

LC Multiblock Copolymers Containing Polysulfone Segments. I. Synthesis and Morphology

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SYNOPSIS

Multiblock copolymers offer the possibility to combine the properties of different polymers. Thus, new materials with tailor-made unique properties are available by coupling of different suitable polymeric segments. The goal of the work discussed in this paper was to combine advantageous properties of liquid-crystalline polymers (LCP) with those of polysulfone (PSU). Therefore, liquid crystalline poly(ethylene terephthalate-co-1,4-oxybenzoates) were connected with PSU oligomers. Chemically homogeneous multiblock copolymers with high molecular weight were obtained by a melt transesterification procedure. It was demonstrated by wide angle x-ray scattering (WAXS), polarizing microscopy, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC) that the properties of the multiblock copolymers (solid phase structure, phase behavior, morphology, glass transition, and melting behavior) can be balanced by the segment length of the incorporated blocks. The investigations clearly reveal the existence of a two-phase structure. However, a change of properties compared to the corresponding homopolymers refers to certain interactions between the phases due to the chemical connection of the LCP and PSU segments. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The number of investigations dealing with synthesis and characterization of multiblock copolymers with liquid crystalline segments has been rapidly increased during the last years. The main intention of that work was the combination of advantageous properties of liquid-crystalline polymers (LCP), e.g., outstanding tensile strength and E-modulus, dimension stability, soft flow, low coefficient of expansion and low shrinkage,¹ with favourable properties of other polymers. In most cases, the chemical coupling of different polymer segments in multiblock copolymers effects special morphologies that are caused by microphase separation.¹ These special morphologies, in addition to the combination of homopolymer properties, may give rise to the development of new, unexpected behavior or synergistic effects of selected properties, thus allowing the de-

velopment of *tailor-made materials* by clever coupling of suitable units.

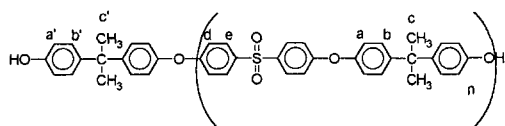
Based on this concept, conventional multiblock copolymers such as poly(urethanes) or poly(ether-esters) were created, resulting in the formation of thermoplastic elastomers.² In a similar manner, polymers with a broad range of properties can be developed by combination of LC segments with several other polymer units (flexible, amorphous-rigid chain or semicrystalline-rigid chain).

Like conventional poly(ether-esters), thermotropic elastomers are formed by coupling of LC units and flexible polyether chains.^{3,4} The elastomeric properties of these polymers are caused by microphase separation into an amorphous polyether phase and an ordered, LC nematic phase.

Particularly, block copolymers containing LC segments are discussed to have potential to realize the concept of molecular or supramolecular self-reinforcement or of molecular composites proposed by Prevorsek.⁵

Recently, LC multiblock copolymers, as well as graft copolymers with polystyrene (PS) segments,

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Formula 1

were prepared in order to study the question whether the compatibility of flexible polymers and rigid chain polymers can be significantly increased by chemical bonds between the polymer segments in the block copolymer.^{4,6-10} It was demonstrated that the modification of thermotropic main chain polyesters by PS chains not only influences the phase stability and morphology of the LCP but also improves the compatibility in PS/LCP blends by changing the morphology.⁷⁻⁹

Compatibilization of polymer blends of high-performance polymers with LCP was one of the main scopes of the development of multiblock copolymers containing poly(phenylene sulfide),^{11,12} poly(phenylene oxide),^{11,13} poly(ether-etherketone),¹⁴ and polysulfone (PSU) units. Structures of LCP/PSU block copolymers described in the literature are reviewed by Auman and Percec.¹⁵ They pointed out the different types of LCP segments chemically coupled with polysulfone segments.

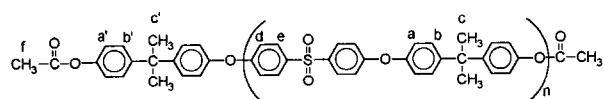
Alternating block copolymers containing LC polyether segments and PSU were prepared by Percec et al. using phase-transfer catalyzed polyetherification reaction of α,ω -di(electrophiles) with OH terminated oligomers.¹⁶⁻¹⁸ The resulting block copolymers show a considerable phase separation as revealed by differential scanning calorimetry (DSC) in spite of incomplete etherification of the monomers.¹⁸ Attempts to prepare poly(*p*-phenylene terephthalamide) (PPTA)/PSU block copolymers by reaction of carboxylic acid chloride terminated PPTA with OH terminated PSU in *N*-methyl pyridoxine (NMP)/LiCl as solvent yielded only a small degree of coupling between the two different blocks, presumably due to phase separation of flexible coil PSU and rigid rod PPTA in the reaction solution.¹⁹

Most of the work done in the field of LCP/PSU block copolymers was gained to the synthesis of polymers containing LC polyester units. This is clearly inspired from the fact that the practically relevant thermotropic LCP are copolyesters. Preformed PSU monomers with reactive end groups are applied for polymer synthesis. These polysulfones are converted into block copolymers with different LC polyester segments by means of various poly-

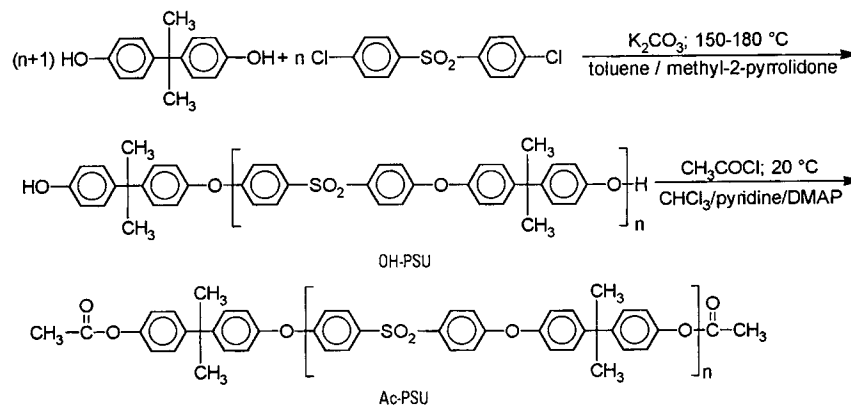
condensation methods. Block copolymers were synthesized either by reaction of the end group functionalized PSU with preformed polyester segments as well as by *in situ* formation of the polyester blocks in the presence of the PSU monomers accompanied and followed by coupling of the chemically different blocks.²⁰ It should be noted that the latter method is preferred in literature because synthesis of LC oligomers with defined end groups is also complicated, and the solubility and melting temperature of such oligomers is critical.

Brenda et al.²¹ and Heitz²² obtained polysulfone block copolymers containing substituted poly(*p*-phenylene terephthalate) segments by high-temperature solution polycondensation of substituted terephthaloyl dichloride with substituted hydroquinone and OH-terminated PSU in diphenyl ether. Block copolymers, including amorphous poly(phenyl-1,4-phenylene-phenyl-terephthalate) units, were discussed to be miscible systems due to the detection of only one T_g in $\tan \delta$ curves of dynamic mechanical analysis, but they did not show LC behavior in the melt. Incorporation of semicrystalline poly(phenyl-1,4-phenylene terephthalate) resulted in biphasic systems showing optical anisotropy. Zhang et al.²³ demonstrated by synthesis of PSU block copolymers with unsubstituted poly(1,4-phenylene terephthalate) units that the minimum needed fraction of mesogenic units, i.e., the minimal LC segment length, strongly depends on the block length of PSU.

PSU block copolymers synthesized by conventional melt polycondensation procedures as applied for LC polyester synthesis using transesterification of acetylated diols, dicarboxylic acids, acetoxy benzoic acids, and acetylated PSU are often reported to be chemically heterogeneous, less-defined products that can be characterized as mixture of nonreacted monomers, corresponding homopolymers, and parts of block copolymer. Auman and Percec¹⁵ pointed out that the melt acidolysis of chloro-hydroquinone diacetate, α,ω -di(acetoxy) PSU and trans-cyclohexane dicarboxylic acid results in real block copolymers only for PSU with molecular weights until 2300 g/mol. With higher molecular PSU, blends of the aromatic polyester homopolymer with chain-extended



Formula 2



Equation 1

PSU were detected. In contrast, McGrath and colleagues^{24–26} succeeded in the preparation of true block copolymers by means of a one-pot acidolysis melt polycondensation using chlorobenzene as a common solvent for both the polysulfone monomer and the aromatic comonomers in the first reaction step. The block copolymers containing PSU segments connected with aromatic poly(oxybenzoate) units showed phase separation. In DSC measurements, one T_g was found, which is caused by the amorphous polysulfone phase, and, in addition, multiple melting endotherms, which represent a semicrystalline solid phase and the transition into an LC phase, respectively. In the case of fully aromatic segments, a careful optimization of reaction conditions seems to be necessary for obtaining chemically homogeneous polymers: aromatic parts should not precipitate before reacting with the end groups of PSU, i.e., the reactivities of aromatic monomers should be comparable to the reactivity of end-group-terminated PSU. Polycondensation of preformed oligomers of such semicrystalline structure with PSU oligomers would not result in true block copolymers.

In contrast, we have used end-group-terminated, semiaromatic poly(ethylene terephthalate-co-oxybenzoate) (PET/HBA) in order to buildup segmented multiblock copolymers with alternating rigid and polysulfone units. PET/HBA polymers were first described by Jackson and Kuhfuss²⁷ and, since then, have been the subject of investigation for a long time.

Beside the known advantageous properties of LCP, they are characterized by a nematic structure with a low degree of classical crystallinity, a low melting temperature in the range of about 200°C, low melt viscosity, and therefore, excellent pro-

cessability. The chemical coupling of such amorphous–nematic PET/HBA segments with amorphous–rigid PSU is assumed to result in products combining the advantageous properties of both polymers. In the following, the synthesis and characterization of such block copolymers is described. In particular, the influence of segment lengths on the resulting morphology, phase behavior, and phase stability of the multiblock copolymers is discussed.

In the next part, we shall describe how the block length influences properties that are important for processing of the polymers, such as melt rheology, dynamic mechanical behavior, and thermal expansion behavior.

EXPERIMENTAL

Synthesis

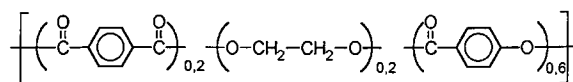
Preparation of α,ω -acetoxy-terminated Polysulfones

In the first step, OH-terminated polysulfones (OH-PSU) were synthesized by reaction of 4,4'-dichlorodiphenyl sulfone (DCDPS) with 2,2'-bis(4-hydroxyphenyl) propane, bisphenol A (BPA). As described by several authors,^{19,28–30} the reaction was carried out in a mixture of methyl-2-pyrrolidone (NMP) as dipolar aprotic solvent and toluene to remove the water formed during reaction by azeotropic distillation. Potassium carbonate was used to generate the phenoxide ion of BPA *in situ*, which subsequently reacts with DCDPS at a higher temperature.³¹ A typical synthesis is described below.

Bisphenol A (0.066 mol), from Aldrich, Steinheim, Germany, mp 158–159°C recrystallized twice from methanol; DCDPS (0.044 mol), from

Table I Chemical Characterization of OH-terminated and Acetoxy-terminated PSU Monomers (OH-PSU and Ac-PSU)

OH-PSU Sample	Molar Ratio (BPA/DCDPS)	Molecular Weight					Inherent Viscosity (dl/g)	Ac-PSU Sample	Molecular Weight					Inherent Viscosity (dl/g)
		\bar{M}_n (calc) (g/mol)	\bar{M}_n (NMR) (g/mol)	\bar{M}_n (titr) (g/mol)	\bar{M}_n (GPC) (g/mol)	\bar{M}_w (GPC) (g/mol)			\bar{M}_w/\bar{M}_n (g/mol)	\bar{M}_n (calc) (g/mol)	\bar{M}_n (NMR) (g/mol)	\bar{M}_n (GPC) (g/mol)	\bar{M}_w (GPC) (g/mol)	
OH-PSU 1	3.00	670	1700	1600	1240	1460	1.18	Ac-PSU 1	1700	1850	1500	1810	1.21	
OH-PSU 2	2.00	670	1660	2100	2160	2830	1.31	Ac-PSU 2	2200	2100	2400	3050	1.27	
OH-PSU 3	2.00	670	1800	2300	2900	4110	1.41	Ac-PSU 3	2450	2250	3300	4630	1.4	
OH-PSU 4	1.15	3140	3700	3800	3770	8300	2.20	Ac-PSU 4	3900	3770	4610	8360	1.81	
OH-PSU 5	1.10	4640	4520	5400	5060	10,100	2.00	Ac-PSU 5	5500	5900	5060	12,000	2.37	
OH-PSU 6	1.05	9040	4900	5730	5240	11,000	2.1	Ac-PSU 6	5900	6190	6650	14,200	2.13	
OH-PSU 7	1.05	9040	6900	8400	5730	29,700	5.18	Ac-PSU 7	8500	11,000	7230	19,100	2.64	



Formula 3

Aldrich, mp 146.5–147.5°C, recrystallized twice from toluene; and dried anhydrous potassium carbonate (0.077 mol) were given into a three-necked round flask equipped with N₂ inlet, condenser with water trap, and stirrer. A mixture of methyl-2-pyrrolidone (110 ml), from Aldrich, bp 202°C, dried over CaH₂, distilled and stored with molecular sieves, and toluene (55 ml), from Merck, Darmstadt, Germany bp 110.8°C, dried with Na and distilled, was added. The reaction mixture was refluxed with stirring at 165°C under nitrogen flow until the water formed during reaction was removed completely by azeotropic distillation (about 4 h). After that time, toluene was removed by distillation, then the mixture was allowed to complete the reaction for 2 h at 180°C. After cooling, inorganic salts were separated by filtration, and the reaction solution was precipitated into the tenfold amount of ethanol. The resulting OH PSU was filtered off, dried, reprecipitated twice from chloroform into ethanol, and finally dried at 50°C in a vacuum oven. OH PSUs were characterized by infrared (IR) and ¹H NMR spectra, by molecular weight determination using end group titration, gel permeation chromatography (GPC) and viscometry (Table I). IR (KBr): 2968 (νCH₃), 1586 (νCH_{ar}), 1323/1295 (ν_{as}O=S=O), 1245 (ν_{as}C—O—C), 1151 (νO=S=O), 1107 (ωCH₂) cm⁻¹, assignments according to Lambert et al.³²

¹H NMR (300.13 MHz, CDCl₃): δ = 7.84 (e,d), 7.24 (b,d), 7.09 (b',d), 7.00 (d), 6.94 (a,d), 6.75 (a',d), 1.69 (c,s), and 1.65 (c',s) ppm; assignments according to Formula 1.

OH end groups of PSU were acetylated in chloroform according to Auman and Percec,¹⁵ using acetyl chloride and dimethylamino pyridine/triethylamine as the catalyst. The resulting acetoxy-terminated PSUs (Ac-PSU) were characterized by infrared (IR) and ¹H nuclear magnetic resonance (NMR) spectroscopy, viscometry, and gel permeation chromatography (GPC). IR (KBr): 3066 (νCH₃), 2968 (νCH₃), 1766/1755 (νC=O), 1586 (νCH_{ar}), 1504/1488, 1324/1295 (ν_{as}O=S=O), 1244 (ν_{as}C—O—C), 1169, 1151, 1106 (ωCH₂) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃): δ = 7.84 (d,e,f), 7.24 (b,b',c,c',d), 7.00 (d), 6.94 (a,a',d), 2.28 (s), 1.69 (s), 1.68 (s) ppm; assignments according to Formula 2.

Table II Chemical Characterization of COOH-terminated (PET/HBA) Oligomers

Sample (PET/HBA)	Excess of TA (mol %)	[COOH] · 10 ⁴ (mol/g)	$\bar{M}_{n,COOH}$ (g/mol)	η_{inh} (dl/g)	$\bar{M}_{n,\eta}$ (g/mol)
PET/HBA 3200	4.4	6.26	3200	0.28	3600
PET/HBA 5400	3.3	3.704	5400	0.35	5200
PET/HBA 5900	2.2	3.380	5900	0.39	6300
PET/HBA 7400	—	2.700	7400	0.46	7700

Synthesis of COOH-terminated LC Poly(ethylene terephthalate-co-4-oxybenzoates) (PET/HBA)

PET/HBA copolymers with a PET/HBA ratio of 40/60 were (Formula 3) synthesized by acidolysis melt polycondensation according to Jackson and Kuhfuss²⁷ as described earlier.³³ COOH end groups were generated by copolycondensation with terephthalic acid. Molecular weights were determined by potentiometric titration of the COOH end groups (assuming complete termination of the polymer chains with COOH groups as detected by ¹³C NMR) in *o*-cresol/chloroform (7/3 v/v) with 0.1N KOH/butanol using a Mettler DL 70 titrator equipped with Mettler DG 113 electrodes, as well as by viscometry (in phenol/1,1,2,2-tetrachloroethane (1/1 v/v), with a polymer concentration of 0.5 g/dl (at 20°C) using Kuhn–Mark–Houwink equation with the exponents given in Leistner et al.³³ ¹³C NMR spectroscopy revealed a nearly random chain sequence distribution.³⁴

Synthesis of PSU-LCP Multiblock Copolymers

Multiblock copolymers were synthesized by acidolysis melt polycondensation of acetoxy-terminated PSU oligomers with COOH-terminated LC poly(ethylene terephthalate-co-4-oxybenzoates) as follows: COOH-terminated PET/HBA (0.001 mol) and Ac-PSU (0.001 mol) of the appropriate molecular weight were put into a three-necked flask equipped with N₂ inlet, stirrer, and distilling head. Before starting the polycondensation, the flask was purged three times with nitrogen. The polycondensation was carried out in two steps. In the first step, the flask was immersed in the metal bath at 230°C, then the temperature was gradually raised to 280°C during 30 min with continuous flow of dry nitrogen and stirring of the reaction mixture. After 45 min, vacuum (133 Pa) was applied for another 1.5 h. After that time, the flask was removed from the metal bath, and the resulting product was cooled down to ambient temperature and cut in a laboratory mill.

Polycondensation in a melt kneader (Brabender Plasticorder PL 2000) was performed as follows: 50 g of the monomers were filled into the preheated (230°C) kneading cell (W50E) equipped with electrical heating, seal piston, and torque registration. The reaction was carried out kneading with a rotative speed of 80 rpm at a constant temperature (250 or 270°C). After 30 min, the pressure within the kneading cell was reduced to about 400 mbar until finishing the reaction. Samples were taken by removing the seal piston and the vacuum.

Preparation of fibers was carried out using a small-scale plunger melt spinning device (for 10 g of polymer) at a spinning temperature of 290–310°C.

Analytical

Infrared spectra were obtained by means of a Bruker FTIR IFS 66 using KBr tablets. The nuclear magnetic resonance (NMR) measurements were carried out on a Bruker AMX 300 spectrometer operating at 300.13 MHz for ¹H and 74.47 MHz for ¹³C. CDCl₃ was used as solvent and lock for the OH- and acetoxy-terminated polysulfones. The spectra were referenced on the residual CHCl₃ signal (7.26 ppm versus tetramethylsilane (TMS)). The number averaged molecular weights of PSU were determined from the integral intensities of main chain and end group signals of aromatic protons. For investigation of block copolymers, they were dissolved in CDCl₃/hexafluoroisopropanol (1/1 v/v). CDCl₃ was used as lock and internal standard (77.00 ppm versus TMS).

Potentiometric titration of OH end groups of polysulfone was carried out similar to the procedure of Wnuk et al.³⁵ using a Mettler Toledo DL 70 Titrator with a DG 113 Ag/AgCl sensor in 2m LiCl, 0.1 molar tetrabutylammonium hydroxide in 2-propanol/methanol (Merck) as titrant, and dimethylformamide as solvent.

GPC investigations were performed by a Knauer GPC (Germany) using for PSU analysis chloroform (1 ml/min⁻¹) as eluent, Merck LiChrogel PS 40 (5 μL) separation columns, RI detection, and

Table III Chemical Composition and Characterization of PSU-PET/HBA Multiblock Copolymers

Polymer	Block Copolymers									
	LC Segment \bar{M}_n (g/mol)	PSU Segment \bar{M}_n (g/mol)	\bar{M}_n (GPC) (g/mol)	\bar{M}_w (GPC) (g/mol)	\bar{M}_w/\bar{M}_n	Inh. Viscosity (dl/g)	T_{soft} (micr.) (°C)	T_m (micr.) (°C)	Phase Behavior	
1a	3200	287	53,100	113,000	2.12	1.09	180	230-260	LC	
1b	3200	1600	39,500	196,500	4.97	1.19	210	270-280	LC	
1c	3200	2100	54,000	209,000	3.87	(partially sol.)	220	300	LC	
1d	3200	2400	19,800	121,000	6.11	1.61	260	315	LC	
1e	3200	3800	25,500	120,000	4.71	(partially sol.)	240	305	LC/350-370i	
1f	3200	5400	42,600	80,100	1.88	0.8	210	225-280	i	
1g	3200	8400	54,700	106,000	1.94	0.84	225	280-310	i	
2a	5400	287	47,500	95,700	2.01	1.00	180	250-260	LC	
2b	5400	3800	33,400	80,600	2.41	(partially sol.)	170	240-245	LC	
2c	5400	5400	67,700	118,500	1.75	1.02	210	260-280	LC/i	
3a	5900	287	39,600	92,800	2.34	0.91	180	230-240	LC	
3b	5900	2400	50,900	105,000	2.06	0.91	190	220-230	LC	
3c	5900	3800	70,200	148,000	2.10	(partially sol.)	230	230-250	LC/i	
3d	5900	5400	64,800	108,500	1.67	1.10	210	250-270	LC/i	
3e	5900	8400	55,400	88,100	1.59	0.79	210	260-280	LC/i	
4a	7400	287	56,200	105,000	1.88	1.09	190	230-260	LC	
4b	7400	3800	71,900	128,500	1.79	1.07	190	240	LC	
4c	7400	5400	61,800	98,100	1.59	0.93	200	220-250	LC	
4d	7400	8400	60,100	102,500	1.71	0.92	230	270-280	LC	

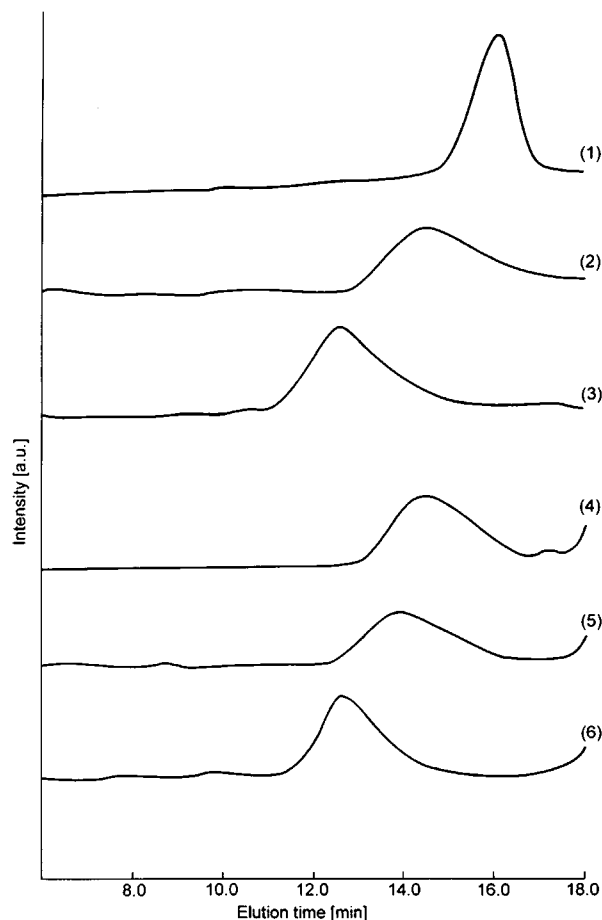


Figure 2 GPC elution curves of multiblock copolymers compared to the corresponding PSU and PET/HBA oligomers: (1) Ac-PSU 2 (2100 g/mol), (2) PET/HBA 3200, (3) block copolymer 1c, (4) Ac-PSU 5 (5400 g/mol), (5) PET/HBA 5400, and (6) block copolymer 2c.

chloroform (1/1 V/V), (polymer concentration 0.25 g/dl (at 20°C).

Softening and melting ranges, as well as the phase behavior of the block copolymers, were observed on a hot stage polarizing microscope (Cambridge Instruments).

DSC measurements were carried out by means of a Perkin Elmer DSC-7 with a scanning rate of 20 K/min in nitrogen atmosphere. The thermal stability of the multiblock copolymers was investigated by a Perkin-Elmer Thermogravimetric system TGA-7 in nitrogen atmosphere at a heating rate of 10 K/min.

WAXS powder diffraction of isotropic samples were performed using $\text{CuK}\alpha$ radiation with the device system X-ray diffractometer HZG 4/A-2 (Seifert-FPM Freiberg i. Sa., Germany) equipped with an energy-dispersive detector EDR 288 (RönTec GmbH Berlin, Germany). Fiber investigations were carried

out by a four-circle-diffractometer P4 equipped with a two-dimensional position sensitive detection system (GADDS, Siemens).

Transmission electron micrographs were recorded by means of a Zeiss EM 912 in the zero-loss-mode ($\Delta E = 0$, elastic scattered electrons only). The samples were prepared as thin films from a polymer solution in TFA/ CHCl_3 by spreading on distilled water.

RESULTS AND DISCUSSION

Polymer Synthesis and Chemical Characterization

The aim to prepare LCP-PSU multiblock copolymers by a melt transesterification procedure as usual for aromatic LC copolyesters^{1,36} requires suitable end-group-terminated oligomers that have melting temperatures within the polycondensation range. Therefore, OH-terminated oligosulfones (OH-PSU) were synthesized by nucleophilic aromatic substitution of 4,4'-dichlorodiphenyl sulfone (DCDPS) with 2,2'-bis(4-hydroxyphenyl)propane (BPA) according to eq. (1). The method of *in situ* formation of the phenoxide ion of BPA by potassium carbonate described by McGrath and colleagues^{28,29} was used. The molecular weight of OH-PSU was controlled by the ratio of BPA and DCDPS (theoretical calculation according to Elias³¹). The respective OH-PSUs were acetylated according to Auman and Percec¹⁵ by acetyl chloride in chloroform. The obtained results are given in Table I.

The experimentally determined molecular weights of OH-PSUs are somewhat higher than the calculated ones. It could be demonstrated by GPC investigation

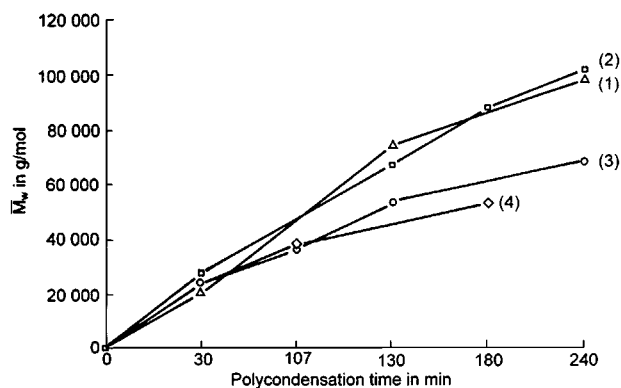


Figure 3 Molecular weight development during polycondensation in a melt kneader: (1) PSU 7100-PET/HBA 7400, 270°C; (2) PSU 5200-PET/HBA 5900, 270°C; (3) PSU 5200-PET/HBA 5900/250°C; (4) PSU 5200-PET/HBA 5900/250°C.

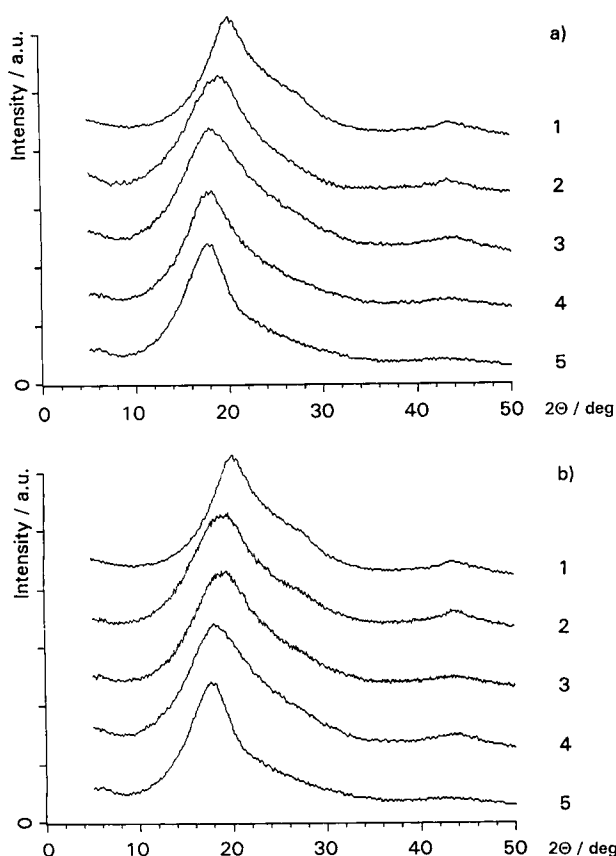


Figure 4 WAXS diffractograms of as-synthesized PSU-PET/HBA multiblock copolymers with different segment lengths compared to the scattering curves of the corresponding oligomers. (a) Influence of PSU length in PET/HBA 3200 block copolymers: (1) PET/HBA 3200; (2) PSU 1600-PET/HBA 3200; (3) PSU 3800-PET/HBA 3200; (4) PSU 8400-PET/HBA 3200; (5) OH-PSU 8400. (b) Influence of PET/HBA length in PSU 3800 block copolymers: (1) PET/HBA 7400; (2) PSU 3800-PET/HBA 7400; (3) PSU 3800-PET/HBA 5400; (3) PSU 3800-PET/HBA 3200; (4) PSU 8400.

that precipitation of the reaction solution from NMP into ethanol causes a fractionation effect; lower oligomers remain in solution. For further reactions, the molecular weights examined by titration were used because the mean error of this method was found to be approximately 1%, whereas the mean error of the calculation based on ^1H NMR peak intensities was about 2–5%. The complete termination of the PSUs by OH groups and, after acetylation, by acetoxy groups, respectively, was proven by ^1H NMR (see the experimental section).

The LC oligomers, poly(ethylene terephthalate-*co*-oxybenzoates) 2, (see Formula 3) with an oxybenzoate content of 60 mol %, were synthesized by melt transesterification of poly(ethylene tere-

phthalate) with 4-acetoxybenzoic acid. As shown earlier, poly(ethylene terephthalate-*co*-oxybenzoates) have a random chain sequence distribution with a slight tendency of oxybenzoate block formation³⁴ and are mainly terminated by COOH groups, which are preferably generated by side reactions occurring during the polymer synthesis.³⁷ The molecular weight of PET/HBA can be controlled by addition of terephthalic acid as illustrated in Table II. For stoichiometric calculation of oligomers for block copolymer synthesis, the $\bar{M}_{n,\text{COOH}}$ values were used.

The amorphous acetoxy-terminated polysulfones soften above their glass transition temperature in the range of 120 to 160°C, and the COOH-terminated poly(ethylene terephthalate-*co*-oxybenzoates) have a melting range from 160–210°C, as revealed by DSC. This melting temperature, together with a low melt viscosity, was assumed to be a good condition to obtain a polycondensation of the oligomers in the melt in a temperature range of 230–280°C. Thus, multiblock copolymers were synthesized by transesterification polycondensation according to eq. (2). End-group-terminated oligomers with different molecular weights were used. For comparison and estimation of reactivity of COOH terminated PET/HBA, polymers with 4,4'-bis(acetoxyphenylene) sulfone (polymers 1a, 2a, 3a, 4a) were prepared as model for PSU.

The chemical coupling of PSU and PET/HBA units resulting in a new ester bond is proved by ^{13}C NMR spectroscopy. For example, the spectrum of block copolymer 1d (Fig. 1) shows up beside two signal groups in the carbonyl region, which are caused according to Jancke et al.³⁴ by ethyl ester diads and oxybenzoate diads as well. A third one at 168.0 ppm can be unambiguously assigned to the ester group which links bisphenol A and PET/HBA. Jancke et al.³⁴ noted that the chemical shift of C=O groups of diads in PET/HBA depends only on the diol component but not on the acid component in the diad. Consequently, ester carbonyls resulting from the linkage of bisphenol A with terephthaloyl units cannot be distinguished from those resulting from bisphenol A-oxybenzoate linkages (only one signal is found). The acetoxy carbonyl signal of bisphenol A units at 174.08 ppm cannot be detected in the block copolymer spectra referring to high molecular weights.

Indeed, molecular weights unusually high for polycondensates have been found by GPC using PS standard for calculation (Table III). The elution curves of block copolymers compared to elution curves of the corresponding PSU and PET/HBA

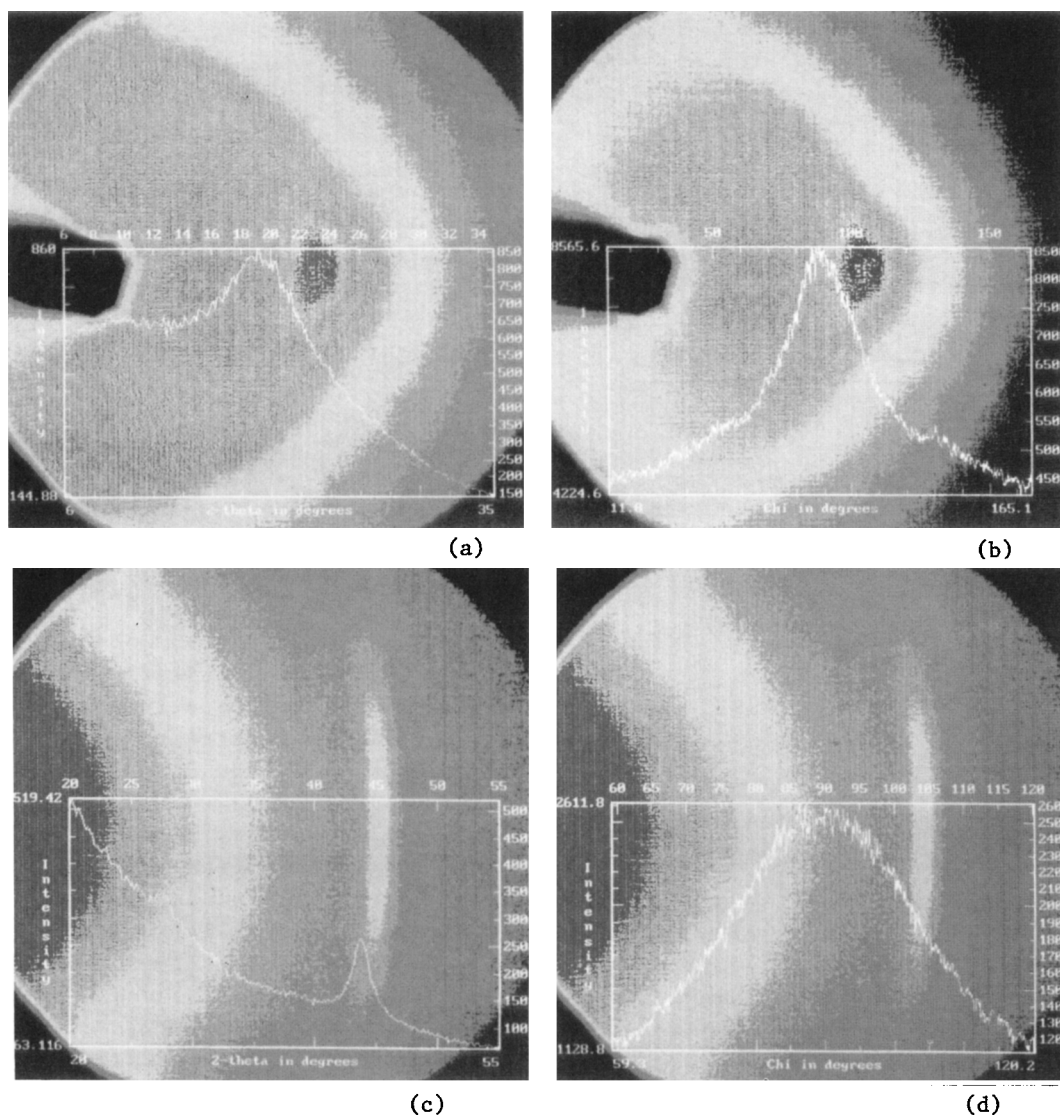


Figure 5 WAXS fiber diagrams of a melt spun of polymer 3d. (a) e: radial scattering intensity distribution. (b) e: azimuthal scattering intensity distribution. (c) m: radial scattering intensity distribution. (d) m: azimuthal scattering intensity distribution.

oligomers in Figure 2 confirm an unimodal molecular weight distribution, i.e., homogeneous multiblock copolymers without residual oligomers. The polydispersities \bar{M}_w/\bar{M}_n are about 2, as expected for polycondensates.

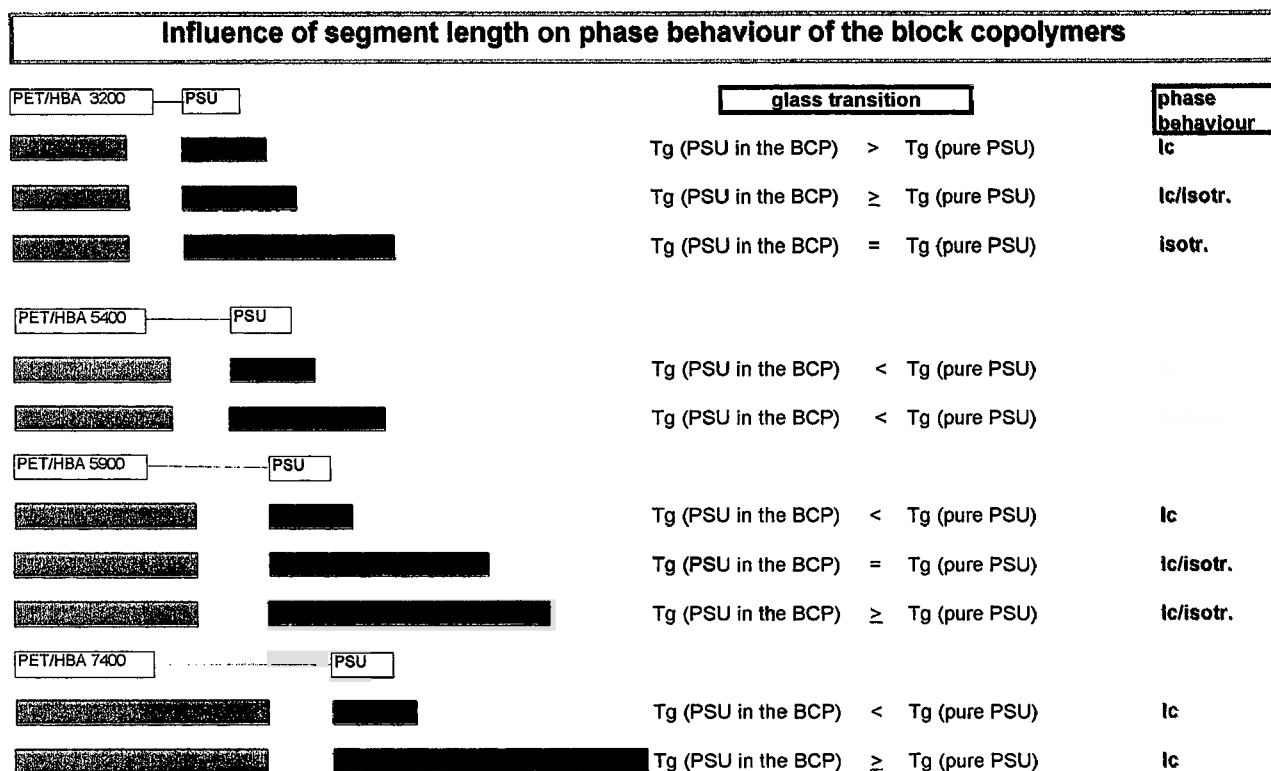
Surprisingly, comparable results were obtained when the reaction was carried out in a melt kneader (Brabender Plasticorder) under air at slightly reduced pressure (400 mbar). Normally, nitrogen atmosphere is used in the first step of polycondensation, and vacuum of 1–2 mbar is applied in the second step in order to obtain good polycondensation results (polymers with high molecular weight without decomposition). During four hours, a continuous increase in the molecular weight of the block copoly-

mers is detected (Fig. 3), accompanied by a continuous increase in torque. The molecular weight of the final products depends on the reaction temperature: with a cell temperature of 270°C, a considerable raise of the molecular weight is found, compared to 250°C.

Thus, homogeneous block copolymers with high molecular weights can be obtained by a relatively simple preparation procedure.

Solid Phase Structure

The solid phase structure of the PSU-(PET/HBA) multiblock copolymers under discussion were first examined by means of wide-angle X-ray diffraction



Scheme 1

of isotropic samples. The as-synthesized polymers can be described as frozen melts. Their scattering behaviour can be interpreted by a superposition of those shown by the respective oligomers. PET/HBA is characterized by a frozen nematic structure (i.e., existence of a lateral order in chain direction due to uniaxial orientation of the mesogenic macromolecules in domains), which is typical for LC copolyesters with random chain sequence distribution. The PSU oligomers are completely amorphous. WAXS diffractograms of block copolymers (Fig. 4) show a continuous change of the scattering maximum from that of PET/HBA to that of PSU.

In order to get more detailed information on the structure of the block copolymers, we tried to prepare uniaxial oriented samples by melt spinning. Fibres of block copolymer 3d have a high degree of orientation (meridional orientational degree of 0.89 relative to the inclined chain axis), figured out by the fibre diagrams recorded by an area detection system (Fig. 5). The diagrams show a broad equatorial reflection at $2\theta = 19.5$ degrees, corresponding to a disturbed pseudo-hexagonal lateral order of the chains. In the azimuthal scattering of the equatorial reflection, weak quadrant reflections are observed referring to the beginning of a three-dimensional ordering.

The meridional scattering is characterized by a relatively sharp reflection at $2\theta = 43.6$ degrees, representing a repeating unit in chain direction. From the azimuthal scattering of the meridional reflection, an inclination of 6 degrees of the chain direction with respect to the fibre axis is concluded to be quite similar to results of HBA/HNA fibres obtained by Gutierrez et al.³⁸

The WAXS results of the isotropic multiblock copolymer samples, as well as of the oriented sample, evidenced a microphase separated structure, which is characterized by a coexistence of an amorphous PSU phase and a lateral ordered nematic PET/HBA phase independent of the length of the connected blocks.

Phase Behavior and Morphology

The investigation of the phase behaviour of the multiblock copolymers was directed on the following questions: 1) How does the combination of different molecular weights of the incorporated segments influence the liquid crystalline behavior of the resulting polymer (LC texture or isotropic melt under the polarizing microscope), as well as the morphology of the polymers (observed by TEM); and 2) how does the chemical composition influence the melting

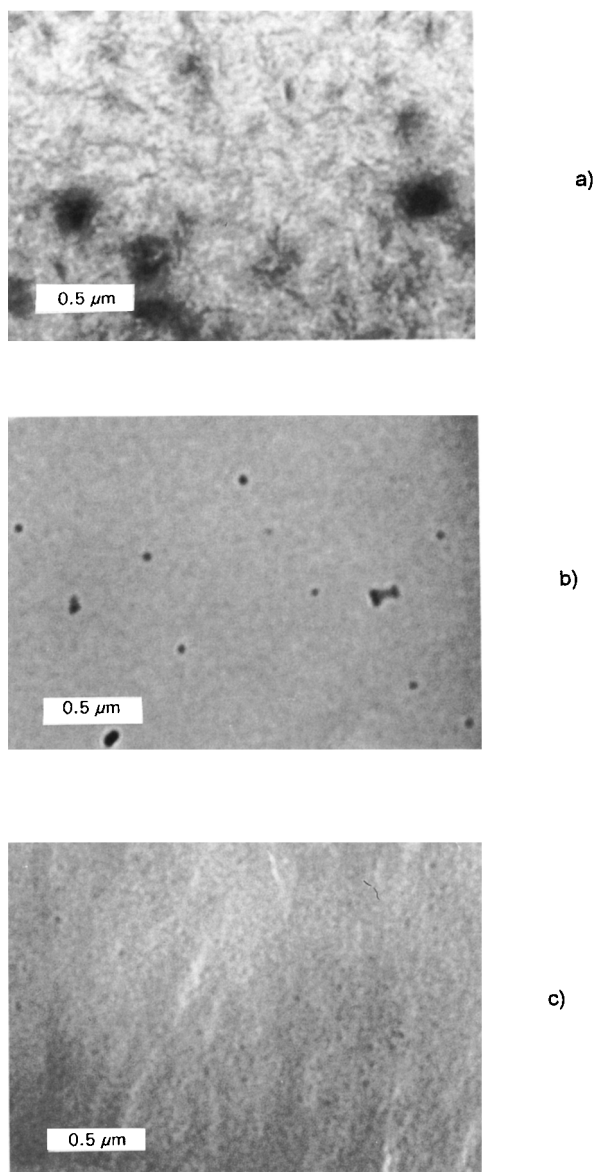


Figure 6 TEM micrographs of multiblock copolymers containing PET/HBA 3200 units: (a) PET/HBA 3200; (b) block copolymer 1c containing PSU 2000 units; (c) block copolymer 1g containing PSU 8400 units.

and glass transition behavior of the polymers (examined by DSC). An overview on the results is given in Scheme 1.

The reaction of 4,4'-bis(acetoxyphenylene) sulfone with COOH-terminated PET/HBA results in a chain extension of PET/HBA macromolecules and, therefore, in a stabilization of the LC phase (polymers 1a, 2a, 3a, 4a). The LC texture is not altered in comparison to the pure LCP. The coupling of short PSU and PET/HBA leads also to a stable

LC melt; whereas the combination of short LC segments with longer PSU chains ($\bar{M}_n > 3800$ g/mol) destabilizes the mesophase, a biphasic texture (coexistence of isotropic and LC regions) is observed by polarizing microscopy. The same result is found for block copolymers containing PET/HBA segments with intermediate molecular weight. Polymers with long PSU segments show isotropic melting behaviour. A stable LC texture of polymers with longer

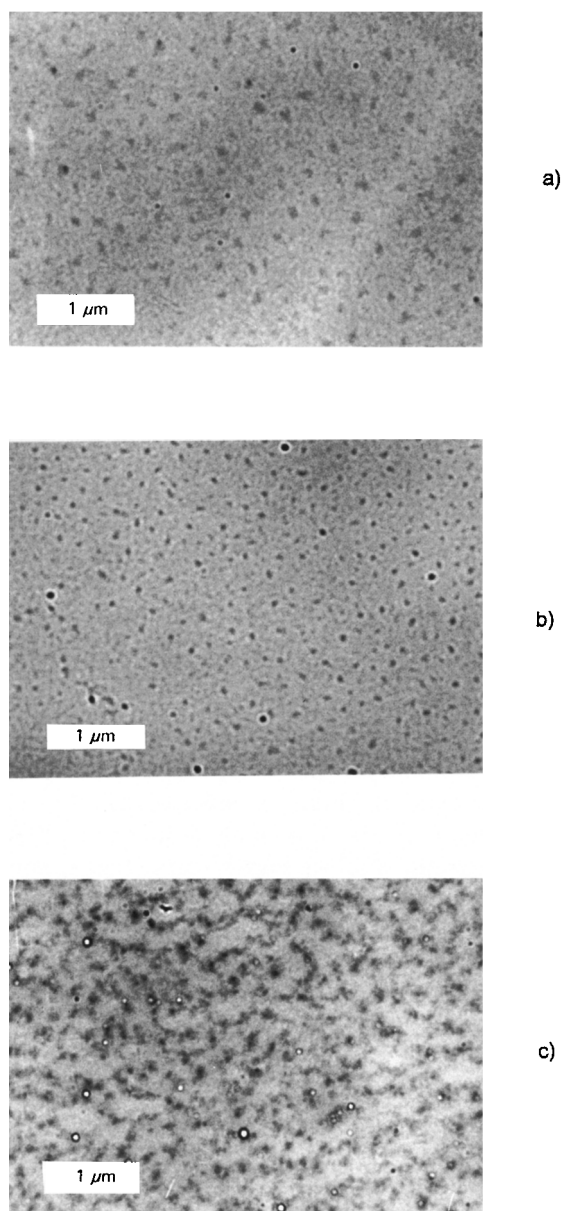


Figure 7 TEM micrographs of multiblock copolymers containing PET/HBA 7400 units: (a) polymer 1a (chain extended by diphenylene sulfone units); (b) block copolymer 4b containing PSU 3800 units; (c) block copolymer 4d containing PSU 8400 units.

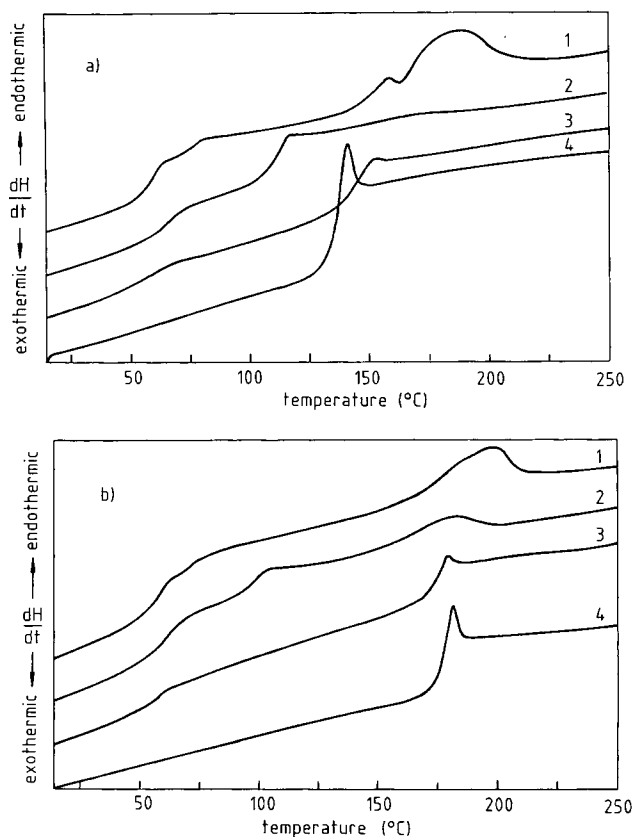


Figure 8 Comparison of the melting behavior (second heating of DSC) of PSU-PET/HBA block copolymers to that of the corresponding oligomers. (a) (1) PET/HBA 3200; (2) polymer 1a (containing 4,4'-bis(oxyphenylene) sulfone units); (3) multiblock copolymer PSU 2000-PET/HBA 3200; (4) PSU 2000; (b) (1) PET/HBA 7400; (2) polymer 4a (containing 4,4'-bis(oxyphenylene) sulfone units); (3) multiblock copolymer PSU 8400-PET/HBA 7400; (4) PSU 8400.

PSU segments is only reached if they are combined with long PET/HBA segments (polymer 4).

Summarizing, it should be noted that the phase behavior of the block copolymers can be controlled by the molecular weights of the coupled segments. Consequently, it was assumed that the morphology of the polymers also depends strongly on their composition. Therefore, TEM investigations were carried out using thin films obtained by spreading TFA/chloroform solutions on water.

Figure 6 illustrates the weak phase separation of multiblock copolymers containing PET/HBA 3200 segments: Only a small difference between the morphologies of polymers with short and long PSU spacers has to be stated. A significant alteration of morphology is observed in multiblock copolymers with PET/HBA 7400 blocks. Although showing

uniform LC textures under the polarizing microscope, a distinct phase separation between PSU phase and aromatic phase can be proved by TEM (Fig. 7). For low and intermediate PSU molecular weights, a dispersive PSU phase is found. At high PSU molecular weights, the morphology is changed into a co-continuous biphasic structure.

Thus, it has to be concluded that the observations taken with polarizing microscopy, i.e., the macroscopic phase behaviour, cannot be compared simply to the morphology of thin films detected by TEM.

The phase separation found by TEM is reflected by the glass transition and melting behaviour, as investigated by DSC measurements. Figure 8 illustrates the thermal behavior of some samples. Whereas pure PET/HBA shows two T_g (phase separation into a PET-rich phase and an oxybenzoate-rich phase³⁹) and a melting transition in the range of 200°C, the amorphous PSU is characterized only by a glass transition that depends strongly on the molecular weight (compare also, Fig. 9). In a simple blend of corresponding homopolymers (1/1 wt/wt), a superposition of the curves of both homopolymers is found due to the complete incompatibility of the components⁴⁰ without significant interactions. In contrast, block copolymer formation results in an alteration of the glass transition and melting behavior. Incorporation of short 4,4'-bis(oxyphenylene) sulfone units results in an increase in T_g of the oxybenzoate-rich phase of (PET/HBA); i.e., the low T_g of that polymer, an inherent disadvantage, can be raised by coupling with the sulfone spacer unit. The crystallinity of the (PET/HBA) component decreases with incorporation of the short sulfone unit, depending on the PET/HBA length [also see Fig. 8(a) 2 and (b) 2]. The coupling of low crystalline PET/HBA segments with PSU suppresses the crystallinity completely. A melting endotherm cannot be observed. This is in agreement with findings of Brenda et al.,²¹ who demonstrated that the crystallinity of the polyester fraction in poly(phenyl-1,4-phenylene terephthalate)/PSU block copolymers is strongly decreased.

Alterations of the glass transition temperature of the PSU phase in the block copolymers refer to interactions between the different blocks, which are caused by their chemical coupling (also see Scheme 1). Figure 9 compares the T_g of the PSU phase and the PET/HBA phase to those obtained for the corresponding oligomers with comparable length.

In the block copolymers, the glass transition temperature of the oxybenzoate-rich phase of PET/HBA cannot be detected. The T_g of the PET-rich phase does not differ from that one found for

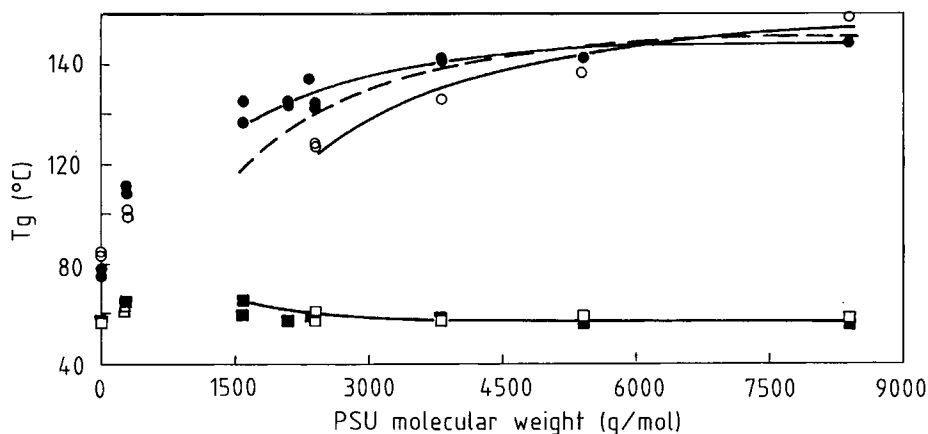


Figure 9 Influence of the segment length on glass transition of PSU-PET/HBA multiblock copolymers (T_g obtained by DSC): — — —, OH-terminated PSU-PET/HBA 3200 block copolymers: \square , PET-rich phase; \bullet , PSU phase. PET/HBA 5900 block copolymers: \square , PET-rich phase; \circ , PSU phase.

the unreacted oligomers. A slight drop has to be noticed with increasing molecular weight of the LC segment. In contrast, the glass transition of the PSU phase is significantly changed in relation to that of OH-terminated polysulfone of corresponding molecular weight. The coupling of short PET/HBA segments with short PSU segments effects an increase of the T_g of the PSU phase in the block copolymer above the T_g of the comparable pure PSU. Obviously, the rigid chain LC phase reinforces the amorphous PSU phase supported by the morphological low degree of phase separation as observed by TEM. T_g 's of block copolymers containing intermediate LC segments are lower in comparison to pure PSU, which can be explained by a softening of the PSU phase due to increasing microphase separation. The PSU glass transition temperatures of multiblock copolymers with long segments move to the value of the corresponding OH-terminated PSU, which has to be discussed in terms of a strong phase separation.

CONCLUSIONS

Multiblock copolymers containing LC poly(ethylene terephthalate-co-oxybenzoate) and polysulfone segments can be prepared by transesterification polycondensation. Chemically homogeneous block copolymers with high molecular weights are obtained using a simple preparation procedure in the melt.

The evidence proves that the block copolymers are two-phase systems on a submicroscopical scale.

Therefore, their properties are determined by a combination of those of the corresponding oligomeric segments with certain alterations due to the chemical bonding between the blocks. It was demonstrated in this work that the properties of the multiblock copolymers can be controlled by combination of suitable molecular weights of both blocks. Thus, the phase behaviour can be chosen between polymers forming isotropic or LC melts offering the possibility to avoid disadvantages of LCP like fibrillation after injection molding without losing the advantages of combination of different polymers. Furthermore, it was shown by TEM that variation of PSU and PET/HBA segment lengths enables control of the morphology of the block copolymers covering the range of less-phase-separated polymers to samples with a high degree of phase separation. The observed influence of the block length on the degree of phase separation obtained by TEM is clearly reflected by the glass transition and the melting behavior of the polymers: the behavior of less-phase-separated systems differ significantly from that of the corresponding homopolymers, whereas the behaviour of extremely phase-separated polymers is more comparable to that of a blend. It will be very interesting to examine the effect of multiblock copolymers of such different morphologies for compatibilization of polymer blends containing PSU and LCP.

In the companion to this article (Part 2), we would like to demonstrate that properties such as melt rheology, dynamic mechanical behavior, and thermal expansion behavior can also be controlled by the segment lengths of the blocks combined in

the multiblock copolymer. The influence of the segment molecular weights on the E modulus and the T_g behavior will be enlightened by dynamic mechanical analysis (DMA) results. Special attention will be attracted to the question how the phase behavior of the polymers (formation of an LC phase or not) influences their relaxation behavior.

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