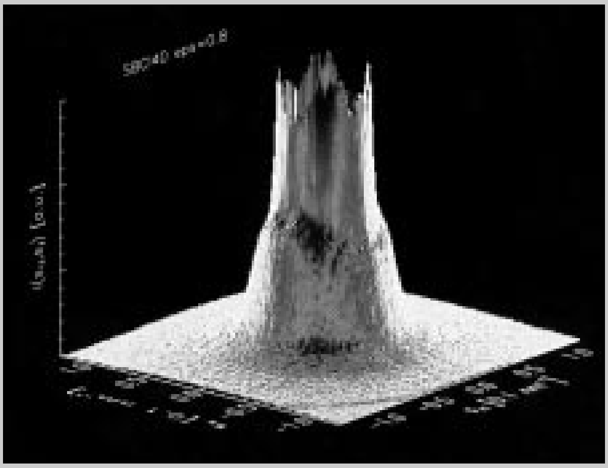
Full Paper: Block copolymers containing ε-caprolactone were synthesized. Mechanical properties as a function of chemical composition and domain structure as a function of elongation were studied. Based on previous optimal conditions determination by factorial design of experiments of ε-caprolactone anionic polymerization, polystyrene-*block*-poly(ε-caprolactone), polyisoprene-*block*-poly(ε-caprolactone), polystyrene-*block*-polybutadiene-*block*-poly(ε-caprolactone) (SBCL), and polystyrene-*block*-polyisoprene-*block*-poly(ε-caprolactone) (SICL) with different compositions where synthesized, and characterized by GPC and DSC. Both the SICL and SBCL materials are thermoplastic elastomers, from which spin-cast films were prepared. Their mechanical properties were determined, small angle X-ray scattering (SAXS) measurements were carried out during straining, and dynamic mechanical analysis (DMA) was performed. All diblock polymers separate into a two-phase structure, but the melting point of crystalline poly(ε-caprolactone) domains in the block polymer is higher than in the case of the homopolymer. According to DMA data, some of the SICL and SBCL materials are three-phase systems, but others are only two-phase systems. The two-phase materials show a considerable depression of the composite hard domain glass transition and, consequently, turn out to be very soft. It appears peculiar that the transition from three-phase to two-phase material is accomplished by decreasing the soft block length. For the soft material SAXS exhibits a lamellar stack nanoscale structure and several reflections of colloidal crystals. As a function of increasing elongation, the crystal reflections broaden, whereas lamellar stacks rotate as a whole.



SAXS pattern of SBCL-40 at 80% elongation.

Synthesis and Properties of some ε-Caprolactone-Based Di- and Triblock Polymers by Anionic Polymerization

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Introduction

Copolymers with an A-B-C block structure, in which the middle block B is flexible and the end blocks A and C are glassy or crystalline at service temperature, are thermoplastic elastomers (A and C may be identical). These materials combine the melt processing characteristics of thermoplastic materials with many of the physical properties of vulcanized rubber. The rubbery nature of the products is a consequence of the thermodynamic incompatibility of thermoplastic and elastic blocks, resulting in a two-phase structure: glassy or crystalline hard domains that act as physical crosslinks dispersed in a rubbery polydiene matrix. The copolymer is easily processed above glass transition temperature of the hard domain phase, which allows recycle of scrap unlike vulcanized or chemically crosslinked polymers.[1,2] The most important thermoplastic elastomers are the styrene-diene block copolymers.

Replacing (some of the) polystyrene blocks with poly(ε-caprolactone) blocks by ring-opening anionic polymerization, the resulting block copolymers become potential engineering materials, because the favorable properties of thermoplastic elastomers[1,2] can be combined with higher ozone-resistance[2] and, probably, bio-

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degradability,[3–6] as is know from the lactide or ε-caprolactone (linear polyesters) based synthetic polymers ("green polymers"). From the point of view of environmental protection the latter would be very important.

Another potential application is the toughening of brittle polymers by incorporation of rubbery particles. Currently styrene-diene block polymers are frequently used for this purpose.[1,2] They possess limited miscibility especially with polymers resulting from polar monomers (e.g. PVC, polyacrylates and methacrylates, etc.). Therefore is desirable to widen the range of miscibility. It is expected that the presence of poly(ε-caprolactone) blocks in the block copolymers will increase the compatibility towards different polymers, broadening the range of applications concerning the toughening of the brittle polymers by blending.

Recently interest has been focused on ε-caprolactone based block polymers, and papers have been published on poly(ε-caprolactone)-*block*-polystyrene,[7,8] poly(ε-caprolactone)-*block*-polybutadiene[9,10] and polystyrene-*block*-polyethylene-*block*-poly(ε-caprolactone), which is in fact hydrogenated polystyrene-*block*-polybutadiene-*block*-poly(ε-caprolactone).[11,12]

The aim of this study was to synthesize and characterize polystyrene-*block*-poly(ε-caprolactone), polyisoprene-*block*-poly(ε-caprolactone), polystyrene-*block*-polybutadiene-*block*-poly(ε-caprolactone), and polystyrene-*block*-polyisoprene-*block*-poly(ε-caprolactone) with different compositions, in order to get new thermoplastic elastomers and to contribute to a better understanding of thestructure-properties relationship of these multi-phase materials.

Experimental Part

Materials

ε-Caprolactone (ABCR GMBH & Co, pure grade) was distilled under vacuum (13 mbar) at 97 °C in a Vigreux column, and kept on activated alumina under high purity argon atmosphere (water and oxygen content less than 5 ppm).[13]

Styrene (CAROM Onesti, Romania, anionic polymerization grade) was treated under argon atmosphere with diluted butyllithium until persistent slight yellow-orange color (the appearance of styryl anion indicating the removal of reactive impurities), and after distilled in vacuum (13 mbar) using a Vigreux column, and collected on activated alumina under argon atmosphere. The entire amount of styrene was consumed during one day.[14]

Isoprene (Fluka, analytical grade) previously treated with diluted butyllithium in presence of 1,10-phenantroline until persistent brown color in order to remove the reactive impurities,[15] was distilled and stored on activated alumina under argon atmosphere.

Butadiene (CAROM Onesti, Romania, anionic polymerization grade) was distilled from the storage-tank into a cylindrical glass reactor (equipped with mixer and cooling jacket) containing cyclohexane, and treated with diluted butyllithium until persistent brown color using 1,10-phenantroline as indicator.[15] The needed amount of pure butadiene was distilled out, dissolved in benzene and the solution was metered into the polymerization reaction vessel.

Benzene (Chimopar Romania, analytical grade) was distilled on Na-K alloy, and kept on activated alumina under argon atmosphere.[13]

Butyllithium (Merck) was diluted with cyclohexane up to 1 mol/l concentration and stored under argon atmosphere in Schlenk-type vessel.

All reagents were handled very carefully under argon atmosphere, as is required for the anionic polymerization in general. The other substances (methanol, phenyl isocyanate, 2,4-di-*tert*-butyl-4-methylphenol) were analytical grade and were used as received.

Polymerization

The polymerization reactions were carried out under argon atmosphere, in a 1 liter cylindrical glass reactor (Büchi, Switzerland) equipped with cooling-heating jacket, thermometer and manometer. The block polymers were synthesized by sequential anionic polymerization in benzene solution, initiated with butyllithium, i.e., only after total consumption of the previous monomer the next one was added. The optimal polymerization periods for every step were computed with previously established kinetic relations[13,16–19] that will be described in the next section. Benzene was chosen as polymerization solvent instead of others, because of the limited solubility of ε-caprolactone monomer in cyclohexane on the one hand, and limited solubility of ε-caprolactone-based block polymers in toluene on the other. At the end of each reaction step, samples were removed from the polymerization reactor in order to determine the monomer conversion (gravimetrically) and the molecular mass of the constituent blocks. The poly(ε-caprolactone) block terminated polymers were deactivated with few drops of phenyl isocyanate. The polymers were precipitated in methanol and dissolved in benzene, repeating both operations several times in order to remove the unreacted ε-caprolactone. The polydiene block containing polymers were stabilized adding 2,4-di-*tert*-butyl-4-methylphenol, 1 wt.-% with respect to the polymer. Finally, by casting from benzene solution followed by slow evaporation of solvent at room temperature for several days, until constant weight,[8] diblock copolymer films containing crystallized poly(ε-caprolactone) blocks were obtained. From polystyrene-*block*-polybutadiene-*block*-poly(ε-caprolactone), and polystyrene-*block*-polyisoprene-*block*-poly(ε-caprolactone) benzene solution approximately 0.5 mm thickness films were obtained by spin casting. The method is described in detail in ref.[21]

Polymer Characterization

The molecular mass, polydispersity and deactivated ("dead") polymers were determined by gel permeation chromatography (GPC) on a Waters-Millipore 244 apparatus, in tetrahydrofuran (flow rate 1 ml/min). The GPC was calibrated with polystyrene standards.

Differential scanning calorimetry (DSC) measurements were performed on a DuPont DSC 910 apparatus, under nitrogen atmosphere. Because the poly(ε-caprolactone) blocks are crystalline ones, the samples were heated from room temperature[7,8] to 300 °C at a rate of 10 °C/min.

Small angle X-ray scattering (SAXS) was measured using synchrotron radiation (wavelength 0.15 nm) from the beamline A2 of the Hamburg Synchrotron Radiation Laboratory (HASYLAB) at DESY in Hamburg.[22] The distance between sample and detector was set to 2783 mm. Two-dimensional scattering patterns were registered on image plates. Exposure time was between 30 s and 2 min. From exposed image plates, an area of 900 × 900 pixels, each with a size of 176 μm × 176 μm, was read out on a Molecular Dynamics image plat scanner and used for evaluation. Valid scattering data were recorded in a circular region of reciprocal plane with a radius of $s = 0.2\ \text{nm}^{-1}$ and the magnitude of the scattering vector being $s = (2/\lambda)\sin\theta$ with λ the wavelength of radiation; and 2θ the scattering angle. Samples of 12 mm width and a thickness of 0.5 mm were fixed in a straining stage with an initial jaw opening of 32 mm. Marks were painted on the films in intervals of 5 mm. Straining rate was set to 30 mm/min. After increasing the jaw opening by 16 mm the stage was stopped, the scattering was recorded and actual thickness and elongation were determined. This procedure was continued until the sample failed.

Dynamic mechanical analysis (DMA) was performed using a DuPont 983 dynamic mechanical analyzer. The sample dimensions were 0.5–0.6 × 8 × 14 mm. The measurements were performed at the resonance frequency (amplitude 0.3 mm) in a temperature interval between –120 and 150 °C and at a heating rate of 5 °C/min.

The tensile properties of thermoplastic elastomer films were determined on standard dumbbell specimens at a jaw separation speed of 0.5 m/min, on a Zwick Mod. 1454 tensile tester. Retractive force was recorded during extension. Hardness was measured with a dead load Zwick hardness meter in the Shore A scale. All mechanical measurements were performed at 25 °C.

Results and Discussion

Block Polymer Synthesis

The hydrocarbon monomer-containing ε-caprolactone-based block polymers can be synthesized only by anionic sequential polymerization. The polycaprolactone block is always the last, because – unlike styrene and diene anionic polymerization – the ε-caprolactone anionic polymerization is not a living one: besides the very fast propagation reaction intra- and intermolecular transesterification reactions occur. In order to obtain poly(ε-caprolactone) blocks having the requested molecular mass and over 95% monomer conversion, parameters for optimum experimental conditions were determined in previous work[13] by factorial design of experiments. From the earlier results a reaction temperature of 20–25 °C and 7–10 min polymerization time followed by phenyl isocyanate deactivation were chosen. The butyllithium concentration is limited because of the desired molecular mass of the other blocks.

According to the literature[2,7,11] it is recommended to add 1,1-diphenylethylene before adding ε-caprolactone, in order to diminish the living end reactivity, but after several trials we observed that it is not absolutely necessary.

The time, t, necessary for practically total monomer consumption (over 99.5% conversion) in polystyrene and polyisoprene block synthesis was calculated with Equation (1), established for toluene as polymerization solvent[16–18]:

$$t = \frac{-\ln(1-X)}{k_p[\mathrm{I}]_0^{0.5}} \tag{1}$$

with X being the monomer conversion in units of mass fraction; k_p is the propagation rate constant in units of $\mathrm{l}^{0.5} \cdot \mathrm{mol}^{-0.5} \cdot \mathrm{min}^{-1}$; $k_p = 4.07 \cdot 10^{10}\ \exp(-63600/RT)$ for styrene; $k_p = 8.21 \cdot 10^{7} \exp(-52000/RT)$ for isoprene; T is the polymerization temperature in K; and $[\mathrm{I}]_0$ is the butyllithium concentration in the reaction mixture, in mol/l. The validity of Equation (1) was checked by both chromatography and gravimetry.

The time needed for polybutadiene blocksynthesis was determined using:

$$t = \frac{-\ln(1-X)}{k_p[\mathrm{I}]_0^{0.3}} \tag{2}$$

established also for toluene as reaction medium.[19] Here $k_p = 7.825 \cdot 10^{15} \exp(-102000/RT)$ is the butadiene propagation rate constant, in $\mathrm{l}^{0.3} \cdot \mathrm{mol}^{-0.3} \cdot \mathrm{min}^{-1}$.

The blocks were synthesized at 50–60 °C, and the above mentioned relations were proved to be valid in benzene too, which is explainable because both toluene and benzene are very similar solvents. The polymerization times necessary to get practically total monomer conversions were 30 to 45 min for styrene, up to 3 h for isoprene and butadiene. Consequently, these block polymers can be obtained in a reasonable synthesis time.

The needed amounts of butyllithium initiator were computed taking account that in living anionic polymerization (valid for styrene, isoprene and butadiene) the molecular mass of the resulting polymer is given by the monomer/initiator ratio. This “kinetic molecular mass” of polymer is very close to the observed weight-average molecular mass.[19]

Except for the styrene-ε-caprolactone diblock polymers, the polystyrene block molecular mass was chosen between 12000 and 14000 g/mol, as is usual for commercial thermoplastic elastomers. The molecular mass of the other blocks varied as a function of block polymer composition.

Table 1 and 2 summarize the synthesis conditions and chemical structure of the block polymers, respectively.

Table 1. Reaction conditions of block copolymer synthesis.

Notation	Block of poly-	BuLi / mmol	Monomer / g	Benzene / ml	Reaction temperature / °C	Reaction time / min	Monomer conversion / %
SCL-50	Styrene	1.7	25	100	50	35	>99
	ε-Caprolactone	–	25	–	20	8	96.3
SCL-75	Styrene	1.8	12.5	100	50	35	>99
	ε-Caprolactone	–	37.5	–	20	8	97.1
ICL-50	Isoprene	1.3	20	100	55	120	>99
	ε-Caprolactone	–	20	–	20	8	96.5
ICL-40	Isoprene	1.0	20	100	60	120	>99
	ε-Caprolactone	–	13.5	–	20	8	98.3
ICL-30	Isoprene	1.0	30	200	60	150	>99
	ε-Caprolactone	–	13	–	20	8	96.4
SICL-50	Styrene	1.1	15	100	50	35	>99
	Isoprene	–	30	200	60	180	>99
	ε-Caprolactone	–	15	–	20	835	98.6
SICL-40	Styrene	1.2	15	100	50	35	>99
	Isoprene	–	45	200	60	180	>99
	ε-Caprolactone	–	15	–	20	8	98.9
SICL-30	Styrene	1.0	12	100	50	40	>99
	Isoprene	–	56	200	60	150	>99
	ε-Caprolactone	–	12	–	20	8	97.7
SBCL-50	Styrene	1.1	15	100	50	35	>99
	Butadiene	–	30	200	55	150	>99
	ε-Caprolactone	–	15	–	20	8	98.5
SBCL-40	Styrene	1.2	15	100	50	35	>99
	Butadiene	–	45	200	55	150	>99
	ε-Caprolactone	–	15	–	20	8	96.9
SBCL-30	Styrene	1.0	12	100	50	40	>99
	Butadiene	–	56	200	55	150	>99
	ε-Caprolactone	–	12	–	20	8	97.8

Table 2. Composition and molecular masses of the synthesized block polymers.

Notation	Total $\overline{M}_n$ / g/mol	$\overline{M}_w/\overline{M}_n$	Styrene/wt.-%; $\overline{M}_n$/(g/mol)	Isoprene/wt.-%; $\overline{M}_n$/(g/mol)	Butadiene/wt.-%; $\overline{M}_n$/(g/mol)	ε-Caprolactone/wt.-%; $\overline{M}_n$/(g/mol)
SCL-50	30000	1.36	50; 15200	–	–	50; 14800
SCL-75	27500	1.43	25; 7300	–	–	75; 20200
ICL-50	30000	1.41	–	50; 15300	–	50; 14700
ICL-40	35900	1.37	–	60; 21600	–	40; 14300
ICL-30	42300	1.26	–	70; 29600	–	30; 12700
SICL-50	56000	1.44	25; 14200	50; 28100	–	25; 13700
SICL-40	67300	1.39	20; 13500	60; 40200	–	20; 13600
SICL-30	82400	1.29	15; 12300	70; 57200	–	15; 12900
SBCL-50	54700	1.43	25; 13900	–	50; 27600	25; 13200
SBCL-40	65600	1.38	20; 13100	–	60; 39600	20; 12900
SBCL-30	80800	1.29	15; 12200	–	70; 56800	15; 11800

Polymer Properties

As a consequence of unavoidable traces of impurities, deactivated ("dead") polymers are observed. According to the GPC results the amount of deactivated polymers does not exceed 2–3% in block polymers. The molecular masses of the second and third blocks in diblock and triblock polymers were computed subtracting the molecular mass of the pervious block(s) from the molecular mass of the diblock and triblock copolymer, respectively. Thus, the polydispersity indexes $\overline{M}_w/\overline{M}_n$ could only be computed for the final block polymers. Values between 1.2 and 1.45 were found, and are close to those observed for usual polystyrene-*block*-polydiene-*block*-polystyrene thermoplastic elastomers.[17–19]

Predicted and measured block polymer compositions are in good agreement (cf. Table 2).

Figure 1 shows the DSC curve of a poly(ε-caprolactone) sample, synthesized previously[13] with $\overline{M}_n = 12800$ and $\overline{M}_w = 18600$. The peak maximum melting point of this polymer is 63 °C. This value is very close to the value of 60 °C, reported in ref.,[11] but much higher than the value of 50 °C from ref.[7]

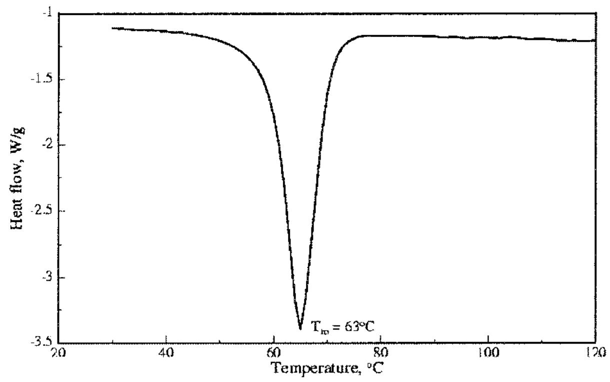

Figure 1. DSC-curve of poly(ε-caprolactone).

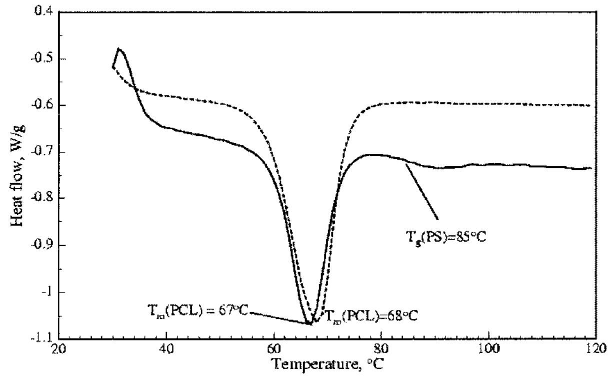

Figure 2. DSC-curves of polystyrene-*block*-poly(ε-caprolactone) polymers. Solid line: SCL-50; dashed line: SCL-75.

The melting point of the poly(ε-caprolactone) block found in the block polymers is 5 °C higher than the melting temperature of the homopolymer (Figure 2 and 3). This finding is very similar to those described for polyisoprene-*block*-poly(tetrahydrofuran).[20] The melting point of the crystalline poly(ε-caprolactone) is defined as the enthalpy of fusion divided by the entropy of fusion. In the block copolymer the entropy of fusion is smaller than that of the homopolymer because the chain conformation is stronger than that of the homopolymer. If the enthalpy of fusion remains constant, then the melting point becomes higher than that of the homopolymer.

A clear glass transition was only detected in the thermogram of the block polymer with 50 wt.-% of poly(ε-caprolactone). Because of the fact that the found transition ($T_g = 85\,°C$) is considerably lower than T_g of pure polystyrene,[7] and because of the fact that SCL-75 does not exhibit any glass transition at all, it is reasonable to assume some miscibility between the polystyrene and poly(ε-caprolactone) blocks.

The DSC curves of diblock polymers containing polyisoprene show a poly(ε-caprolactone) peak melting point close to the one found with the diblock polymers containing polystyrene. An example is presented in Figure 3. It is important to remark that these diblock polymers do not exhibit cold flow, unlike the anionic polyisoprene with the same molecular mass. This observation indicates that the poly(ε-caprolactone) blocks are able to form domains, but the material is no elastomer, because different domains cannot be interconnected by diblock polymer chains.

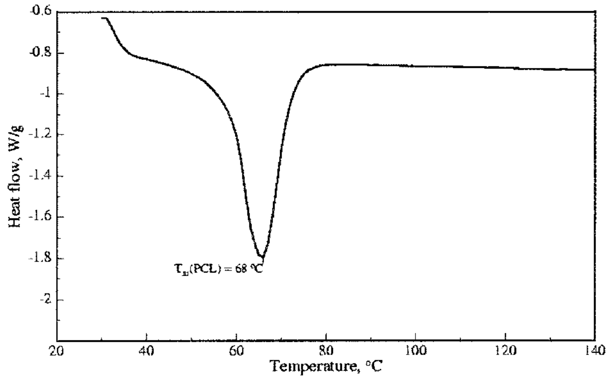

Figure 3. DSC-curve of ICL-30 polyisoprene-block-poly(ε-caprolactone).

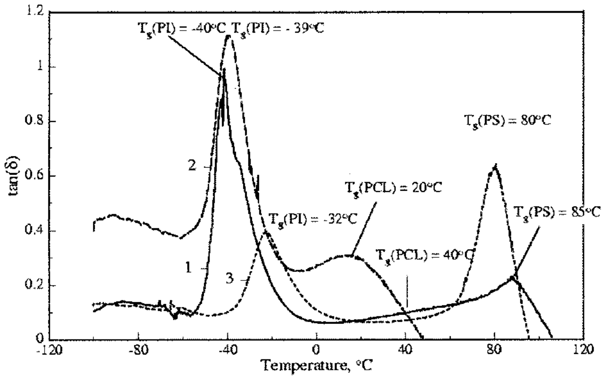

Figure 4. Loss tangent angle vs. temperature curves of SICL-40 (curve 1); SICL-50 (2); and a linear SIS with 40 wt.-% polystyrene block content (3).

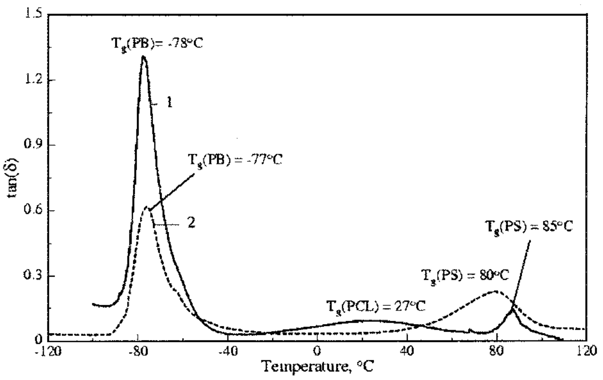

Figure 5. Loss tangent angle vs. temperature curves of SBCL-40 (curve 1) and a linear SBS with 40 wt.-% polystyrene block content (2).

Dynamic mechanical analysis (DMA) is more appropriate for the analysis of the glass transition than DSC. Figure 4 and 5 present loss tangent angle vs. temperature curves from the DMA data of several polystyrene-*block*-

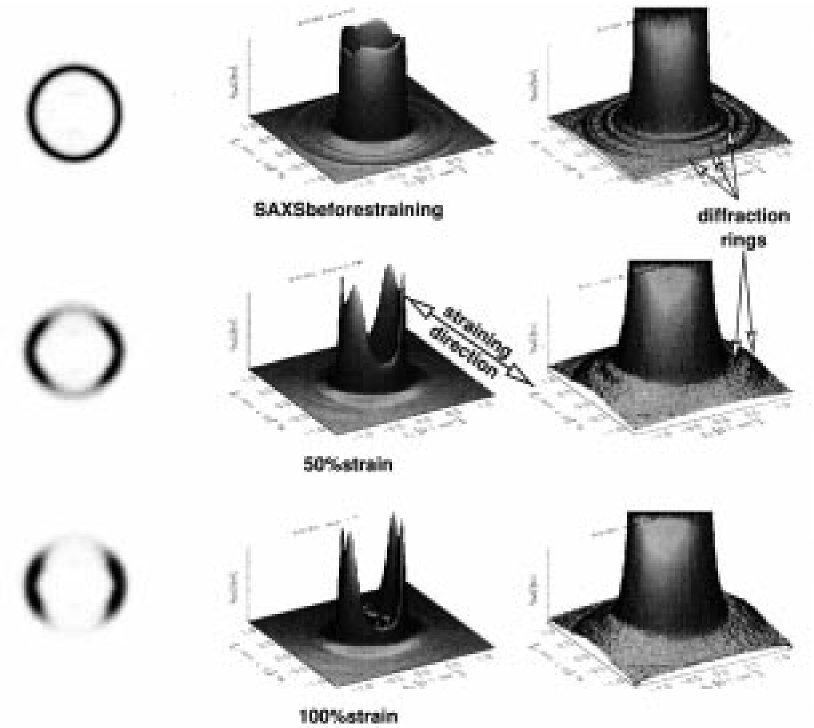

Figure 6. High resolution synchrotron radiation SAXS patterns. SICL-50 at various elongation (from top to bottom as indicated) and in different representations. Left: As on photographic film; Center: 3D, full scale; Right: 3D, zoomed scattering intensity.

polydiene-*block*-poly(ε-caprolactone) and styrene-diene triblock polymers. No DMA results are available for the SBCL-50 material because of insufficient stiffness.

Unlike polystyrene-*block*-polyisoprene-*block*-polystyrene, SIS (Figure 4 curve 3), and polystyrene-*block*-polybutadiene-*block*-polystyrene, SBS (Figure 5 curve 2), which are two-phase systems, SICL-40 and SBCL-40 are three-phase materials with three glass transition peaks. For these two copolymers the peak position assigned to the polydiene phase glass transition temperature is almost the same as for SIS and SBS whereas the peak position of the polystyrene domain glass transition temperature is shifted towards little higher values.

Much more interesting is the result concerning the glass transition temperature of poly(ε-caprolactone) domains. Compared to the transition temperature of the same blocks in a diblock material and to poly(ε-caprolactone) homopolymer, in the three-phase triblock materials with 40 wt.-% of hard domain blocks (SICL-40 and SBCL-40) it is much lower and the peaks are very broad. Such a result is characteristic for an impure phase caused from poor phase separation during material processing. This explanation appears reasonable, because the samples were prepared in a spin casting process, far from thermodynamic equilibrium.

The tanδ vs. temperature curve of SICL-50 (Figure 4 curve 2) is totally different. Whereas the glass transition peak of the polyisoprene phase is recovered at the usual temperature, only one additional peak is found. The material appears to be two-phase, with the glass transition of the “hard” domains at unexpectedly low 20 °C. This phenomenon can be explained by the assumption of a mixed phase containing both polystyrene and poly(ε-caprolactone). Concerning the change of chemical structure, the chain length of the middle polyisoprene block has been shortened with respect to the SICL-40 material. It is known that chain shortening, in general, increases miscibility. But because the hard domain components are, in principal, unchanged, the effect could only be explained by synergy.

In order to check reproducibility, SICL-50 and SBCL-50 materials were synthesized four times. For all samples the same softness and the corresponding mechanical properties were found.

All materials were studied by X-ray methods as well. Wide-angle diffraction from crystalline regions was never observed. Small-angle scattering data were insufficient for most of the samples, because of the fact that the nanostructure of most of the materials cannot be resolved by the SAXS beamline. Ultra small-angle X-ray scattering will be performed in the future. Only sample SICL-50 yields interesting results, but fails rather early in the straining experiment at the beamline. The early failure is caused by the unavailability of appropriate clamps for such soft materials. The SAXS data from the straining experiment are presented in Figure 6.

Elongation increases from top to bottom. The left column shows the data in the usual representation of a photographic film. The central column shows corresponding 3D-surfaces covering the full scale of the dynamic range. In the right column the intensity range is zoomed in order to visualize the low intensity features more clearly. Every surface representation covers a region of $-1.3\ \text{nm}^{-1}$ to $1.3\ \text{nm}^{-1}$ both in equatorial, s_{12}, and meridional, s_3, direction of the scattering vector. The meridional direction is equal to the straining direction and indicated in the central drawing.

The original material is almost isotropic. Slight deviations can be explained from subtle pre-straining during the soft material handling. The main feature is a circular long period reflection corresponding to a long period $L = 22$ nm. Moreover, a peculiar observation is made: the material shows three narrow Debye-Scherrer rings of diffraction in the small-angle regime. Their *d*-spacings according to Bragg's law are 8.0, 10.5 and 12.1 nm. This finding can be explained if we assume an ensemble of colloidal crystals with lattice constants in the order of 10 nm that are randomly oriented in the sample.

External force during the straining process causes the structure to change. But this change is a peculiar one as well: The intensity of the main SAXS reflection remains positioned on the Debye-Scherrer ring known from the unstrained sample, but becomes more and more anisotropic. The diagrams indicate that stacks built from lamellae are rotating whereas the distance between neighboring layers remains constant. At an elongation at 100% most of the stacks axes are pointing in a direction almost perpendicular to the straining direction.

Nevertheless, the colloidal crystal diffraction rings remain isotropic during the straining process: Two broad but isotropic rings can be separated in the pattern at 50% strain, whereas at 100% strain there is still one broad and isotropic reflection. Thus straining appears to break colloidal crystals into smaller parts until they vanish without imprinting measurable orientation on the ensemble, whereas more extended lamellar structures are oriented. Such complex finding requires the development of novel data evaluation methods.[23] One now may start to speculate on hard domain lamellae built from a lattice of polystyrene enriched domains in a polystyrene depleted matrix (or vice versa), but it will be difficult to elucidate the reason for the colloidal crystal structure from the scattering data, because its effect is small as compared to the scattering intensity of the lamellar system.

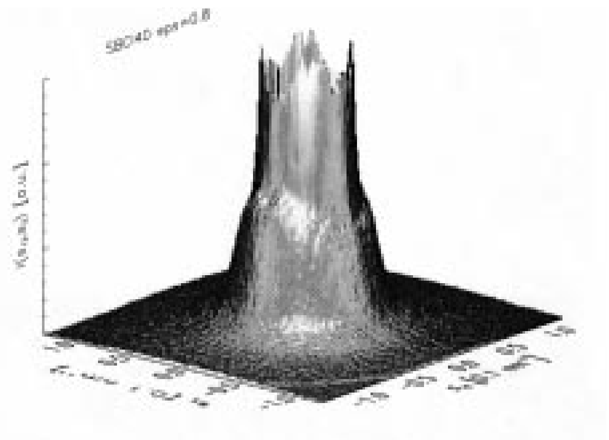

Figure 7. SAXS pattern of SBCL-40 at 80% elongation.

Figure 7 presents the SAXS pattern of SBCL-40 block polymer at 80% elongation. One observes a strong central SAXS, partly hidden behind the beam stop. The central SAXS is a function of the external strain. Additionally, scattering from tilted lamellar stacks was observed. The very high long period observed for this material can only be resolved using ultra small-angle X-ray scattering.

Only part of polystyrene-*block*-polydiene-*block*-poly(ε-caprolactone) linear triblock polymers, namely SICL-40 and SBCL-40, exhibit the basic properties of a thermoplastic elastomer (cf. Table 3, Figure 8 and 9). But even the mechanical properties of these materials are inferior to the corresponding styrene-diene triblock polymers having similar hard block content.

Hardness and tensile strength of SICL-40 and SBCL-40 are about one half of the values recorded for the corresponding styrene-diene triblock polymers. Because the hardness is a function of the volume fraction and hardness of polystyrene and poly(ε-caprolactone) phases, respectively, the lower hardness of three component block polymers can be due to the considerable softness of the poly(ε-caprolactone) blocks introduced.

As shown in Figure 8 and 9, the stress-strain curves of SICL-40 and SBCL-40 have similar shape to those recorded for SIS and SBS copolymers, respectively. In all cases initial yielding (destruction of interconnections among the hard domains) was observed that is typical for spin cast films.

Table 3. Mechanical properties of polystyrene-*block*-polydiene-*block*-poly(ε-caprolactone) triblock polymers.

Property	SICL-30	SICL-40	SBCL-30	SBCL-40	SBCL-50
Hardness/°ShA	27	31	28	45	26
Tensile strength/MPa	3.2	5.5	5.7	12.1	3.6
Modulus at 300% elongation/MPa	0.21	0.44	0.35	0.6	0.19
Elongation at break/%	750	1 020	1 200	1 700	650
Set at break/%	160	125	145	100	180

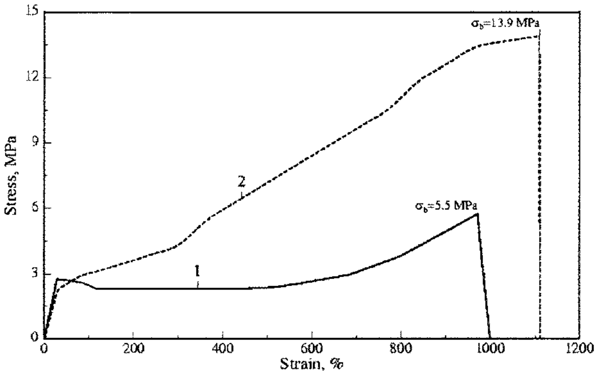

Figure 8. Stress-strain curves of SICL-40 (curve 1) and a linear SIS with 40 wt.-% polystyrene block content (2).

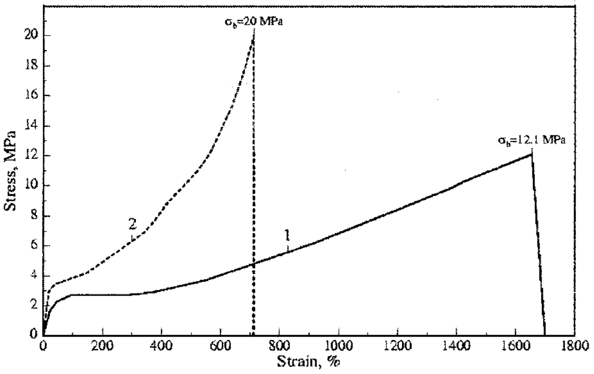

Figure 9. Stress-strain curves of SBCL-40 (curve 1) and a linear SBS with 40 wt.-% polystyrene block content (2).

The tensile strength (which is a measure of the necessary force to disrupt hard domains and entanglements, with respect to the initial cross section area of the sample) is significantly lower for the ε-caprolactone based triblock polymers, as compared to styrene-diene triblock polymers, probably because cohesion forces within the polycaprolactone domains are much weaker as within the polystyrene domains.

The tensile modulus at 300% elongation, defined as the retractive force divided by the initial cross section area of the dumbbell specimen at 300% elongation, is considered a measure of elasticity, in the terms of the high elasticity of rubber: the lower the tensile modulus, the higher the elasticity.[21,24] For SIS and SBS the tensile modulus is ca. 1 and 3 MPa, respectively, if the polystyrene block content is 30 wt.-%; for a polystyrene content of 40 wt.-% usual values are 3 and 6 MPa, respectively. According to the data from Table 3, all ε-caprolactone based triblock polymers exhibit lower tensile moduli. Thus, at a first glance, these materials might be considered more elastic than the styrene-diene triblock polymers.

Set at break, determined ten minutes after sample failure as the ratio between the length of the broken test specimen and its initial length,[21,24] can be an indication of the material elasticity as well. For styrene-diene triblock polymers the set at break is usually below 50%. Consequently, considered from this point of view the SICL and SBCL samples are less elastic than SIS or SBS. Nevertheless, the determination itself is subject to a relatively high error.

The elongation at break for the SBCL-40 material (1700%) is more than double the value of common SBS (700%). We do not have a satisfactory explanation for this finding. Generally this parameter can be increased by stimulation of lubricating phenomena in the polydiene matrix, but we cannot imagine such a process to have occurred in our material. For the other ε-caprolactone based triblock polymers the observed elongation at break is in the usual range.

Conclusions

ε-Caprolactone based di- and triblock polymers were synthesized by sequential anionic polymerization with not using 1,1-diphenylethylene before adding the ε-caprolactone monomer.

All diblock polymers exhibit phase separation into two-phase systems, and, because the conformational space of the block copolymer chain is more restricted than that of the homopolymer chain, the melting point of poly(ε-caprolactone) in the block polymers is higher than in the case of homopolymer.

The polystyrene-*block*-polydiene-*block*-poly(ε-caprolactone) triblock polymers with relatively good mechanical properties are thermoplastic elastomers with application potential especially in hot melts. According to the DMA data, some of the materials are three-phase systems, but others are only two-phase systems. The two-phase materials show considerable depression of the hard domain glass transition and, consequently, turn out to be very soft. It is peculiar that the transition from three-phase to two-phase material is accomplished by increasing the hard block content.

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