

LC Multiblock Copolymers Containing Polysulfone Segments. II. Material Properties

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ABSTRACT: The synthesis of multiblock copolymers containing liquid crystalline, semi-aromatic polyester segments of poly(ethylene terephthalate-*co*-oxybenzoate), and polysulfone segments with different segment molecular weights was recently described. Such block copolymers should make it possible to combine properties of the base homopolymers, e.g., the high strength of liquid crystalline polymers (LCP) with the high thermostability of polysulfone (PSU). Investigations of melt rheology and relaxation behavior discussed here demonstrated that the properties of the block copolymers are intermediate between those of the homopolymers and can be tailored by using PSU and LCP segments of suitable molecular weight. The high melt viscosity of PSU is lowered by block copolymer formation, allowing good processability by injection molding. The material properties of the resulting samples are characterized by a combination of PSU thermostability and improved strength. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 619–630, 1997

Key words: multiblock copolymers; polysulfone; liquid crystalline polymers; phase separation

INTRODUCTION

The combination of different polymers having known chemical structures offers us the opportunity to develop materials with new characteristics and a wider range of properties in shorter amounts of time. This combination can be realized either by mixing two different polymers in polymer blends, or different polymer segments can be combined by chemical coupling via terminal groups in multiblock copolymers. Often, the mechanical properties of such polymer blends are found to drop below the level of the pure blend partners due to immiscibility or incompatibility of the polymers mixed. Therefore, synthesis of multiblock copolymers is regarded to be a possibility for avoiding this disadvantage and achieving

true combination of properties. In addition, the combination of chemically incompatible segments should result in polymers with phase-separated morphologies, which give rise to special synergistic properties occurring beside the simple combination of properties.¹ Therefore, investigations were carried out in order to combine the advantageous properties of liquid crystalline copolyesters (i.e., high E-modulus, high stiffness, good processability in the melt due to low melt viscosity, low thermal expansion coefficient) with the high thermal and chemical stability of polysulfones.

Recently, we reported that multiblock copolymers containing polysulfone (PSU) segments and segments of the semiflexible, liquid crystalline polyester poly(ethylene terephthalate-*co*-oxybenzoate) (PET/HBA) show a phase-separated morphology.² The degree of phase separation is strongly dependent on the molecular weights of the segments incorporated. Multiblock copolymers with low phase separation are formed by coupling short segments, while the coupling of longer segments results in highly phase-sepa-

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rated systems. Furthermore, it was demonstrated that the glass transition and melting behavior are influenced by morphology, i.e., by the length of the segments. Particularly, it was observed that the phase behavior in the melt (formation of a liquid crystalline or an isotropic melt) is distinctly determined by the lengths of the PSU and the (PET/HBA) blocks.

From those investigations, the question arose as to whether or not the morphology of the multiblock copolymers and, consequently, their chemical composition, influences the macroscopical properties.

Therefore, using the rheological behavior in the melt as the first guide for processability, the dynamic-mechanical behavior, the thermomechanical behavior, and the thermal stability are discussed in the following article. Finally, preliminary results regarding mechanical properties of injection-molded samples are presented. Special attention was paid to the comparison of properties of multiblock copolymers to those of the corresponding homopolymers. Thus, the results obtained allow a first estimation of the material properties of PSU-PET/HBA block copolymers.

EXPERIMENTAL

Materials

Poly(ethyleneterephthalate-*co*-oxybenzoates) (PET/HBA 40/60) were prepared and characterized according to Leistner et al.³ High molecular polysulfone (PSU, MW 30,000 g/mol) was obtained from Polysciences Europe GmbH (Eppenheim, Germany).

The multiblock copolymers investigated were synthesized by polycondensation of acetoxy-terminated polysulfones of different molecular weight with COOH-terminated poly(ethyleneterephthalate-*co*-oxybenzoates) and chemically characterized as described elsewhere.² The block copolymers had comparable molecular weights M_w in the range of 100,000 g/mol with a polydispersity of approximately two. Amounts of about 50 g with comparable properties were obtained by using a melt kneader (Brabender Plasticorder, 280°C, 80 rpm) equipped with a vacuum pump.

Injection molding was carried out using an Engel injection molding machine ES 200H/80V/50 HL-2F (Germany) with a screw diameter of 15 mm, equipped with a special mold for small amounts at temperatures in the range of 280 to 340°C.

Analytical

Rheological Characterization

Melt flow curves were obtained by means of a RMS 800 rheometer (Rheometrics, Inc., U.S.A.) at 280°C. Measurements of the complex viscosity η^*

$$\eta^*(\omega) = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \quad (1)$$

were realized with a disc and plate device (ϕ 25 mm, 2 mm gap, 30% strain amplitude) in small oscillatory shear within the frequency range of 0.1 to 100 rad/s.

Transmission Electron Microscopy

Polymer films were prepared by spreading trifluoroacetic acid/chloroform solutions onto water. The films were transferred to grids and investigated both as casted and annealed (annealing: 30 min at 165 and 190°C, respectively, on a Linkam hot stage with nitrogen atmosphere). TEM investigations were carried out with a Zeiss EM 912 in the zero-loss-mode ($\Delta E = 0$, elastic scattered electrons only).

Dynamic Mechanical and Thermal Analysis

Dynamic mechanical relaxation spectra of multiblock copolymers were obtained using an Eplexor 150 N Dynamic Mechanical Analyzer of GABO Qualimeter Testanlagen GmbH (Ahlden/Germany). The measurements were carried out in the temperature range from -100 to 180°C with a heating rate of 2 K/min and at a frequency of 1 Hz. The foils with a typical sample geometry of $6 \times 15 \times 0.5$ mm were prepared by melt pressing.

Thermomechanical analysis was performed with TMA 40 foil equipment (Mettler-Toledo, Switzerland). The thermal stability was investigated by means of a Perkin-Elmer thermogravimetric system TGS 7 with nitrogen atmosphere at a heating rate of 10 K/min. Differential Scanning Calorimetry (DSC) investigations were performed using a Perkin-Elmer DSC-7 with a scanning rate of 20 K/min. Tensile strength, E -modulus, and elongation were determined according to DIN 53455 using S2 tensile specimens at a Zwick tensile test machine.

RESULTS AND DISCUSSION

Melt Rheology

The melt viscosity behavior of liquid crystalline polymers (LCP) can normally be described as dis-

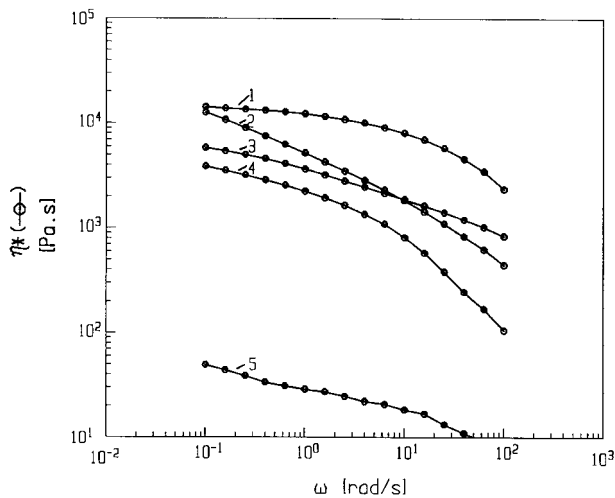


Figure 1 Comparison of melt viscosities of (1) PSU 30,000, (2) multiblock copolymer PSU 7,100/PET/HBA 7,400, (3) multiblock copolymer PSU 5,400/PET/HBA 5,900, (4) physical blend PSU 30,000 and PET/HBA 13,000 (50/50 wt/wt), and (5) PET/HBA 13,000.

tinctly different from that of conventional polymer melts.⁴⁻⁷ The liquid crystalline melts show power-law viscosity behavior for the entire shear rate range at a given temperature. At higher temperatures, their flow curves are characterized by three sections, whereby region I is the low shear rate region of shear thinning behavior, region II is the

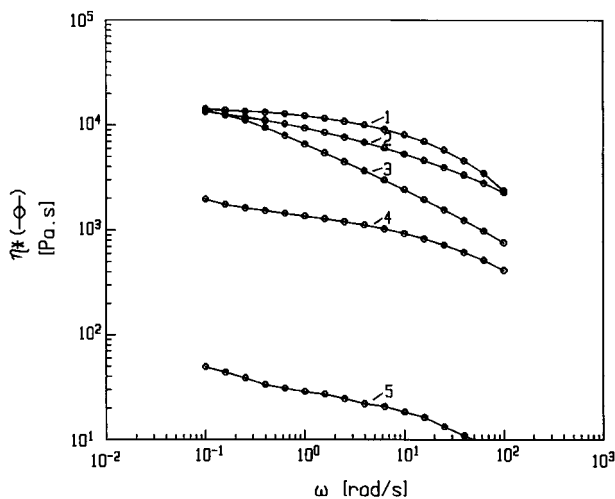


Figure 2 Complex viscosities of PSU-PET/HBA multiblock copolymers with constant PET/PHB length in dependence on the length of PSU segments (measuring temperature is 280°C): (1) PSU 30,000, (2) multiblock copolymer PSU 8,400/PET/HBA 5,900, (3) multiblock copolymer PSU 5,700/PET/HBA 5,900, (4) multiblock copolymer PSU 2,400/PET/HBA 5,900, and (5) PET/HBA 13,000.

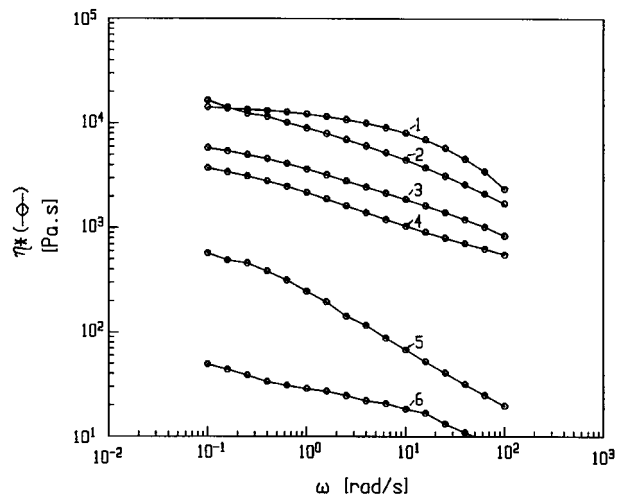


Figure 3 Influence of the length of PET/HBA segments on the complex viscosities of PSU-PET/HBA multiblock copolymers with constant PSU segment length: (1) PSU 30,000, (2) multiblock copolymer PSU 5,400/PET/HBA 3,200, (3) multiblock copolymer PSU 5,400/PET/HBA 5,900, (4) multiblock copolymer PSU 5,700/PET/HBA 7,400, (5) PET/HBA 7,400, and (6) PET/HBA 13,000.

plateau of nearly constant viscosity at intermediate shear rates, and region III is characterized by shear thinning at higher shear rates.⁷ In contrast, isotropic melts formed by conventional polymers only exhibit a decrease starting at a critical shear rate. The melt viscosity of LCP at higher shear rates is therefore much lower compared to that of isotropic melts. This is due to the easier orient-

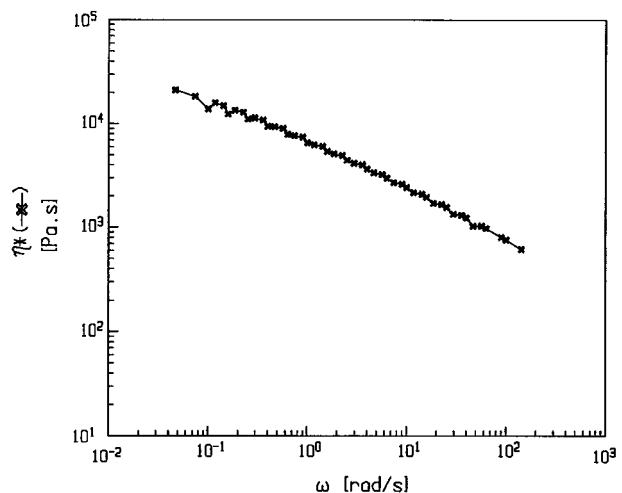


Figure 4 Master curve of the multiblock copolymer PSU 5,700/PET/HBA 5,900 (reference temperature is 280°C) calculated according to the time-temperature superposition principle.

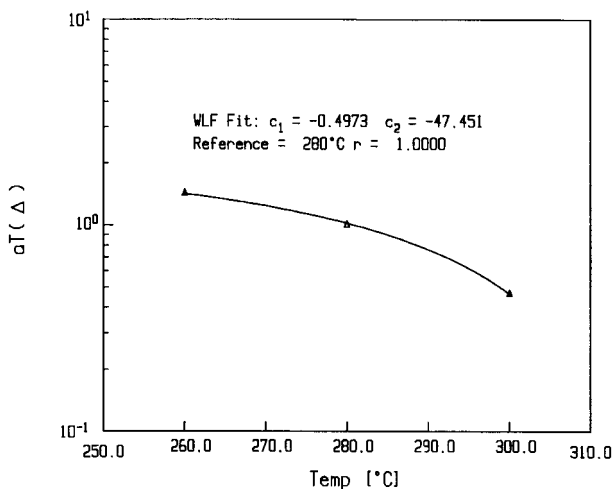


Figure 5 Fit of the temperature dependence of the shift factor a_T with the WLF equation for multiblock copolymer PSU 5,700/PET/HBA 5,900.

ability of the LCP macromolecules in shear direction. The viscosity behavior of the PSU-LCP multiblock copolymers under investigation (consisting of n parts of two immiscible polymer segments) is expected to be comparable to that of an immiscible polymer blend of the polymers discussed above (i.e., may be intermediate between that of the components).⁷ The influence of the liquid crystalline segments on the melt viscosity of PSU-LCP multiblock copolymers with different segment lengths was studied in order to estimate the processing behavior during injection molding.

The viscosity behavior of the PSU-LCP multiblock copolymers was examined by a disc/plate rheometer using frequency sweep mode at 280°C. Thus, the measuring temperature is comparable to the temperature applied during synthesis.

Figure 1 reflects the comparison of the complex viscosities of PSU and LCP with high molecular weight, a physical blend of both (50/50 wt/wt), and multiblock copolymers with comparable weight ratio with respect to the segment molecular weight. LCP and PSU homopolymers show a significant difference in their melt viscosities. The multiblock copolymers have higher melt viscosities than the comparable physical blend, occupying up an intermediate position. This difference cannot be explained only by the higher molecular weight of the block copolymers. Different levels of phase separation of blend and block copolymer must also be taken into account.

Figure 2 demonstrates the influence of the molecular weight of the PSU segment on the melt viscosity of multiblock copolymers with constant (PET/HBA) blocks. The coupling of LCP with

PSU results in a significant increase of the LCP viscosity. The melt viscosity continuously rises with increasing polysulfone segment length. By increasing the molecular weight of the LCP segment, the melt viscosity is approximately that of pure PET/HBA (Fig. 3). In contrast to the behavior of flexible chain polymers, the LCP viscosity drops with increasing molecular weight, which is caused by a higher orientability of longer LCP chains. The temperature dependence of the melt viscosity was investigated using the block copolymer PSU 5,700/(PET/HBA) 5,900. A master curve was constructed according to the temperature time superposition principle (Fig. 4).⁸ The temperature dependence of the shift factor was fitted best using the known Williams-Landel-Ferry (WLF) equation (Fig. 5). Therefore, it can be concluded that the multiblock copolymer represents a thermorheologically simple fluid; i.e., all rheological material functions depend on the temperature in the same manner. Furthermore, it should be noted that morphological alterations do not occur exclusively within the temperature range investigated (260 to 300°C).

It can be stated that the flow behavior of the multiblock copolymers can be tailored by the length of the coupled oligomeric LCP and PSU segments. The coupling results in a decrease of the melt viscosity of pure PSU and therefore in an increased processability.

Thermal and Relaxation Behavior

In general, the relaxation behavior of block copolymers is directly influenced by their morphology. The first results of morphological investigations, discussed previously, were obtained by using films spread from TFA/ CHCl_3 onto a water surface. Multiblock copolymer films formed by this method are considered not to be in thermodynamic equilibrium. It was assumed that the relaxation behavior (examined by dynamic-mechanical analysis of melt pressed films) could not be exactly related with regards to the morphology of such solution casted films. On the other hand, thin sections of melt pressed films observed by TEM and SEM did not show a very clear structure. In all cases, a particle structure was found independent of the length of the block copolymer segments. In order to generate comparable morphologies, the as casted solution films were annealed at temperatures ten degrees below and ten degrees above the glass transition temperature of the PSU phase in the block copolymer. In particular, it was interesting to see whether or not the

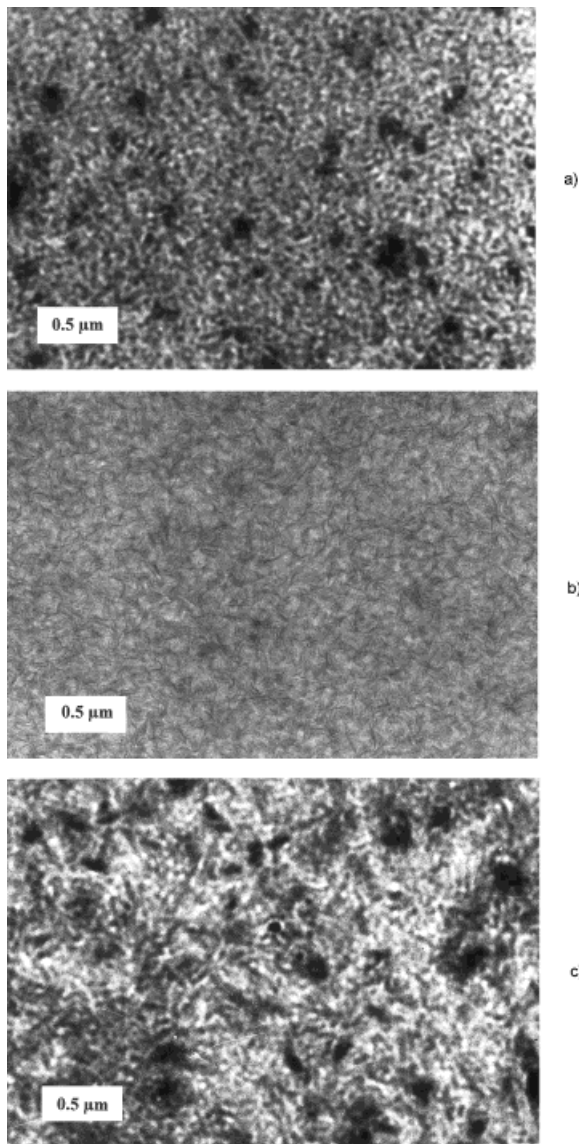


Figure 6 TEM micrographs of as casted and annealed PET/HBA: (a) PET/HBA 7,400, (b) PET/HBA 7,400 annealed (165°C), and (c) PET/HBA 3,200.

phase separation observed in the as casted solution films was intensified by annealing.

For comparison, Figure 6 shows transmission electron microscopy (TEM) micrographs of as casted and annealed LCP (PET/HBA) films. It should be noted that the morphology of PET/HBA depends on its molecular weight. Whereas PET/HBA with a molecular weight of 7400 [Fig. 6(a)] initially shows an unspecific structure, changing after annealing, into a typical nematic domain structure [Fig. 6(b)], the low molecular weight sample (PET/HBA) 3,200 forms that structure without annealing [Fig. 6(c)]. Annealing of both samples results in a typical nematic structure

characterized by uniaxial orientation within aspheric domains, which are isotropically distributed in the sample. Identical morphologies were observed in PET/HBA polymers, which were chain extended by bis(4-hydroxyphenylene) sulfone units (as the model for polysulfone oligomers).

Annealing of a short segmented multiblock copolymer [PSU 3,800/(PET/HBA)] 3,200 at 165°C (i.e., below the glass transition of the polysulfone phase) causes segregation of the co-continuous structure of the as casted film [Fig. 7(a), as casted; Fig. 7(b), annealed at 165°C]. Annealing

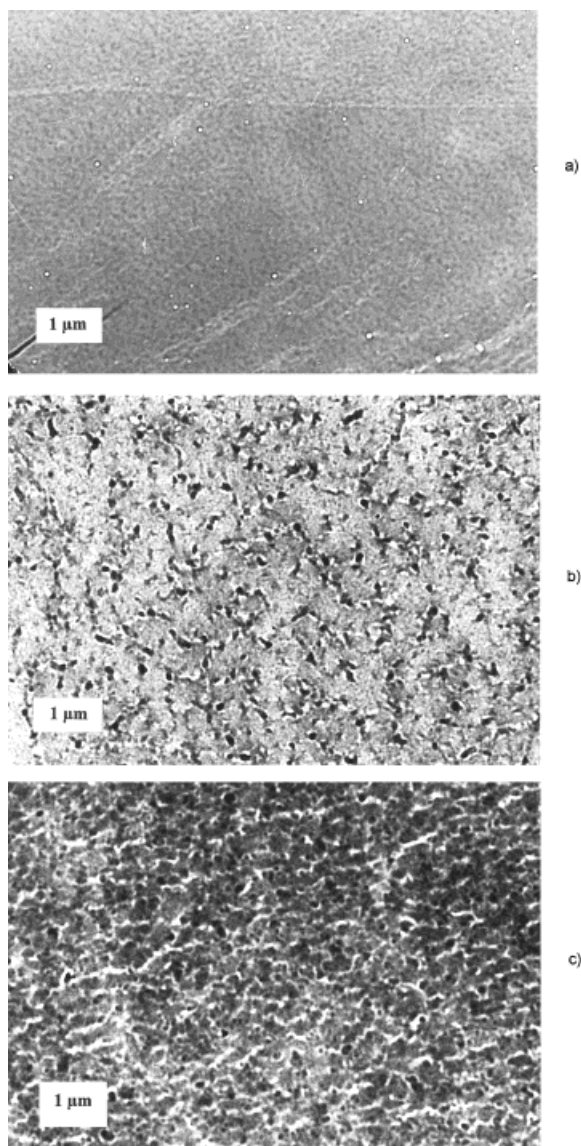


Figure 7 TEM micrographs of short segmented multiblock copolymer PSU 3,800/PET/HBA 3,200: (a) as casted, (b) annealed (165°C, $T < T_{g,PSU}$), and (c) annealed (190°C, $T > T_{g,PSU}$).

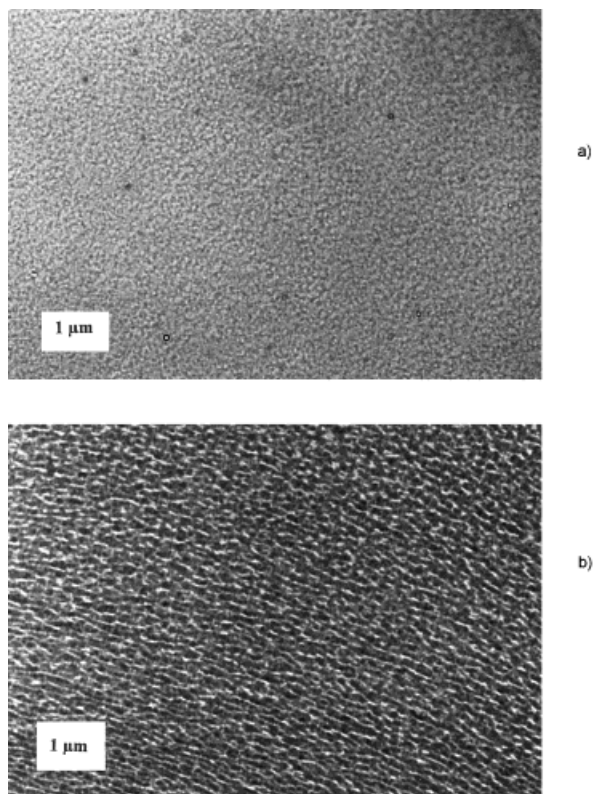


Figure 8 TEM micrographs of long segmented multiblock copolymer PSU 8,400/PET/HBA 7,400: (a) as casted and (b) annealed (165°C).

above T_g of the block copolymer PSU phase (190°C) increases the segregation process and results in the formation of a three-phase structure [Fig. 7(c)] in which the aspheric domains change into small spheric ones.

In contrast, the distinctly phase separated, co-continuous structure of multiblock copolymers with long segments (PSU 8,400/(PET/HBA) 7,400) is not significantly altered by annealing [Fig. 8(a) and (b)].

The two-phase morphology of the multiblock copolymers is reflected by the relaxation behavior of the polymers examined by dynamic-mechanical analysis of hot pressed melting films.

First, the relaxation spectra of the uncoupled (PET/HBA) oligomers were investigated. The storage modulus E' as a measure of the stiffness of polymers drops with increasing molecular weight of the LC oligomer (Fig. 9), which is in contrast to the expectations because it was assumed that rising molecular weight would result in increasing mechanical characteristics. This result has to be discussed in terms of slight deviations in chemical composition of the LC oligomers. For generation of low molecular weight oligomers,

small amounts of terephthalic acid were added to the reaction mixture of PET and 4-acetoxy benzoic acid.² The stiff aromatic terephthaloyl units mainly form end groups of the oligomer and, in addition, increase the rigidity of the whole polymer chain (i.e., E'). Moreover, strong interactions between the carboxylic end groups have to be taken into consideration. The lower the desired molecular weight of the (PET/HBA) oligomers, the higher the content of terephthalic acid, which leads to oligomers with higher stiffness and interactions, which in turn results in higher modulus values. This assumption is supported by the morphological observations. As in the transmission electron microscopy (TEM) micrographs [Fig. 6(a)–(c)] previously described, PET/HBA 3,200 (synthesized adding an amount of 4.4% TPA) is characterized by a more pronounced domain structure (with large domains of uniaxial orientation) in comparison to PET/HBA 7,400 (without additional terephthalic acid (TPA)).

The multiphase structure of PET/HBA, which has been extensively discussed in the past (see, for instance, Sugiyama et al.,⁹ Benson and Lewis,¹⁰ and Gedde et al.¹¹), is reflected by the heterogeneous shape of the glass transition peak in the $\tan \delta$ curve (Fig. 10) representing both the PET-rich and HBA-rich phases. This result is consistent to that found by DSC (Fig. 11).

Pure PSU was only examined with high molecular weight (8,400 and 30,000 g/mol) as the acetoxy-terminated oligomers used for multiblock copolymer synthesis were too brittle to give melting films. Measurements revealed a single glass transition in the temperature range of 100 to 170°C.

The coupling of COOH-terminated (PET/HBA) oligomers with polysulfone oligomers to form multiblock copolymers results in storage modulus curves that can be characterized by two steps reflecting the separation of the polymer into two main phases. The first step between 50 and 100°C is assigned to the glass transition of the LC phase. The second step corresponds to the glass transition of the amorphous PSU phase of the block copolymer, depending on the PSU segment molecular weight.

Generally, the linking of the LC units with amorphous PSU segments leads to a significant drop of the modulus of the block copolymer compared to the high stiffness (E') of the original LCP (demonstrated in Fig. 12 for multiblock copolymers with PSU 3,820 units). This effect is discussed in terms of restricted crystallization of the LC phase (also confirmed by DSC), as well as in terms of disturbance of the LC phase behavior

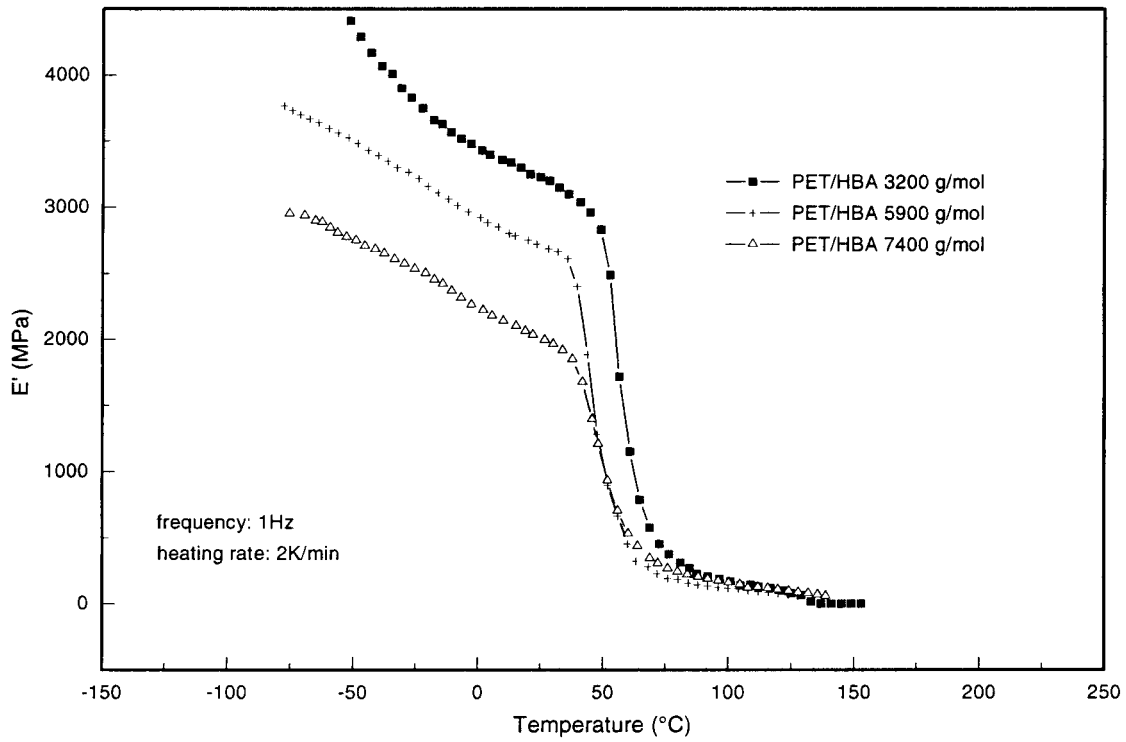


Figure 9 Storage modulus E' of poly(ethyleneterephthalate-*co*-oxybenzoates) with different molecular weights.

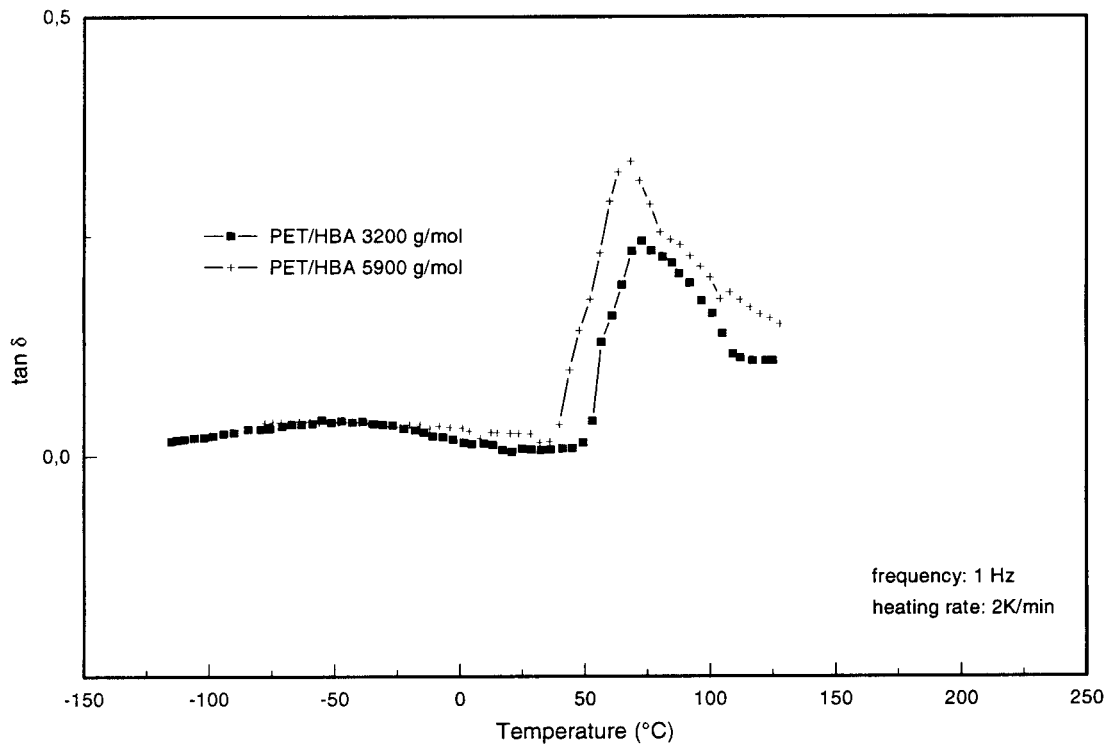


Figure 10 $\tan \delta$ curves of poly(ethyleneterephthalate-*co*-oxybenzoates) with different molecular weights.

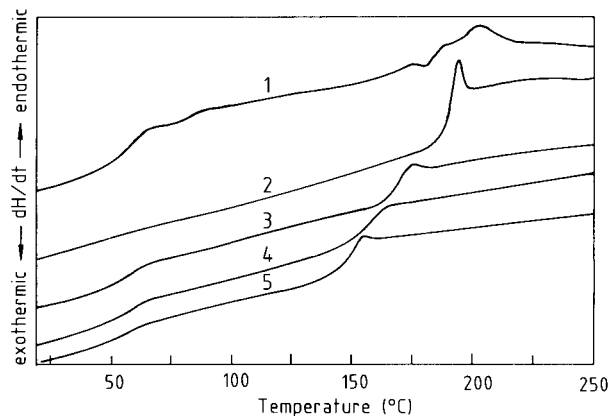


Figure 11 DSC traces (second heating) of PSU-PET/HBA block copolymers in comparison to uncoupled PET/HBA and PSU oligomers: (1) PET/HBA 7,400, (2) PSU 30,000, (3) PSU 8,400/PET/HBA 7,400, (4) PSU 5,800/PET/HBA 5,900, and (5) PSU 2,000/PET/HBA 3,200.

in the multiblock copolymers. The ability of the chains to orientate and to form uniaxial oriented domains is higher with increasing molecular weight of PET/HBA segments. Consequently, the modulus of multiblock copolymers below $T_{g,PET/HBA}$ rises with increasing LCP length.

As it can be seen in the $\tan \delta$ curves (Fig. 13), the glass transition temperature of the PET/HBA

phase is hardly altered by block copolymer formation. Its relaxation intensity is lower than expected, which can be explained by the hindered mobility of the block copolymers due to chemical coupling. This decreased relaxation intensity leads to small values of thermal expansion coefficients above $T_{g,PET/HBA}$ and to an increased thermostability in comparison to pure (PET/HBA) (Fig. 14).

The influence of the PSU segment length on the storage modulus is discussed for block copolymers containing PET/HBA 3,200 segments (Fig. 15). The glass transition temperature of the PSU phase increases with rising molecular weight of the PSU segment and reaches the T_g of high molecular PSU in block copolymers with long segments (PSU 8,400 g/mol), indicating strong phase-separated structures as reported in the first part of this investigation.²

The results of the dynamic-mechanical investigations showed that E modulus, as well as thermal expansion behavior of PSU/LCP multiblock copolymers, can be controlled by variation of the molecular weight of the blocks.

The averaged thermal expansion coefficient α of all multiblock copolymers is approximately constant with about $100 \cdot 10^{-6} \text{ K}^{-1}$ in a broad temperature range from -50 to 120°C . Although somewhat higher than for pure PET/HBA, α is low

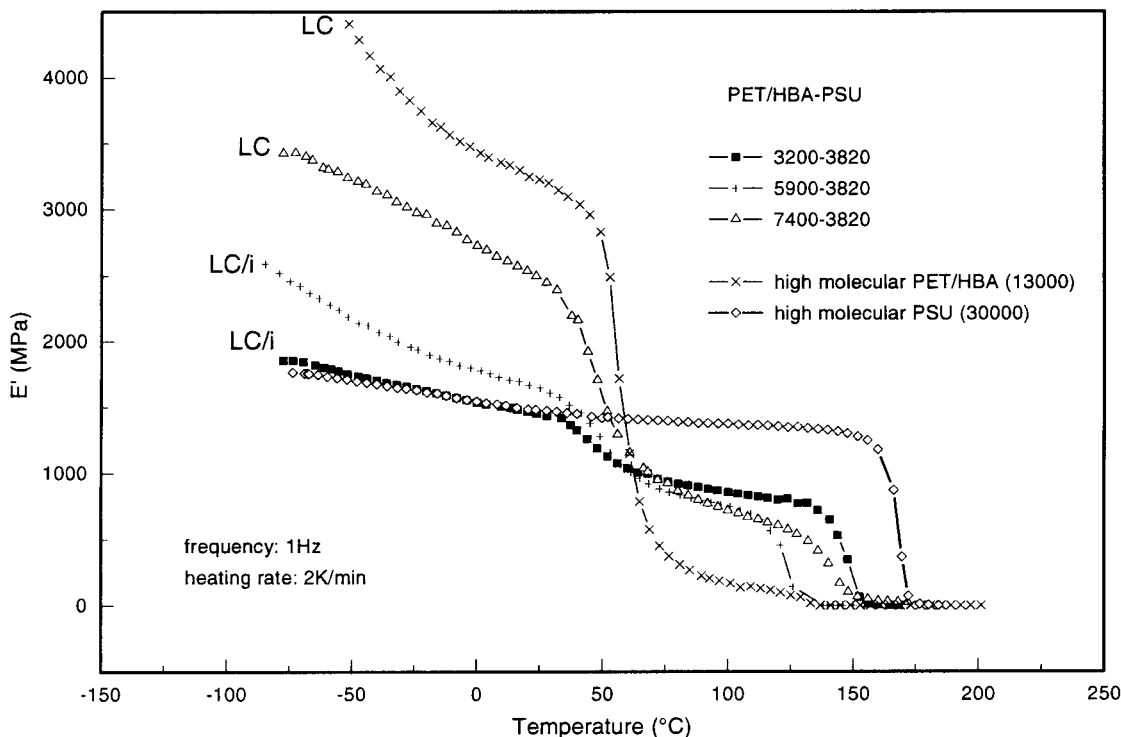


Figure 12 Storage modulus curves of PSU-PET/HBA multiblock copolymers in dependence on the molecular weight of the LC segments.

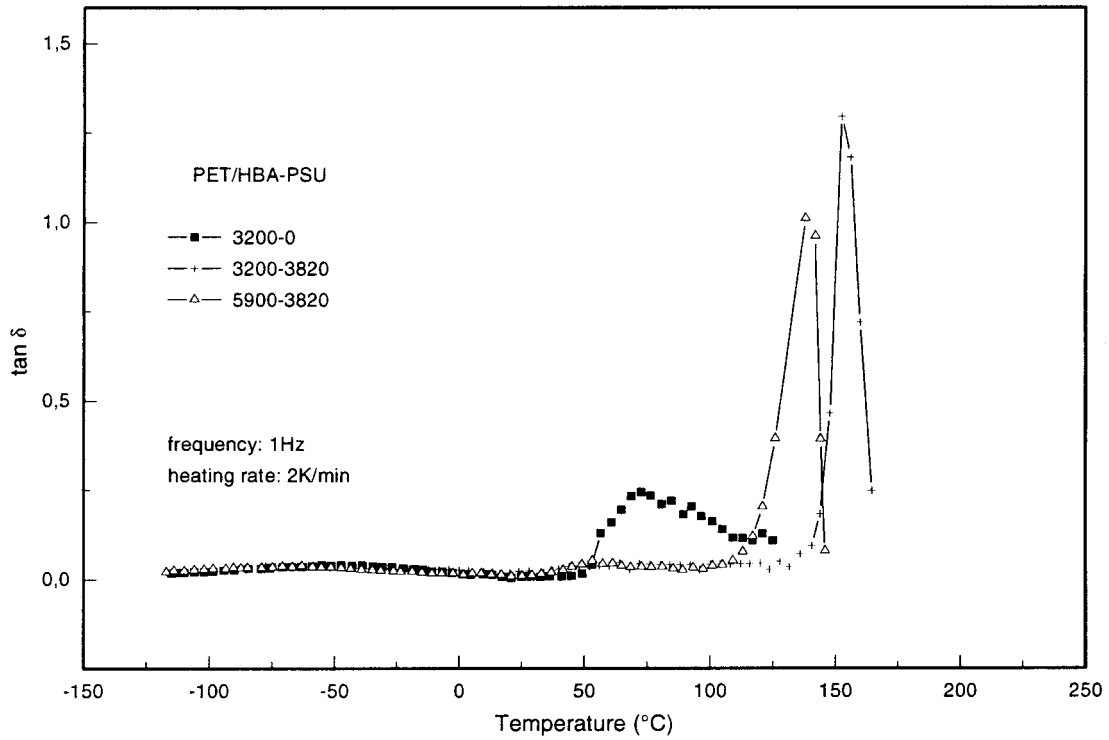


Figure 13 Tan δ curves of PSU-PET/HBA multiblock copolymers in dependence on the molecular weight of the LC segments.

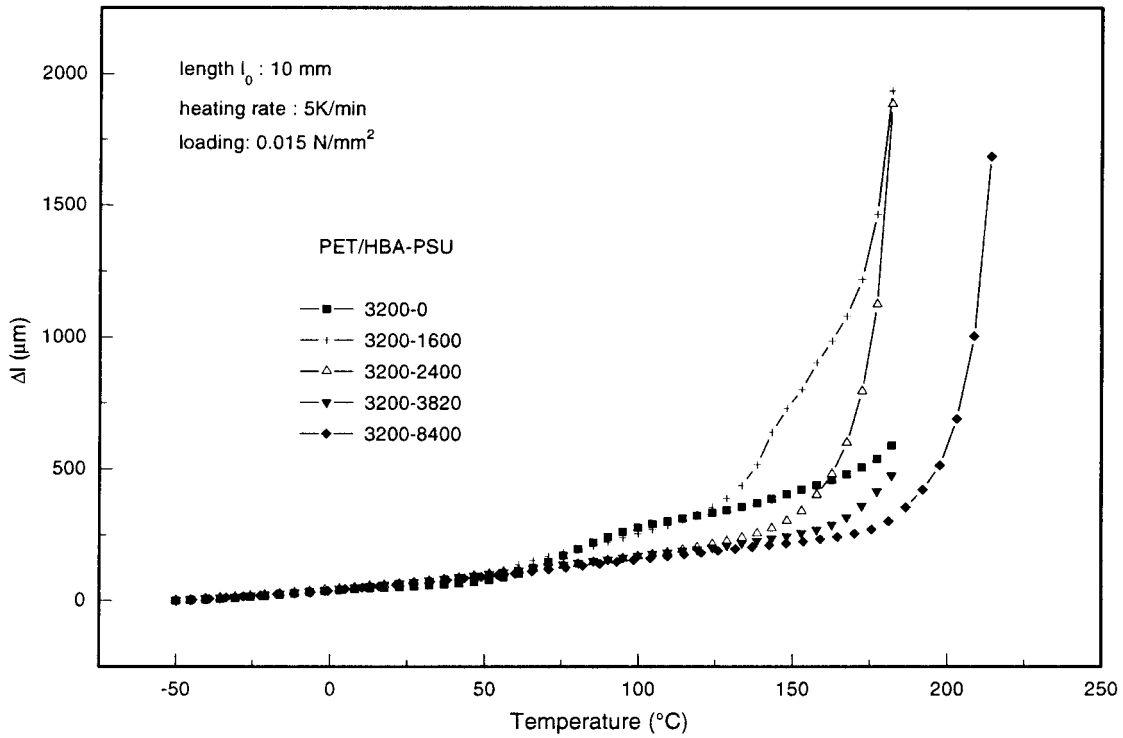


Figure 14 Expansion behavior of PSU-PET/HBA multiblock copolymers with different lengths of the PSU segments examined by thermomechanical analysis.

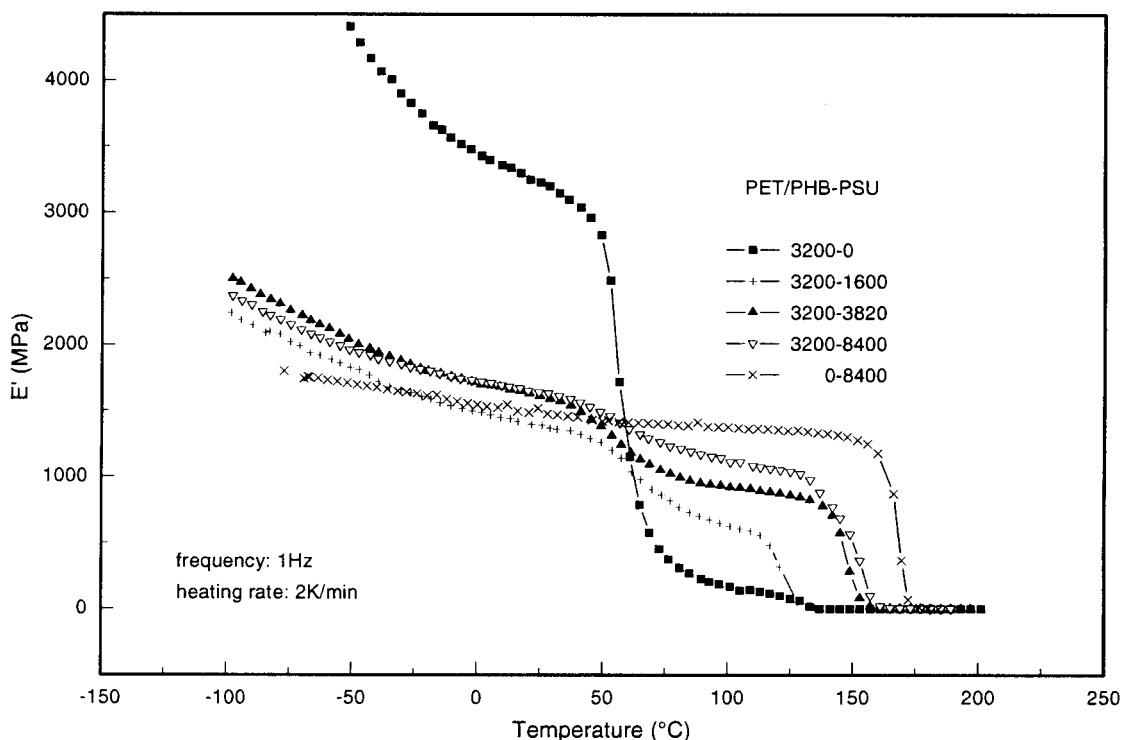


Figure 15 Influence of the polysulfone segment length on the storage modulus of PSU-PET/HBA multiblock copolymers.

enough to meet the requirements of applications in the field of electronics.

Moreover, the thermal stability as examined by thermogravimetry is quite high. Table I illustrates that the temperature of 1% weight loss is above 380°C for all samples independent of their composition.

Mechanical Properties

The PSU-PET/HBA multiblock copolymers under discussion were injection molded into test bars

for tensile tests at 300°C. Table II compares the mechanical properties (tensile strength, E-modulus, elongation) of pure PSU and LCP with those of their blends, as well as with a corresponding block copolymer.

Whereas the tensile strength of the PSU/LCP blend (50/50 wt/wt) drops below the level of the homopolymers, the multiblock copolymer takes an intermediate position, i.e., the tensile strength is higher than for PSU. E-modulus and fracture strength show a significant increase. The raised E-modulus of the block copolymer causes low elon-

Table I Thermostability of Some PSU-PET/HBA Multiblock Copolymers Examined by Thermogravimetry

Polymer	$T_{1\% \text{ weight loss}}$ (°C)	$T_{10\% \text{ weight loss}}$ (°C)	$T_{\text{DTG, max}}$ (°C)/ Weight Loss (%)
PSU 30,000	473	521	543/28 635/59
PET/HBA 13,000	395	433	453/27 517/61
PET/HBA 3200/PSU 2000	388	433	456/25
PET/HBA 5900/PSU 5800	391	440	450/15
PET/HBA 7400/PSU 8400	387	442	449/13 526/48

Table II Mechanical Properties of Injection-molded LCP and PSU Test Bars in Comparison to the Corresponding Blend and Multiblock Copolymer

No.	Sample	E-Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)	Fracture Strength (MPa)
1	PSU	2.566	72.38	5.74	48.26
2	PET/HBA	14.447	141.24	1.82	138.86
3	Blend PSU/PET/HBA 50/50 wt/wt	4.256	51.13	1.84	51.02
4	BCP PSU 5000/PET/HBA 5000	6.644	78.69	2.00	77.64

gation values as observed for materials with high modulus.

Thus, a combination of properties of PSU and LCP within the block copolymer can be stated.

CONCLUSIONS

The investigation of multiblock copolymers containing polysulfone segments and liquid crystalline poly(ethyleneterephthalate-co-oxybenzoate) units clearly indicated that processing, as well as material properties of the polymers, can be tailored by coupling of segments with suitable molecular weight.

The block copolymer properties are characterized by a true combination of the E-modulus of LCP with the thermostability of polysulfone. Dynamic mechanical investigations showed that the decrease of E-modulus of the block copolymers below the very high value of LCP can be compensated by incorporation of longer PET/HBA segments into the block copolymer.

The thermostability of polysulfone caused by the high glass transition temperature of the polymer is maintained in the block copolymers due to the depression of the relaxation in the T_g range of PET/HBA.

The disadvantageous high melt viscosity of PSU is decreased by block copolymer formation. As a result, the products can be processed by injection molding and fiber spinning.

Besides this, films can be prepared from solution. Because of the amorphous-nematic solid phase structure of the polymers, application as membranes showing increased mechanical strength can be proposed. The separation processes in such membranes could be influenced by the phase-separated morphologies of the block copolymers, which can be controlled by the molecular weight of the coupled segments. Zeta potential measurements of multiblock copoly-

mer films revealed an isoelectrical point between pH 3 to 4; i.e., the polymers possess an acidic surface. Further investigations regarding the dependence of surface properties on multiblock copolymer composition are in progress.

Another interesting application of the multiblock copolymers under discussion could be as compatibilizer in blends of LCP with PSU. Recently, it was suggested by Noolandi¹² that multiblock copolymers should be effective as polymeric surfactants, provided that their blocks are large enough to form loops that extend well beyond the original homopolymer interface. First, experiments have been carried out in order to investigate the effect of PSU-LCP multiblock copolymers in blends of PSU and LCP, which are known to be immiscible.¹³ Some interesting results have been found, demonstrating that a certain miscibility between the phases can be reached. These and other results will be included in our next publication.

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