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Composites. 2. Reinforcement of Poly(ϵ-caprolactone) via Lyotropic Blends of Rigid-Rod Polyesters Derived from Substituted Terephthalic Acids

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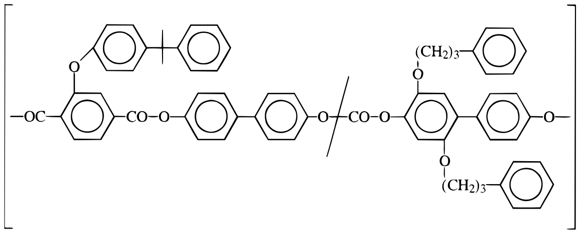
ABSTRACT: Two aryloxyterephthalic acids and two 2,5-bis(alkoxy)terephthalic acids were synthesized and polycondensed with hydroquinone (HQ), methylhydroquinone (MeHQ), phenylhydroquinone (PhHQ), or 4,4′-dihydroxybiphenyl (DHBP). Eleven out of the possible 16 polyesters were selected for the preparation of blends with commercial poly(ϵ-caprolactone), PCL, as the matrix. The properties of blends containing 1, 2, 4, or 8 wt % of the rigid-rod polymer were studied. The optical microscopy revealed birefringence for the entire blend below the melting temperature (T_m) of the rigid-rod polymer. The lyotropic character vanished and phase separation took place above the T_m of the rigid-rod polymer. The lyotropic blends (PCL acting as a solvent) showed a significant mechanical reinforcement effect, when examined by melt rheology and stress−strain measurements. This effect depended largely on the aromatic character of the substituents. The most surprising and important finding is the formation of lyotropic blends from a rigid-rod polyester which is not liquid crystalline as a neat material.

Introduction

In the past decade blends or composites of isotropic thermoplastic materials (the so-called matrix) and rigid-rod polymers (usually liquid crystalline polyesters, LCPs) have attracted much interest.[1−11] The purpose of these studies is to utilize the excellent but anisotropic mechanical properties of the relatively expensive LCPs for a mechanical reinforcement of the less expensive, isotropic, and mechanically weaker engineering plastics. Typical engineering plastics used for such studies are polyethylene, polypropylene, polystyrene, polycarbonates, or poly(ether sulfones). The most widely used reinforcing components are the commercial LCPs: Rodrun, Econol, Sumicosuper, and Vectra. For thermodynamical reasons the isotropic matrix polymers and the LCPs are not miscible.[12−14] Hence the blends containing 10−40% of a LCP (the most widely studied compositions) are two-phasic systems. When such a biphasic blend is in the molten state without being influenced by mechanical forces, the LCPs are dispersed in the form of nematic droplets. Upon shearing (e.g., extrusion or injection molding) and cooling the nematic LCP phase is transformed into rigid fibrils which can be isolated and studied after selective dissolution of the matrix material.

The ideal case from the viewpoint of reinforcement is a perfect molecular dispersion (i.e., solution) of the LCP in the matrix, the so-called concept of molecular reinforcement.[15,16] Because of the incompatibility of isotropic and liquid-crystalline materials, this concept is difficult to realize with commercial engineering plastics and LCPs. However, one sort of blend showing a partial miscibility of the polyether matrix (Ultem) and of the LC polyester (Granlar) has recently been reported.[17−19] This concept of molecular reinforcement is worth studying further at least for fundamental reasons. On the basis of theoretical calculations a significant improvement of the compatibility has been predicted for rigid three-dimensionally star-shaped polymers.[20] Unfortunately such reinforcing components are difficult and expensive to synthesize. Another approach which comes close to the ideal molecular reinforcement despite a total incompatibility of matrix and LCP has recently been described by the first author of the present work.[21,22] This experimental approach consisting of the formation of "lyotropic blends" was based on the coprecipitation of a substituted LC copolyester **1** (identical with **5c** of the present work) with various matrix polymers. The present work was designed to serve two purposes. Firstly, the existence of "lyotropic blends" should be confirmed, and their properties should be studied in more detail. Secondly, the structure of the rigid-rod polyesters (RPPs) used as reinforcing additives should be systematically varied to elucidate their influence on the formation and stabilization of the "lyotropic blends".



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Experimental Section

Materials. Hydroquinone (HQ), methylhydroquinone (MeHQ), phenylhydroquinone (PhHQ) and 4,4′-dihydroxybiphenyl (DHBP) were purchased from Aldrich Co. (Milwaukee, WI) and used as received. They were silylated with chlorotrimethylsilane and triethylamine in refluxing toluene and isolated by distillation in vacuo. Their properties have been described.[23−26] Cumylphenoxyterephthaloyl chloride (mp 124−126 °C) and biphenyloxyterephthaloyl chloride (mp 76−78 °C) were synthesized from dimethyl nitroterephthalate (Aldrich Co.) as described previously.[27] 2,5-Bis(dodecyloxy)terephthal-

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oyl chloride (mp 62−64 °C) and 2,5-bis(3-phenylpropoxy)-terephthaloyl chloride (mp 101−103 °C) were prepared from diethyl 2,5-dihydroxyterephthalate (Aldrich Co.) according to the literature.[28] Poly(ϵ-caprolactone) (mp 60−62 °C) was also purchased from Aldrich Co. The poly(methyl methacrylate) was a mainly syndiotactic product prepared by anionic polymerization at −75 °C. $M_w = 155\,000$, $M_w/M_n = 1.08$. Poly(m-hydroxybenzoic acid) with $\eta_{inh} = 0.63$ dL/g and T_g 136 °C was prepared by thermal polycondensation of trimethylsilyl 3-acetoxybenzoate in bulk at 290 °C.[29]

Polycondensations. A bissilylated diphenol (20 mmol), a substituted terephthaloyl chloride (20 mmol), and benzyltriethylammonium chloride (20 mg) were weighed into a cylindrical glass reactor equipped with stirrer and gas-inlet and gas-outlet tubes. The reaction vessel was placed into a metal bath preheated to 150 °C where most polycondensations slowly started. The temperature was raised to 270° in steps of 10 °C over a period of 2 h. The final temperature of 270 °C was maintained for 30 min without and for additional 30 min with vacuum. The cold polyester was dissolved in CH_2Cl_2/trifluoroacetic acid, TFA (volume ratio 4:1), and precipitated into methanol.

Preparation of the Polymer Blends. A 4% blend was prepared as follows. A rigid-rod polyester (RRP) (0.04 g) was dissolved in dichloromethane (40 mL), and if necessary, trifluoroacetic acid (TFA, 5 mL) was added. Poly(ϵ-caprolactone) (0.96 g) was added, and the suspension was stirred until a clear solution was obtained. This solution was added dropwise with rapid stirring to cold methanol (500 mL). The precipitated blend was isolated by filtration and dried at 40 °C in vacuo. The yields were in all cases around 98−99%.

The 1%, 2%, and 8% blends were prepared analogously.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C.

The DSC measurements were performed on a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

The dynamic mechanical analyses (DMA) were conducted with a Rheometrics RSAII. The temperature was varied from −110 to +60 °C in steps of 2 °C/min at constant frequency of 1 Hz. For these measurements films of 50 × 5 × 2 mm size were pressed at 80 °C for 15 min in vacuo.

The stress−strain measurements were performed with films of 50 × 40 × 1 mm size pressed at 80 °C in vacuo. Standardized (DIN 53455) dog-bone-type specimens (length 40 mm, width 4 mm) were cut from these films. A Zwick Md 1445 was used for all measurements, and neat poly(ϵ-caprolactone) samples were used for comparison in all series of measurements.

The rheological measurements were conducted on a Rheometrics RMS-800 with plate−plate geometry under nitrogen. The disks used for these measurements had a diameter of 25 mm and were pressed from 0.7 g of the blend at 80 °C in vacuo (hydraulic press Schwabenthan Polystat 100). Prior to any frequency sweeps, time and strain sweeps were conducted to find the area of linear dependency. The frequency sweeps were conducted isothermally between 70 and 140 °C in steps of 10 °C. The frequency was varied from 100 to 0.025 rad/s.

Lower frequencies were prevented due to low torque values. The isotherms were combined to a master curve at a reference temperature (T_{ref} = 80 °C) by the computer program LS-SHIFT.[30]

Results and Discussion

Syntheses and Characterization of Rigid-Rod Polyesters. All RRPs used in the present work were prepared by polycondensation of substituted terephthaloyl chlorides and silylated diphenols as examplified by the synthesis of **1** in eq 1. This polycondensation reaction is catalyzed by chloride ions and has proven its usefulness for the syntheses of numerous liquid-crystalline polyesters in several previous studies.[27,31,32]

In this way the homopolyesters **1**, **2a**−**d**, **3a**−**b**, and **4a**−**d** and the copolyesters **5a**−**d** were obtained. As demonstrated by the data compiled in Table 1 high yields, satisfactory inherent viscosities and acceptable elemental analyses were obtained in all cases (Table 1).

Table 1. Yields, Viscosities, and Elemental Analyses of the Rigid-Rod Polyesters

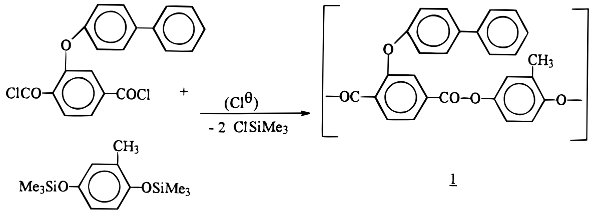
polymer no.	yield (%)	η_{inh}[a] (dL/g)	elem formula (form wt)	elemental analyses		
					C	H
1	94	0.80	$C_{27}H_{17}O_5$	calcd	76.77	4.30
			422.4	found	76.59	4.28
2a	96	0.99	$C_{30}H_{24}O_5$	calcd	77.57	5.21
			464.5	found	76.49	5.51
2b	89	0.81	$C_{35}H_{26}O_5$	calcd	79.83	4.98
			526.6	found	79.70	5.46
2c	90	0.95	$C_{35}H_{26}O_5$	calcd	79.83	4.98
			526.6	found	79.69	4.44
3a	96	1.72	$C_{33}H_{30}O_6$	calcd	75.84	5.79
			522.6	found	75.85	5.88
3b	93	0.78	$C_{38}H_{32}O_6$	calcd	78.06	5.52
			584.7	found	77.94	5.64
4a	87	1.14	$C_{38}H_{56}O_6$	calcd	74.96	9.27
			608.9	found	74.70	9.11
4b	92	1.89	$C_{39}H_{58}O_6$	calcd	75.32	9.40
			621.9	found	75.01	9.46
4c	88	0.93	$C_{44}H_{60}O_6$	calcd	77.16	8.83
			685.0	found	76.70	8.90
4d	95	0.54	$C_{44}H_{60}O_6$	calcd	77.16	8.83
			685.0	found	76.87	8.88
5a	98	1.16	$C_{67}H_{54}O_{11}$	calcd	77.74	5.26
			1035.2	found	76.58	5.24
5b	95	0.92	$C_{68}H_{56}O_{11}$	calcd	77.84	5.38
			1049.2	found	76.24	5.53
5c	90	0.80	$C_{73}H_{58}O_{11}$	calcd	78.90	5.26
			1111.3	found	79.31	5.43

[a] Measured at 25 °C with c = 2 g/L in CH_2Cl_2/TFA (volume ratio 4:1).

Table 2. Thermal Properties and Solubilities of the Rigid-Rod Polyesters

polymer no.	T_g[a] (°C)	T_m[a] (°C)	T_i[a] (°C)	T_i[b] (°C)	soluble in CH_2Cl_2
1	n.d.	281	297	305−310	⊕
2a	93	210	320	330−335	⊕
2b	106	220			⊕
2c	n.d.	377	460	455−460	⊖
3a	91	247	267	275−280	⊕
3b	72	257	358	360−365	⊖
4a	n.d.	158	208	210−215	⊕
4b	112	176	192	195−200	⊕
4c	96	123			⊕
4d	n.d.	198	270	275−280	⊕
5a	n.d.	175	273	275−280	⊖
5b	n.d.	139	258	255−260	⊕
5c	90	174	380	390−395	⊖

[a] DSC measurements with a heating rate of 20 °C/min. [b] Optical microscopy with a heating rate of 20 °C/min.



(1)

The structures of these RRPs were selected for the following reasons. Substitution of the hydroquinone is required in combination with monosubstituted terephthalic acid to achieve a good solubility in inert organic solvents. Also 4,4′-dihydroxybiphenyl improves the solubility relative to unsubstituted hydroquinone, because its length is quite different from that of the terephthaloyl unit and reduces the stability of the crystal lattice. The solubility data listed in Table 2 indicate that most RRPs were indeed soluble in neat

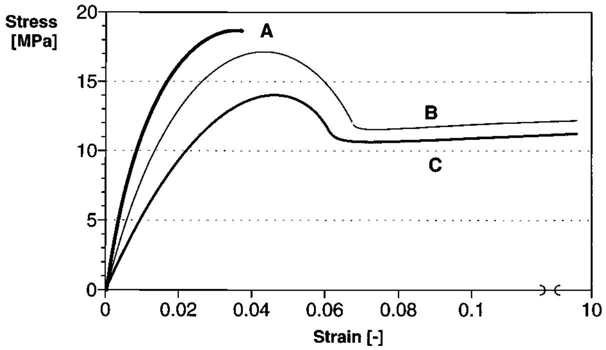
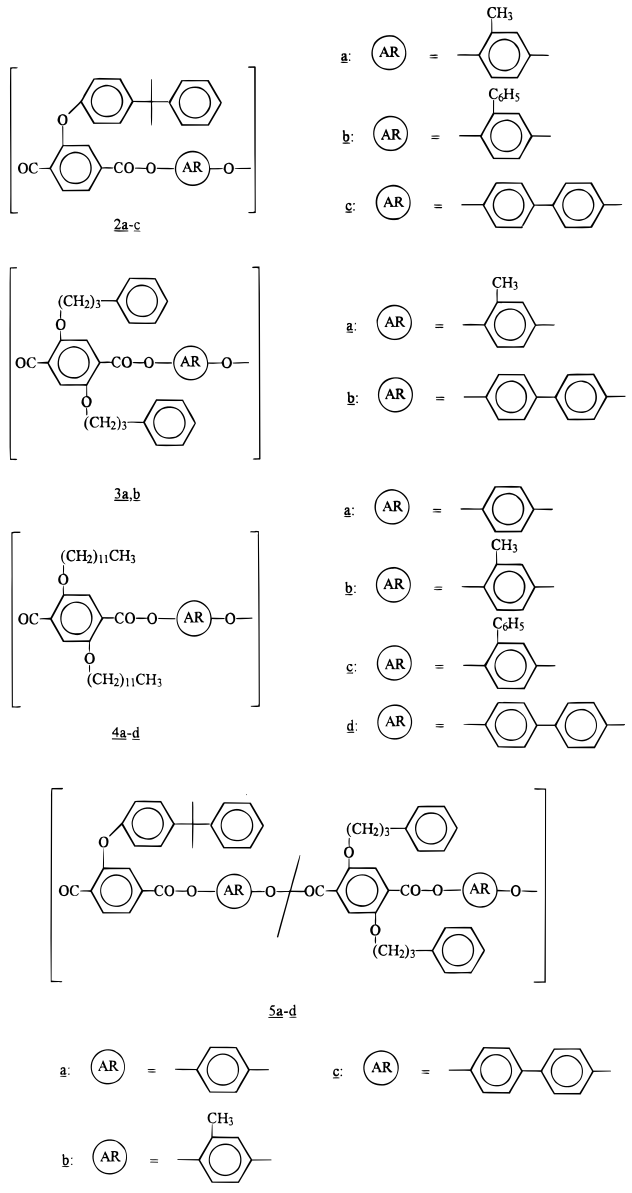


Figure 1. Stress–strain measurements of (A) 4% blend containing RRP **2c**, (B) 4% blend containing **2a** or **2b**, and (C) neat PCL.

Table 3. Influence of Trifluoroacetic Acid in the Solvent Mixture on the Properties of the Blend[a]

expt no.	vol %[a] of TFA	E-modulus[b] (MPa)	max stress[b] (MPa)	η_{inh}[c] (dL/g)
1	0	780	15.5	1.14
2	2	810	16.7	1.11
3	5	820	17.0	1.0
4	10	785	15.7	0.96
5	20	820	16.5	0.94

[a] Poly(ϵ-caprolactone) containing 8 wt % of RRP **2a**. [b] The given values are averaged over five measurements. [c] Measured from the neat matrix at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1).



dichloromethane. In a few cases addition of a small amount of TFA was required to obtain clear solutions.

The existence of crystallinity and the thermal properties of all polyesters were determined by means of WAXS powder patterns (after annealing at 115 °C), DSC measurements, and optical microscopy. The observation of a melting endotherm in the DSC heating traces (listed as T_m in Table 2) indicated together with the WAXS powder patterns that most polyesters were semicrystalline materials despite the nonsymmetrical substitution patterns. This finding agrees with previous studies of rigid-rod polyesters derived from monosubstituted terephthalic acids.[27] The glass-transition temperatures (T_g in Table 2) were so low that drying of the freshly precipitated samples at 115 °C had an annealing effect.

The chemical structure of the RRPs of this work also required that a liquid-crystalline (LC) melt, whenever it was formed, was nematic. The textures observed by optical microscopy with crossed polarizers indeed showed the schlieren texture and mobility expected for a nematic LC phase. Noteworthy are the RRPs derived from phenylhydroquinone, because their melting temperatures (T_m in Table 2) are extraordinarily low and they do not form a liquid crystalline melt. This finding was not surprising (and was in fact intended) because it has been shown previously[33] that substitution of both terephthalic acid and hydroquinone is less favorable for the formation of a LC phase than double substitution of one sort of monomers.

Preparation of Blends. In order to obtain a monomolecular "solution" of the RRPs in the matrix polyester (PCL) or at least a blend close to this ideal case, both the PCL and the RRPs were dissolved in one cosolvent, precipitated into methanol, and dried at 40 °C in vacuo (the low T_m of PCL (60 °C) prevented a higher temperature). For the preparation of most blends neat CH_2Cl_2 served as solvent, but in the case of **2c**, **3b**, **5a**, and **5c**, TFA had to be added to the CH_2Cl_2 solution. Small amounts of TFA were difficult to remove from the precipitated blends due to the low drying temperature. Therefore, the question arose to what extent residual TFA might affect the properties of the blends, in as much as stress–strain measurements showed that the elongation at break was particularly low for blends of **2c**, **3b**, **5a**, or **5c** (Figure 1). In other words blends of these RRPs were particularly brittle.

Therefore, systematic measurements were conducted with a 8% blend of **2a**. This blend was prepared either from neat CH_2Cl_2 or from CH_2Cl_2/TFA mixtures with increasing concentration of TFA. The mechanical measurements revealed that the TFA did not have a systematic influence on the properties of the blend (Table 3). However a slight degradation of the PCL matrix was detectable from viscosity measurements (Table 3).

Mechanical Measurements. Mechanical measurements of blends containing 1, 2, 4, or 8% of a RRP were conducted in two ways, either by dynamical mechanical (DMA) of hot-pressed films or by stress–strain measurements of doggy-bone-type specimens. The DMA measurements were conducted at a frequency of 1 Hz in the temperature range of −110 up to +40 °C. The storage modulus (E') reflecting the elasticity, the loss moldulus (E'') reflecting the transformation of mechanical energy into heat, and their quotient, tan δ, were recorded (Figure 2). Four blends contained 4 wt % of a

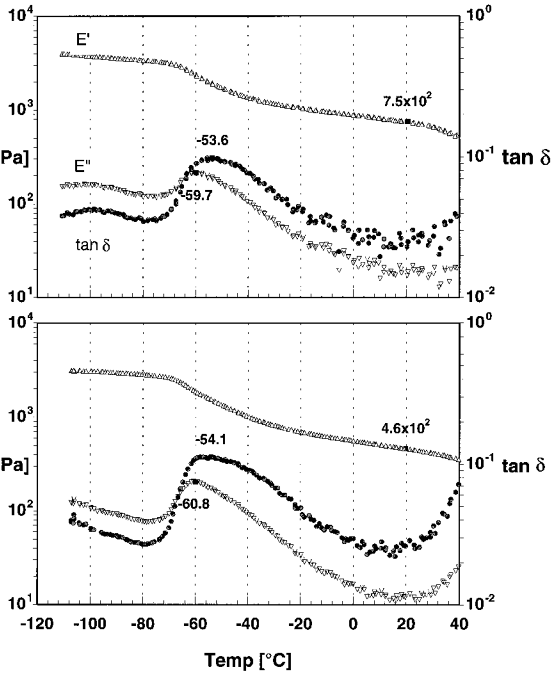


Figure 2. DMA measurement of a blend containing 4 wt % of RRP **2a**. Neat PCL measured under identical conditions gave a storage modulus (E') of 4.6 × 10^2 MPa (E'' = loss modulus).

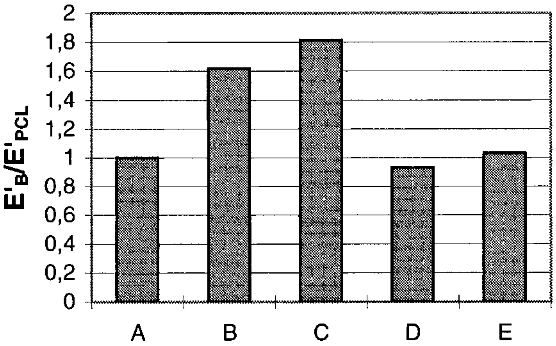


Figure 3. Normalized storage moduli of (A) neat PCL, (B) 4 wt % of **2a**, (C) 4 wt % of **1**, (D) 4 wt % of poly(3-hydroxybenzoic acid), and (E) 4 wt % of poly(methyl methacrylate).

RRP, namely, **1** or **2a**, the third blend contained 4 wt % either of poly(3-hydroxybenzoic acid) or of poly(methyl methacrylate), sPMMA. Figure 2 displays examplary the measurements of the **2a** blend. Compared to neat PCL (Figure 2b) the loss modulus was almost unchanged but the storage modulus showed an 80% gain at low temperatures. A comparison of all five measurements with normalized storage modulus is presented in Figure 3. It is obvious that only the para-linked RRPs bring about a significant mechanical reinforcement, whereas the nonrigid polymers do not. This finding is remarkable because the segmental mobility of poly(3-Hybe) and sPMMA is much lower than that of PCL as indicated by their high T_g which are 190 and 140 °C, respectively, higher than that of PCL ($T_g \sim -55$ °C).

A first series of stress−strain measurements were conducted in such a way that blends containing an increasing weight percentage of **2a** were examined. In a parallel series the RRP **2b** was used as the reinforcing component. The results displayed in Figure 4 carry two interesting pieces of information. Firstly, the stiffening effect of the RRP is additive for concentrations below 10%. Secondly, the reinforcing effect of **2b** is nearly as high as that of **2a** when both polyesters are compared

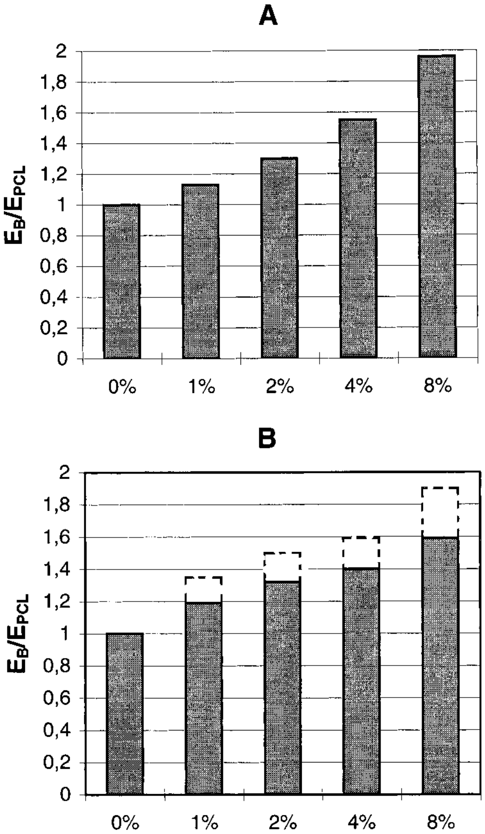


Figure 4. Normalized elastic moduli (stress−strain measurements) of blends containing (A) increasing concentrations of **2a** and (B) increasing concentrations of **2b**. The dotted columns are values calculated for equimolar concentrations of the repeating units of **2b** and **2a**.

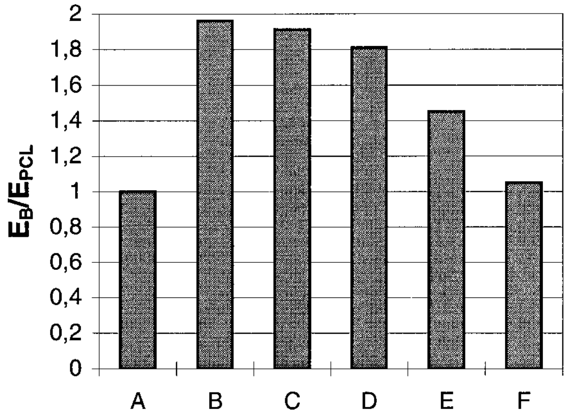


Figure 5. Normalized elastic moduli (stress−strain measurements) of blends containing 8 wt % of RRPs derived from methylhydroquinone: (A) neat PCL; (B) **2a**; (C) **1**; (D) **3a**; (E) **5b**; (F) **4b**.

on the basis of equimolar amounts of the repeating units (white columns in Figure 4B). It is obvious that the stiff polymer backbone of the RRPs is responsible for the enhancement of the elastic moduli, and thus, any fair and accurate comparison of two RRPs requires equimolar amounts of repeating units. Since the weight of the repeating unit of **2b** is by 13.5% higher than that of **2a** (Table 1), blends with identical weight percentages will show poorer results for **2b**. The observed reienforcing effect of **2b** is particularly remarkable, because this polyester does not show LC character itself.

In a third series of stress−strain measurements five RRPs all containing methylhydroquinone but different terephthalic acids were compared (Figure 5). The most conspicuous result of this series is the finding that the

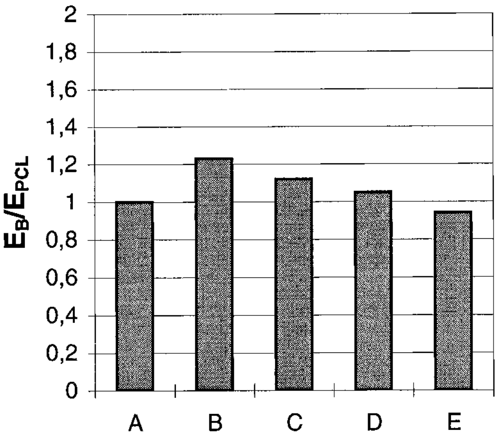


Figure 6. Normalized elastic moduli (stress–strain measurements) of blends containing 8 wt % of RRPs derived from 2,5-bis(docecyloxy)terephthalic acid: (A) neat PCL; (B) **4d**; (C) **4a**; (D) **4b**; (E) **4c**.

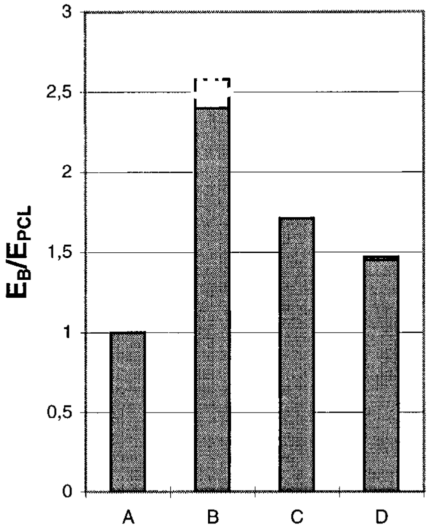


Figure 7. Normalized elastic moduli (stress–strain measurements) of blends containing 8 wt % of a copolyester: (A) neat PCL; (B) **5c**; (C) **5a**; (D) **5b**. The dotted columns represent values calculated for equimolar concentrations of repeating units relative to **5a**.

RRP derived from 2,5-bis(dodecyloxy)terephthalic acid is ineffective. This finding was confirmed by a fourth series of measurements involving all four RRPs derived from 2,5-bis(dodecyloxy)terephthalic acid (Figure 6). The polyester containing the stiff 4,4′-dihydroxybiphenyl (**4d**) is the only RRP of the series which shows a reinforcing effect clearly outside the margin of error (±10%). Therefore, these measurements demonstrate for the first time that the nature of the side chains plays a key role for the interaction between the RRPs and the matrix polymer. Obviously, the aromatic side chains are advantageous due to an electronic interaction between the aromatic π-electrons and the polar ester groups of the PCL. A further discussion of these results is presented below in connection with the microscopic observations.

Finally, the mechanical effect of the three copolyesters **5a**–**c** was compared (Figure 7). These measurements show far more clearly than those of Figure 6 that also the structure of the diphenol has an influence on the mechanical properties of the blend. Again the 4,4′-dihydroxybiphenyl yielded the highest modulus obviously due to the higher rigidity of the repeating unit.

Rheological Measurements. For neat PCL time sweeps gave constant values for $G'$and G'', and the strain sweeps remained constant up to a strain of 50%. Consequently, time–temperature superposition was valid and allowed the shifting of isotherms to a master curve at the reference temperature of 80 °C. The curves correspond to the rheological response of a polydisperse polymer with a broad transition from the plateau region to the terminal relaxation region. The latter was not finally reached because the slope of G' does not approach a factor of 2.

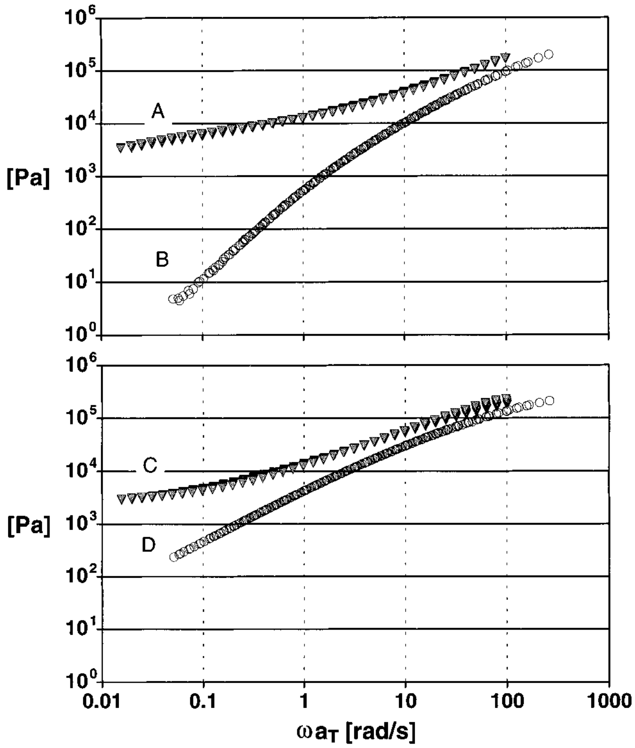


Figure 8. Rheological measurements (80 °C) of neat PCL and of a blend containing 1 wt % of **2a**: (A) storage modulus of the blend; (B) storage modulus of PCL; (C) loss modulus of the blend; (D) loss modulus of PCL.

The behavior of all blends was significantly more complex. Strain sweeps showed no plateau indicating an intrinsic nonlinear character of theses blends. Therefore, all measurements were performed at a constant strain of 10%. The time sweeps at a frequency of 1 Hz showed generally a slow increase of both G' and G'' and reached constant values after 2 h. The increase in G' was 30% of the inital value for blend containing 1% **2a** at 80 °C. The reason for that increase is not known at the moment. It may be one reason for the bad shifting behavior of the blends in comparison to the matrix polymer. It is well-known that main chain LC polymers deviate largely from the rheological behavior of isotropic polymers. It has recently been demonstrated by Schneider et al.[31] that LC polymers show a satisfactory temperature–frequency superposition only when extremely long relaxation intervals are applied (>1 day). Nevertheless the differences between the master curves of different blends are discussed here because these differences are significantly larger than the uncertainty due to the slowly changing blends. The comparable long relaxation times could even indicate that the lyotropic blends possess a distinct anisotropy or, in other words, that these blends behave like a LC phase.

The blend containing 1% **4b** shows a viscoelastic behavior (Figure 9), for which G'' is close to that of neat PCL. Yet, the storage modulus (G') deviates at lower frequencies (ωa_T < 2 rad/s) considerably from that of PCL, reaching a secondary plateau value at around 100

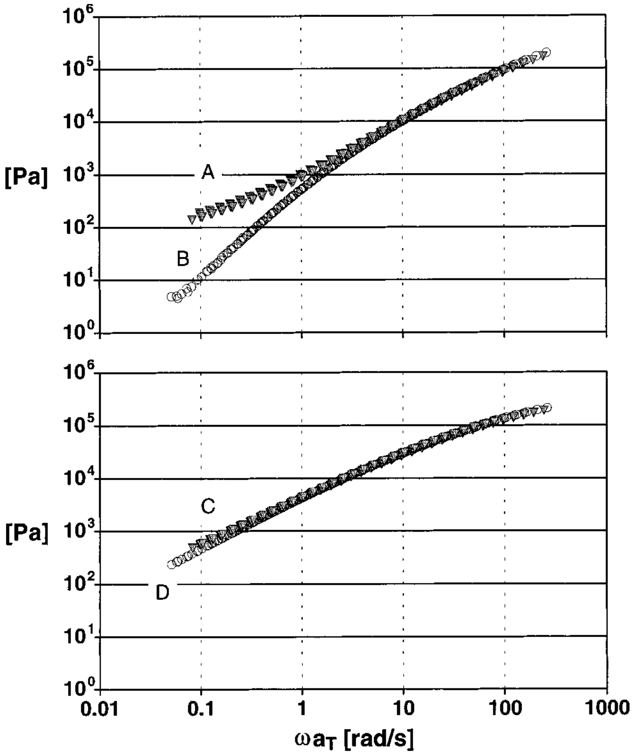


Figure 9. Rheological measurements (80 °C) of neat PCL and of a blend containing 1 wt % of **4a**: (A) storage modulus of the blend; (B) storage modulus of PCL; (C) loss modulus of the blend; (D) loss modulus of PCL.

Pa. The shift factors a_T of this blend could be fitted to a WLF plot.

The 1% **2a** blend gave very small a_T values which could not be fitted to WLF or Arrhenius equations. Nevertheless master curves were constructed, which show a large deviation from neat PCL (Figure 8). Both moduli show higher values in the plateau region and reach a broad secondary plateau below ωa_T values of 0.1. The value of G' of the secondary plateau can be extrapolated to 2000 Pa, more than 20 times higher than that of the 1% **4b** blend.

The blends containing 4% of LCP **2a** and **4b** gave results similar to the 1% blends, but the differences to the PCL are more pronounced. For the 4% **4b** blend the WLF fit of the a_T factors was still acceptable, the difference to the 1% blend consisted of slightly higher moduli over the whole frequency range and thus a higher value of the secondary plateau of 300 Pa. The increase in moduli is even greater for the 4% **2a** blend, which has a value of the secondary plateau around 20000 Pa (G').

Shearing of the samples at elevated temperatures (time sweep for 2 h at 180 °C, 1 Hz, and 10% strain) prior to the rheological investigation leads to significant changes in the rheological response of the blends. The curve of a 1% **4b** blend had a shape similar to that of neat PCL, although both moduli remained higher at low frequencies. The 1% **2a** blend showed a completely different behavior after the same treatment at 180 °C, both moduli were nearly two times higher in both time and frequency sweep at 80 °C. From these results we concluded that shear-induced morphological changes have a significant influence on the properties of these materials. The type of change or a morphological picture cannot be forwarded at this time.

Shearing of the 4% **2a** blend at 220 °C for 2 h showed a behavior similar to the **4b** blends. Obviously there is a connection between the transition temperature of the LCP (180 °C for **4b**, 220 °C for **2a**) and the breakdown of orientation and thus reinforcement in the blends. This corresponds to similar observations at the polarizing light microscope.

Without having rheooptical measurements providing information about the morphological or orientational changes causing the rheological response, the observed rheological behavior is difficult to understand. At this time we can only exclude a couple of scenarios by the following considerations.

One of these scenarios is concerned with the behavior of fully phase separated polymer blends. Usually the relative increase (in comparison to the matrix viscosity) of viscous properties of two-phase blends due to the presence of rigid inclusions is explained by the Einstein equation. That increase should be of the order of $^5/_2\,\Phi$ for the concentration considered here. For an 1% blend this model predicts an increase of the viscosity by 2.5%, a value hardly detectable in this way. In our case we did not reach the zero shear viscosity necessary for this calculation. Nevertheless, the viscosity corresponding to the lowest frequency measured is much higher than the theoretical value. Therefore it may be concluded that this model is not suitable for a description of lyotropic blends, and obviously, another morphology causes the strong changes in the rheological response.

The second scenario which merits a discussion is based on the hypothesis that the dispersed polymer (LCP) is distributed throughout the matrix like a network or a cobweb, which is characterized by a certain characteristic length L_c. In analogy to the theory of temporary networks of linear polymers we use the following equations to calculate a molecular weight of a web strand M_x and subsequently its characteristic length L_c

$$M_x = \rho RT/G'_{sp}$$

and

$$L_c = (M_x/M_0)L_0$$

In these equations ρ is the density of the dispersed polymer, R the gas constant, and T the absolute temperature at which the modulus is measured. G'_{sp} is in our case the value of the secondary plateau discussed previously. M_0 is the molecular weight of the repeat unit of the LCP (464.46 g/mol) and L_0 the all-trans length of this unit (about 1.1 nm).

This calculation yields L_c values of up to 70 μm, which can hardly be found in such a material. From this we conclude that such a morphological picture also fails. In consequence, the question for the morphological picture that explains the dramatic effects observed in dynamic mechanical measurements remains open.

Not surprisingly, the LCP, which has the strongest effect on the rheological properties, has also the most pronounced effect during mechanical testing; again LCPs with aromatic side chains were much more effective than those bearing alkyl side chains.

Optical Microscopy. The thermal properties of PCL are those of a normal semicrystalline polymer which forms an isotropic melt above its T_m. As demonstrated in a recent publication[22] dealing with blends of a rigid-rod copolyester and various matrix polymers, even blending with only 1 wt % of a RRP may suffice to generate birefringence in 15−25% of the total volume. This birefringent "phase" can be sheared and oriented above the T_m of the PCL and, thus, needs to be considered as a mobile anisotropic phase. In the present

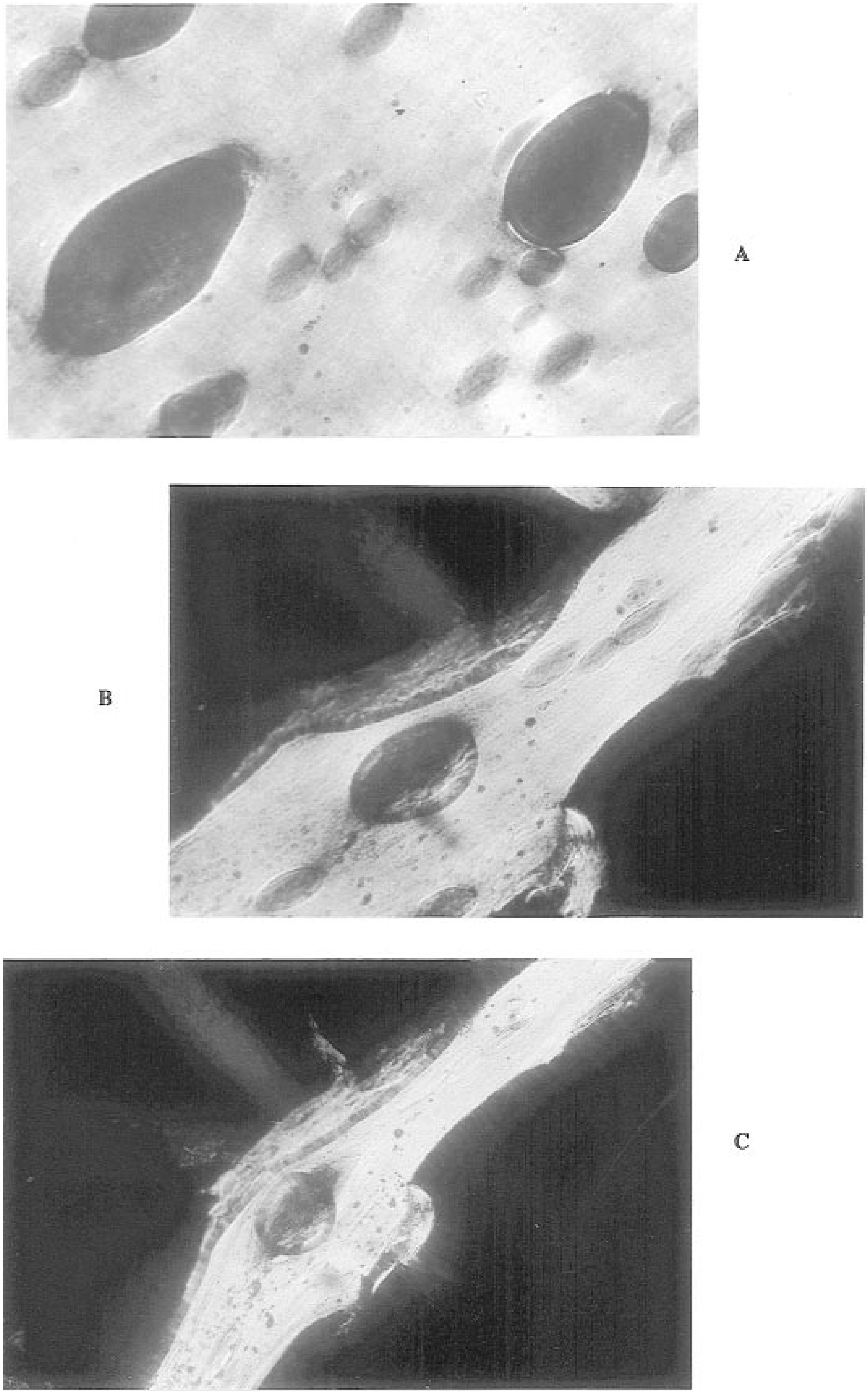


Figure 10. Pictures taken from an optical microscope with crossed polarizers (×200): (A) 4% blend of **2a** and PCL at 200 °C; (B) the same blend (and spot) after heating to 255 °C; (C) again the same blend (and spot) after heating to 280 °C.

work the photograph of Figure 10A should demonstrate that a 4% blend of **2a** and even more an 8% blend may induce birefringence in the entire volume of the blend. This birefringence is diffuse and not combined with a classical texture, such as the threaded nematic schlieren texture of the neat polyester **2a** (Figure 11). The homogeneous birefringence is stable at temperatures below 150 °C for many hours (its final dissappearance has never been observed) but slowly vanishes when the temperature approaches the T_m of the RRP (Figure 10B). The contraction of the birefringent phase intensifies above the T_m of the RRP (Figure 10C) and the schlieren texture of the neat RRP (here **2a**) may become detectable. This process was irreversible in all cases regardless, if the cooling rate was high or extremely slow (1 °C/min).

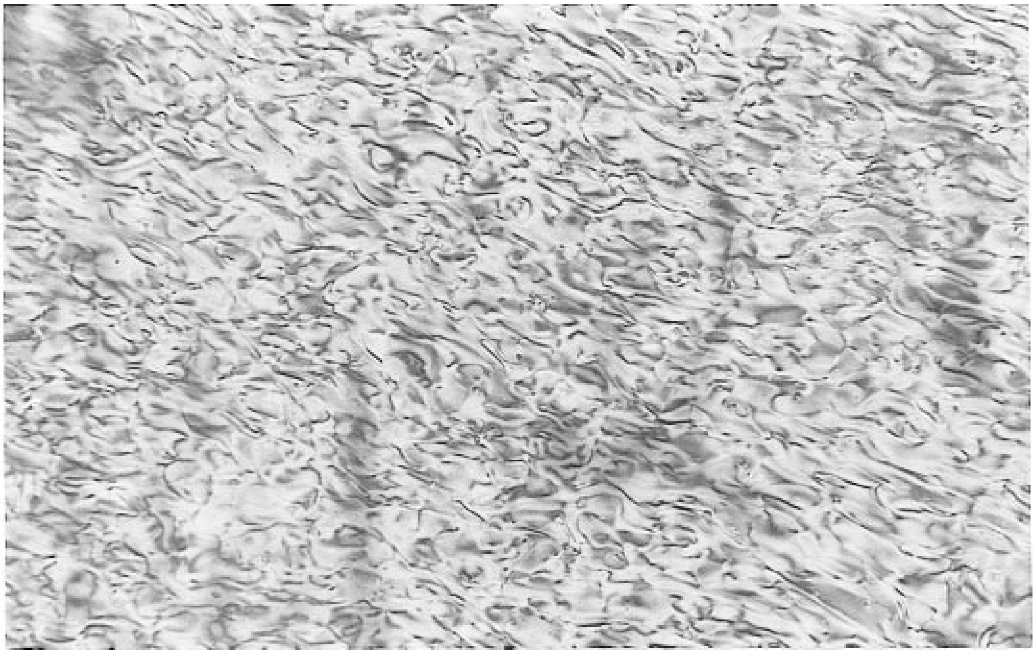


Figure 11. Schlieren texture of molten polyester **2a** at 300 °C.

These observations suggest that an initially homogeneous finely dispersed phase of RRPs in PCL undergoes an irreversible phase separation at temperatures around the T_m of the RRP. This suggestion is in principle obvious, because it is well-known from the work of Flory[12−14] and numerous experimental studies that isotropic and liquid-crystalline phases are thermodynamically not compatible and miscible, respectively. The novel aspect of the blends described in this work and previous studies[21,22] is thus the existence of a rather stable mobile birefringent phase below the T_m of the RRP but above the T_m of the matrix polymer. This property of the blends is based on the coprecipitation of both components from a cosolvent and cannot be produced by blending in an extruder or kneader. Furthermore, the formation of the birefringent phase depends on the chemical structure of the added polymer. No birefringence was, of course, detectable, when PMMA or poly(3-hydroxybenzoic acid) were added to PCL. All synthesized LCPs **1**−**5** including the RRP **2c** and **4b**, which are not liquid crystalline as a neat material, yielded a birefringent blend. Therefore, it can be concluded that optical anisotropy seems to be required for the observed mechanical properties but is not sufficient alone. Only those blends containing aromatic substituents show a significant reinforcing effect.

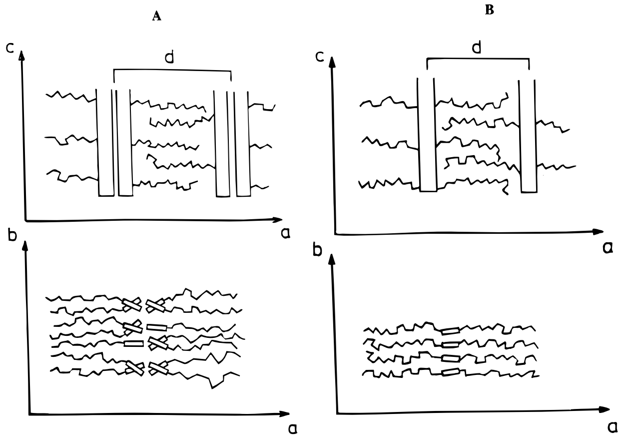


Figure 12. (A) Schematic illustration of the double stacks formed by polyester derived from monosubstituted terephthalic acids. (B) Schematic illustration of the stacks and layer structure of polyesters derived from 2,5-substituted terephthalic acids.

All the aforementioned experimental findings can be consistently interpreted by the following hypothesis. The coprecipitation of PCL and a RRP having more or less aromatic substituents yields a blend with a nearly molecular dispersion of the RRP. Small bundles or (more likely) stacks of a few RRP chains may be formed during the precipitation process. This stacks possess most likely the order known from the solid state of the neat RRPs.[35−40] They form double stacks (Figure 12A), when the terephthalic acid is monosubstituted or monostacks (Figure 12B) when the terephthalic acid is disubstituted. The individual RRP chains or the stacks of few chains are “solvated” by PCL chains which are more or less aligned parallel along the RRP chains (Figure 13A). This orientation of the PCL chains along the RRP chains induces anisotropy in the matrix surrounding the RRP chains (or stacks). Therefore, a birefringent mobile phase is created which encompasses a much larger volume than the neat RRP itself and allows shearing above the T_m of PCL (Figure 13B). The induced anisotropy of the matrix may also contribute to the mechanical reinforcement. Without these assumptions it is difficult to explain how only 1 wt % of a RRP can turn 20−25 vol % of the matrix birefringent[18,19] and how only 1 wt % can significantly improve the storage modulus (Figure 8). The electronic interactions between the aromatic side chains of the RRP and the matrix stabilize the blends below the T_m of the RRP and prevent a rapid phase separation. Furthermore, this interaction contributes to a transfer of the mechanical forces between the matrix and the RRPs. In this connection it is worth mentioning that the partially miscible system Ultem/Granlar[17−19] is based on a LC polyester containing hydroquinone units with aromatic substituents. Obviously, aromatic substituents may play the role of compatibilizers for various matrix materials.

Particularly remarkable is the formation of lyotropic blends from two isotropic components, namely, PCL and the RRP **2c**. A speculative explanation can be based on the theory of Ballauff and Flory[41] who have predicted

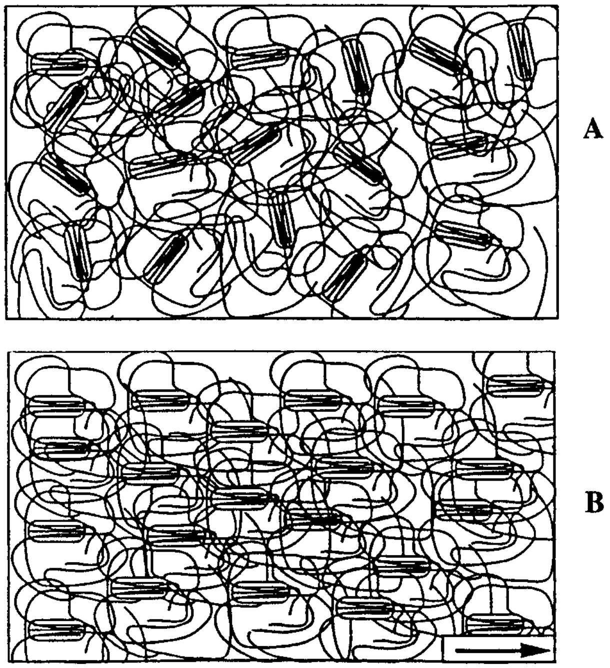


Figure 13. Schematic illustration of the molecular order in lyotropic blends of **2a** (and other RRPs) in PCL: (A) ground state after precipitation; (B) after shearing above the T_m of PCL.

that the formation of a LC phase depends strongly on the free volume of a neat LCP. Obviously the melt of **2c** contains too much free volume above the T_g. The intensive "solvation" by more or less parallel aligned PCL chains will improve the stiffness of this aggregate and reduce its free volume so that it obeys again the requirements of a nematic order.

Conclusion

The coprecipitation of PCL and rigid-rod polyesters derived from substituted terephthalic acid (and possibly hydroquinones) yields blends which may possess a lyotropic character. These blends obviously contain an extremely fine dispersion of the RRPs most likely in the form of individual chains and stacks or bundles of a few chains. The RRP chains are solvated by a more or less parallel alignment of PCL segments supported by a strong interaction between the PCL and the aromatic substituents of the RRP. This special "solvation" enhances the stiffness of the RRP chain and induces in turn anisotropy in the matrix directly surrounding and solvating the RRPs. The consequences are the formation of a mobile birefringent phase and an extraordinary mechanical reinforcement, when only 1−4 wt % of a suitable RRP is present. After phase separation at temperatures above the T_m of the RRP, the anisotropic properties vanish irreversibly. These properties, which are different from those of all classical blends, justify the label "lyotropic blends".

Finally three characteristic differences between a normal lyotropic phase and the lyotropic blends of the present work should be emphasized. Firstly, a normal lyotropic phase is a thermodynamically stable system, whereas the lyotropic blends are a kinetically stabilized system of two thermodynamically incompatible components. Secondly, a lyotropic blend may be formed from two isotropic components and does not need a true liquid-crystalline polymer. Thirdly, in the case of lyotropic blends the dispersed RRP induces anisotropy in the surrounding matrix.

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