASTM 412 D, elongated by 300%, and fracturated at 77 K. B is a magnification of the front view of a "stair" visible on A.



C 3 G = 100,000

Figure 8. Transmission electron micrograph of the PS–PCL diblock copolymer containing 56 wt % PCL and cast from benzene (sample C3, see Table I). PCL is observed as dark phases,[7] and the mean size of the microdomains is 500 Å.

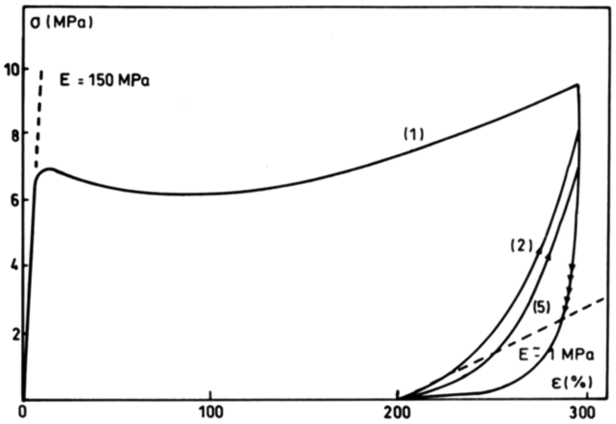


Figure 9. Stress–strain curve of the amorphous PS–polyester diblock copolymer (sample A1, see Table I). The sample has been molded at 433 K into a 150-μm-thick film and tested at 293 K at an extension rate of 9 cm min^{-1}. (1), (2), and (5) refer to the first, the second, and the fifth deformation cycle, respectively.

and XCL. By use of the polymerization pathway reported for the synthesis of PS–PCL copolymers, a PS block of 90 000 molecular weight has been associated to a random copolyester block of 110 000 molecular weight comprizing 60 wt % XCL. This amorphous diblock copolymer (A1) has the same polyester content (55%) as the semicrystalline copolymer designated as C3 in Table I. The stress–strain curve is shown on Figure 9, which unfortunately does not allow a straightforward comparison with the curves of Figure 3. Indeed, the two types of copolymer have not been available at the same time, and they have been tested under different experimental conditions. Nevertheless, Figure 9 provides meaningful information. The amorphous diblock copolymer can be extended up to approximately 600%, and beyond the yield point, it shows a partially recoverable deformation rather than a distinct drawing region as does semicrystalline copolymer C3. This is supported by a hysteresis loop when the extension is limited, for instance, at 300% (Figure 9). At that time, the copolymer recovers by ca. 33%, and a 10-fold drop in the initial modulus is observed. When the deformation cycle is repeated from the unrecovered 200% elongation, the hysteresis loop does not change very much and the sample recovers the deformation completely. It ensues that replacing a semicrystalline polyester block by an amorphous one is unfavorable to the occurrence of a clearly defined drawing region. This means that the spherulite-to-fibril transformation of the crystalline PCL phases is the major contribution to the drawing of the PS–PCL diblock copolymers. Moreover, the drop in the initial modulus between the first and the second deformation cycle for the sample in Figure 9 is an indication of the rupture of some rigid structure during the initial extension step. Hysteresis loops are usually observed when poly(styrene-*block*-butadiene-*block*-styrene) copolymers are loaded and their stress–strain curve recorded.[17,18] In that case, the unrecovered elongation is, however, much smaller due to the physical cross-linking of polybutadiene by the dispersed glassy domains of PS. Nevertheless, the origin of the mechanical hysteresis has been attributed to PS domains which are not isolated but interconnected by thin paths of PS, although the copolymer composition is dominated by polybutadiene.[17,18] When the PS structural interconnections are broken, the material becomes rubberlike, and this explains why the mechanical response reported in Figure 9 no longer changes significantly.

Conclusion

Block copolymerization is a very useful tool to extend the service range of two polymers otherwise limited in their applications. Combining in a ratio of ca. 55 wt % a ductile polyester (PCL) that flows above 50 °C to a very brittle component like PS leads to a material that enjoys the ductility of PCL but with an increase in the initial modulus and a substantial delay in the occurrence of flow. The opportunity to impart a fibrillar structure to the material is not the least advantage, and its high impact resistance even at low temperature would deserve further investiga-

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tion. 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 continuous phase changes. Nevertheless, the minor component does not form systematically dispersed microdomains, especially at compositions close to the phase inversion. When 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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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 heterogeneities, large enough to exhibit 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 χN, where χ is the segment–segment interaction parameter and N 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, the nature of these 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 (R_g) 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 χ, the Flory–Huggins segment–segment interaction parameter, can be obtained. The success of these macroscopic measurements in establishing χ 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 both systems are in the homogeneous state. Whereas mean-field theories predict that polymer–polymer mixtures can macroscopically phase separate when the parameter χN exceeds 2 (ref 2; N is the degree