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Polymer Liquid Crystals. Contribution of the Links between Mesogenic Units and Flexible Spacers to the Structure–Properties Relationship in Poly(ether ester) Liquid Crystals

Zbigniew Jedliński,* Jan Franek, and Antoni Kulczycki

Institute of Polymer Chemistry, Polish Academy of Sciences, ul. M. Curie-Skłodowskiej 34, 41-800 Zabrze, Poland

Augusto Sirigu and Cosimo Carfagna

Dipartimento di Chimica, Universita di Napoli, Via Mezzocannone 1, 80 134 Napoli, Italy.

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ABSTRACT: The effect of ether and ester bonds linking an aromatic mesogenic unit and a flexible spacer in poly(ether ester) liquid crystals is presented. Two groups of polymers, each of them possessing the same aromatic ester mesogen and the same 8-membered oligooxyethylene spacer, but different linkages between mesogen and spacer (ester and ether bond), have been studied by DSC, polarizing microscopy, X-ray, and IR spectroscopy. The structure analysis reveals the formation of the smectic phase when the spacer is attached to a rigid mesogenic unit by an ester bond, whereas in the case of ether bond the nematic phase can be observed. IR spectra of polymers in the solid, liquid-crystalline, and isotropic phases suggest the conformational changes in the polymer chain during the transition to mesomorphic state. The formation of a smectic phase is accompanied by an increase of the number of gauche conformers. The lack of essential conformational changes in the case of nematic polymers with ether bridges can be explained by a low-energy barrier to rotation characteristic of ether bonds.

Introduction

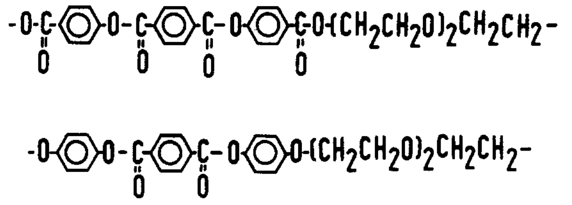
Great attention has been paid to the studies on the structure–properties relationship in liquid-crystalline main-chain polyesters having linear flexible spacers.[1-11] Especially the influence of composition, structure of a mesogen, and type and length of a spacer on the polymer properties has been extensively studied.

The contribution of the mesogen, especially its polarity, rigidity, and geometry to polymer properties, has been investigated.

The correlation between the geometry of a mesogen and the melting point of a polymer is simple: the longer the aromatic unit, the higher the melting point.[2] The decrease of the length-to-diameter ratio in the case of substituted mesogenic units leads to the reduction of transition temperatures.[3,4] Rigidity and planarity of the mesogen have significant effects on the clearing points, e.g., polymers that have an aromatic ester triad as the mesogen melt and clear at lower temperatures than the polymers with shorter but more rigid terphenyl groups.[6,7]

As far as the nature of the spacer is concerned, the following factors are of significant importance: flexibility and length of a spacer and even–odd as well as substitution effects.[8] There is some information about the contribution of linkages between the rigid mesogen and the flexible spacer to the properties of main-chain thermotropic polyesters. Krigbaum et al.[11,12] studied the influence of the ester bonds linking mesogenic groups and aliphatic spacers in the polymers synthesized from 4,4′-dibenzoic acid and aliphatic glycols and 4,4′-dihydroxydiphenyl and aliphatic diacids. Lenz et al.[8] reported recently on the polymers having hydroquinone–bis(benzoyl) and terephthalic–bis(phenylene) (ester triad type) mesogenic units and decamethylene spacers, possessing ether or ester links between the mesogen and the spacer. For those polymers, some differences in melting and clearing temperatures and also the different formation ability of the smectic phase have been observed. However, no detailed explanation has been given.

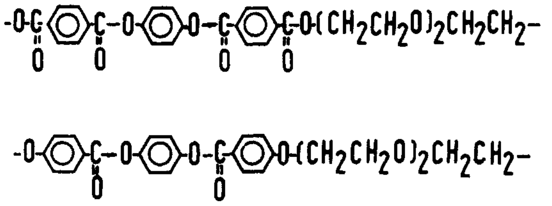
Scheme I
Structure of Polymers with the Terephthalic Acid Residue as the Central Unit of the Mesogen



Ia

Ib

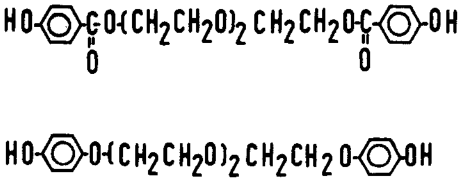
Scheme II
Structure of Polymers with the Hydroquinone Residue as the Central Unit of the Mesogen



IIa

IIb

Scheme III
Structure of Reactive Oligomeric Diols



IIIa

IIIb

In our previous paper,[10] some indications on the role of linkages connecting mesogen and spacer moieties have been provided. In the present work, this problem has been studied more thoroughly. As model polymers for this study we have chosen two groups of poly(ether esters). Within each pair of polymers (I and II), there is a common mesogenic unit; the oligoether spacer is the same in all four polymers. The general formulae of polymers studied are shown in the Schemes I and II.

The mesogenic units of polymers presented in Schemes I and II differ from each other with respect to their central units which may be terephthalic acid residue (series Ia, b) or hydroquinone residue (series IIa, b). All polymers contain the same 8-membered oligooxyethylene (CH$_2$C-

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* To whom correspondence should be addressed.

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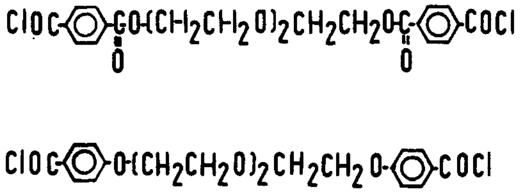
Table I
Physical Properties of Polymers

polymer	$\eta_{\text{inh.}}$[a]	melting temp, °C[b]	clearing temp, °C[b]	mesophase range	melting enthalpy, J/g	clearing enthalpy, J/g	clearing entropy, J/(g K)	mesophase
Ia	0.24	209 (202)	298 (280)	89	44.4	11.9	0.022	smectic
Ib	0.52	233 (223)	303 (295)	70	38.3	2.6	0.0046	nematic
IIa	0.34	219 (209)	273 (246)	54	31.2	1.4	0.0025	smectic
IIb	0.32	229 (208)	296 (286)	67	32.0	3.6	0.0063	nematic

[a] Measured on 0.4 g/dL solutions in a mixture of *p*-chlorophenol–tetrachloroethane (2:1 w/w) at 25 °C. [b] By DSC determined from the maximum of the given transition endotherm; in parentheses, onset slope temperatures.

Scheme IV
Structure of Reactive Oligomeric Diacid Chlorides



IVa

IVb

$H_2OCH_2CH_2OCH_2CH_2$) flexible spacer. The linkages between flexible spacer and mesogenic unit are either ester (Ia, IIa) or ether (Ib, IIb) bonds. The polymers were synthesized by polycondensation of reactive oligomeric diols (IIIa, b) with terephthaloyl chloride and oligomeric diacid chlorides (IVa, b) with hydroquinone (Schemes III and IV).

Some novel phenomena concerning the structure–properties relationship in main-chain thermotropic poly(ether esters) having oligoether moieties as flexible spacers will be discussed.

Experimental Section

Polymer Preparation. All polymers were obtained by a low-temperature polycondensation procedure, as described previously.[10,13]

Polymer Characterization. Inherent viscosities were determined at 25 °C using 0.4 g/dL solutions of polymers in a mixture of *p*-chlorophenol/tetrachloroethane (2:1).

Texture studies were performed by using the Boethius polarizing microscope equipped with a hot stage.

Differential scanning calorimetry data were recorded by using a Du Pont 1090B instrument at scanning rates of 10 and 30 deg/min; indium was used for calibration.

IR spectra were taken by using a Perkin-Elmer 580B spectrometer. All measurements were performed in the range 250–4000 cm^{-1} at 25 °C and at higher temperatures specified in the text.

X-ray diffraction patterns were recorded by a photographic method using a flat-film camera. For high-temperature measurements, the polymer sample was kept under nitrogen atmosphere inside a sealed glass capillary by utilizing a temperature-regulated microfurnace. Temperatures were defined within ±2K. . Cu Kα radiation was utilized.

Results and Discussion

DSC and Polarizing Microscopy Observations. Thermodynamical data are listed in Table I. The DSC thermograms of all polymers (Figures 1 and 2) show, apart from the broad and complex melting endotherms as frequently observed with partially crystalline thermotropic main-chain polymers, an additional endotherm which could be correlated to the transition from the liquid-crystalline phase to the isotropic melt.

Comparing the isotropization transitions of polymers Ia and Ib, which only differ by the chemical group binding the flexible spacer to the mesogenic unit, strong differences in the clearing enthalpy are found. The clearing enthalpy for polymer Ia (with ester linkage) amounts to 11.9 J/g, while for polymer Ib (with ether linkage) it is only 2.6 J/g.

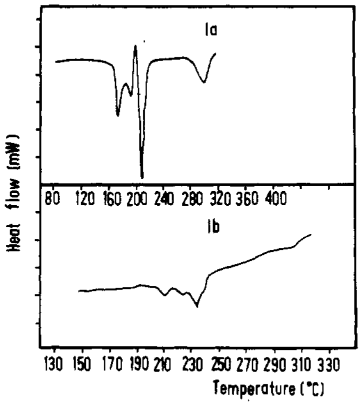


Figure 1. DSC curves for Ia and Ib polymers with the terephthalic acid residue as the central part of the mesogen.

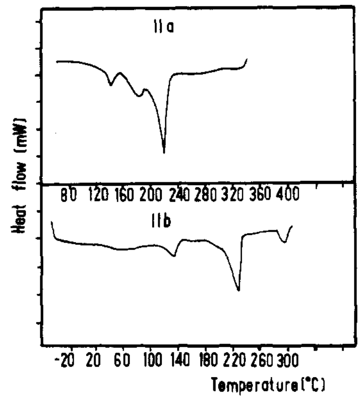


Figure 2. DSC curves for IIa and IIb polymers with the hydroquinone residue as the central part of the mesogen.

The microscopic observations in polarized light confirm that polymer Ia forms a smectic phase (A or C), while polymer Ib melts to a nematic phase.

Polymers of group II exhibit similar behavior when studied by using a polarizing microscope. Polymer IIa (ester linkage) exhibits at melting fan shape texture characteristic of the smectic mesomorphism, and microscopic images of polymer IIb (ether linkge) were typical of the nematic phase. However, for polymer IIa, a biphasic structure occurs in a large temperature region above the melting endotherm. Isotropic areas are observed in the microscopic picture, and the extension of the anisotropic regions is rather small. The biphasic character of the melt is coherent with the small clearing enthalpy measured for polymer IIa. It amounts to 1.4 J/g, notwithstanding the smectic nature of the mesophase.

Summarizing the results of the DSC and microscopic measurements, it may be stated that polymers with different linkages between mesogen and spacer (system a–b) coherently possess different abilities in the formation of a mesophase. Polymers Ia and IIa with ester linkages are smectogenic, while polymers Ib and IIb with ether linkages form only a nematic liquid-crystalline phase.

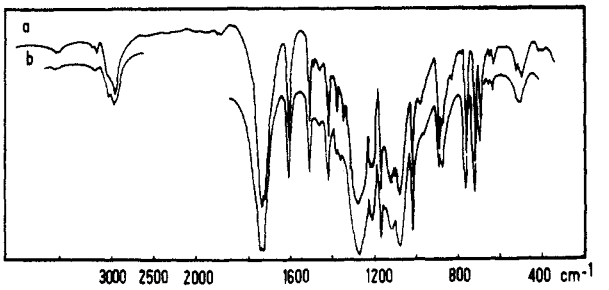


Figure 3. IR spectra for Ia polymer: (a) temperature, 25 °C (solid phase), (b) temperature, 250 °C (liquid-crystalline phase).

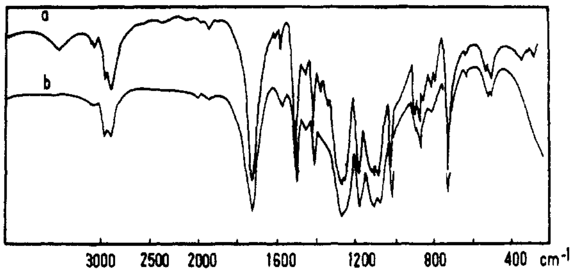


Figure 4. IR spectra for IIa polymer: (a) temperature, 25 °C (solid phase), (b) temperature 270 °C (smectic + isotropic biphasic system).

Table II
Absorption Intensity Changes in the IR spectra for (a) Ia and (b) IIa Polymers[a]

wavenumbers, cm^{-1}			
solid phase at 25 °C	mesophase at 250 °C	isotropic phase at 300 °C	interpretation
	Section a		
520	520 ↓	–	
784	–	–	
830	830 ↓↓	–	t CH_2 rock.
860	860	860	g CH_2 rock.
875	875 ↑	875 ↑	g CH_2 rock.
890	890 ↓	890 ↓↓	t CH_2 rock.
980	–	–	t CO stretch. asym.
1020	1020 ↑	1020 ↑↑	g CO stretch. asym.
1100	1100 ↓↓	–	t CO stretch. sym.
1114, 1120	1110	1105 ↑	g CO stretch. sym.
–	1145	–	g CH_2 twist.
1310	1310 ↓↓	1310 ↓↓	
1340	1340 ↓↓	1340 ↓↓	t CH_2 wag.
1360	1360	1360	g CH_2 wag.
1380	1380 ↓	1370	
1455	1455	1455 ↑	g CH_2 bend.
1490	1480 ↓	–	t CH_2 bend.
2850	–	–	t CH_2 stretch.
2875	2875 ↑	2878 ↑	g CH_2 stretch.
2900	2908 ↓	2908 ↓↓	t CH_2 stretch.
2960	2960 ↑	2960 ↑	g CH_2 stretch.

wavenumbers, cm^{-1}		
solid phase at 25 °C	biphasic system at 270 °C (smect. + isotrop.)	interpretation
	Section b	
500	500 ↓↓	
790	786 ↓	
804	804 ↓↓	t CH_2 rock.
820	820	
850	850	g CH_2 rock. (overlap with 875)
875	875 ↑	g CH_2 rock.
890	890 ↓	t CH_2 rock.
982	–	t CO stretch. asym.
1020	1020 ↑	g CO stretch. asym.
1100	1100 ↑	g CO stretch. sym.
1120	1120 ↓	t CO stretch. sym.
1335	1335 ↓↓	t CH_2 wag.
1350	1350 ↑	g CH_2 wag.
1370	1370 ↓↓	
1450	1450 ↑	g CH_2 bend.
1485	1485 ↓	t CH_2 bend.
1610	1610 ↓↓	
2850	2850 ↓	t CH_2 stretch.
2870	2870 ↑	g CH_2 stretch.
2900	2900 ↓	t CH_2 stretch.
2970	2970 ↑	g CH_2 stretch.

[a] g = peak characteristic for gauche conformation, t = peak characteristic for trans conformation, ↑ = increase of absorption intensity, ↓ = reduction of absorption intensity, – = disappearance of a given absorption band.

X-ray Analysis. The X-ray diffraction patterns recorded for all polymers at room temperature shows their semicrystalline structure. For two of them, some modifications of the spectra recorded at high temperature (at 195 °C for IIa; at 183 °C for IIb), but below melting, indicate the occurrence of solid-state polymorphism. However, this point will not be discussed in any detail since it is not central to the purpose of the present work.

The X-ray diffraction patterns recorded at temperatures within the range of stability of the mesophase give significant indications about the nature of the mesophase in coherence with the optical observations.

A diffuse halo centered around sin θ/λ = 0.105 (5) Å^{-1} and a short Bragg diffraction ring corresponding to a 28.0-Å lattice distance are the relevant features for polymer Ia at 245 °C. This is coherent with the smectic nature of the mesophase.

The X-ray diffraction patterns as well as the observation in polarized light of polymer Ia do not indicate the transition from the smectic phase to the nematic phase at a temperature of 203 °C as claimed by Lenz et al.[9] This discrepancy may be due to the different synthetic method used and consequently the different end groups in both polymers (Lenz's and ours).

A diffuse halo around sin θ/λ = 0.105 (5) Å^{-1} is present in the diffraction pattern of polymer IIa at 240 °C. A very faint diffraction ring at 28-Å lattice distance is also observable. Attempts to record more intense spectra were frustrated by some chemical damage to the sample as a consequence of the long exposure time at high temperature. Nonetheless, the X-ray diffraction data are compatible with the optical observation of a biphasic (smectic + isotropic) system. The comparatively low intensity of the 28-Å diffraction ring is also coherent with a reduced fraction of the sample being in the smectic phase.

Polymers Ib at 254 °C and IIb at 250 °C are characterized by a diffraction pattern whose essential feature is a diffuse halo centered around sin θ/λ = 0.105 (5) Å^{-1}. This is coherent with a nematic structure of the liquid.

IR Measurements. The IR spectra of polymers Ia and IIa were measured at 25, 250, and 300 °C and at 25 and 270 °C, respectively. The spectra of solid phase and liquid mesomorphic phase are presented in Figure 3 and 4. At the transition from the solid through the liquid crystalline phase to the isotropic phase, modifications in the IR spectra were observed. In the solid phase, the maxima are more intensive in comparison with those in liquid-crystalline and isotropic states.

After transition from the solid phase to the liquid-crystalline phase, the disappearance of certain maxima and simultaneous increase of intensity of other maxima were observed. Differences between IR spectra in the liquid-crystalline and isotropic states were very small.

The characteristic maxima and changes in the intensity of absorption bands for polymers Ia and IIa are summarized in Table II.

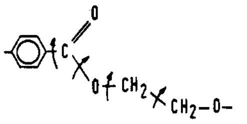


Figure 5. Conformational transitions in poly(ethylene terephthalate).

Changes in the degree of ordering of macromolecules are often accompanied by changes of chain conformation; hence, the differences in the IR spectra of the solid and liquid-crystalline phases could be ascribed to this fact.[14] The possible conformational transitions have been taken into consideration (Figure 5) using poly(ethylene terephthalate) chains as the model. According to the literature data,[15-19] it could be assumed that changes in the spectra of polymers Ia and IIa were due to the macromolecular fragments reorientation and namely the transition from trans to gauche (T–G) conformation of OCH_2CH_2O groups (Figure 5). The characteristic maxima for trans and gauche forms are given in Table II. The number of gauche conformers increases at the transition from solid state to liquid-crystalline mesophase, along with degree of freedom of the mesogenic units which enables them to properly align and form the smectic layers.

High intermolecular attractions, e.g., dipole–dipole interactions and dispersion forces in the polymers having ester linkages (Ia and IIa), obviously favor the formation of smectic arrangement, which is difficult for polymers with mesogens linked by flexible ether bonds (Ib and IIb), exhibiting low van der Waals interactions.

For Ib and IIb polymers, no essential changes in IR spectra between 25 and 270 °C characteristic for conformational changes were observed. This result suggests that in the case with ether bridges gauche conformations occur in the solid state as well as in the liquid-crystalline state and the transition to liquid-crystalline state does not result in large conformational T–G changes in the polymer chain. This observation is probably due to the low rotation energy due to weak van der Waals interactions of ether bonds; hence, the conformational changes are reversible and proceed at low energy.

In the specific case of polymers Ib and IIb, a gauche conformation for the OCH_2CH_2O group contiguous to mesogenic segments does not severely alter the possibility for the polymer chain to preserve an overall elongated conformation.

Conclusions

In the present paper, attention is called to the effect of the type of bonds connecting a mesogenic group with a flexible spacer on the liquid-crystalline properties in poly(ether esters). Suitable polymer models having the same mesogen structure and the same spacer but connected either by ether bonds (Series b) or by ester bonds (Series a) were selected for these studies. As a result of DSC, X-ray, and microscopic measurements it was found that polymers with ester bridges (Ia and IIa) tend to form a smectic phase, whereas in the polymers with ether bridges (Ib and IIB) the nematic phase was preferred. IR measurements of the polymers studied in the solid, liquid-crystalline, and isotropic phases suggested that in the case of polymers with ester linkages the transition to mesophase is accompanied by the increase of gauche conformations in the polymer chains (Ia and IIa). In the case of polymers with ether bridges; no essential conformational changes were observed during the transition to mesophase. This phenomenon could be explained by a low-energy barrier to rotation characteristic for the ether bonds, the conformational changes being reversible and proceeding at much lower energy then in the case of more rigid polymers with ester linkages.

The above conclusions based on IR measurements are in good agreement with theoretical calculations of Yoon and Bruckner,[20] as well as with considerations of other authors.[7,21] Based on their considerations and our experiments, it may be stated that the type of linkage between the mesogenic group and the flexible spacer is a very essential structural parameter influencing chain conformations and, consequently, the type and behavior of the mesophase formed by a polymer.

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Registry No. Ia (copolymer), 105709-24-8; Ia (SRU), 84329-77-1; Ib (copolymer), 105709-26-0; Ib (SRU), 105689-43-8; IIa (copolymer), 105709-30-6; IIa (SRU), 105689-47-2; IIb (copolymer), 105744-18-1; IIb (SRU), 105689-48-3.

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