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Chiral liquid crystal polymers. VIII Thermotropic poly(ester-β-sulphide)s based on variously spaced twin *p*-oxybenzoate diads

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Chiral liquid crystal polymers

VIII†. Thermotropic poly(ester-β-sulphide)s based on variously spaced twin p-oxybenzoate diads

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The synthesis and characterization both in solution (chiroptical properties) and in bulk (thermotropic properties) of a new series of structurally defined chiral liquid-crystalline poly(ester-β-sulphide)s are described. The functional polyesters are constituted by repeating units consisting of two p-oxybenzoate diads interconnected by a linear segment of m methylene groups (m = 6–10, 12), and strictly sequenced by the chiral (R)-3-methyl-1,6-hexanedithiyl spacer. The thermotropic behaviour deviates from the regular profiles generally established in homologous series of mesomorphic polymers and results in peculiar alternations of the liquid-crystalline properties, enantiotropism being exhibited by only a few, mainly odd-numbered, homologues of the series.

1. Introduction

The thermotropic mesomorphism of main chain liquid-crystalline polymers is now well established. The majority of such materials exhibit nematic phases, although there are a few examples of smectic and cholesteric polymers. Semiflexible cholesteric polyesters have been prepared almost exclusively from (R)-3-methyladipic acid, as the chiral precursor [1–4]. We have described several chiral thermotropic polyesters and copolyesters derived from optically active propylene glycol ethers (monomer, dimer and trimer) [5] and glycerol ethers [6], in which the cholesteric helical array was affected by temperature in an unusual way [7]. Indeed, due to the unique properties of such twisted phases, cholesteric polymers appear of particular interest for applications in thermochromic displays, reflective filters and polarizers, while chiral twisted smectics might serve as ferroelectric materials in electro-optic devices with memory properties.

Along this line, and following our interest in establishing structure–property correlations in functional liquid-crystalline polymers, we have prepared a series of chiral poly(ester-β-sulphide)s $C_mS_6^*$ containing two bis(p-oxybenzoate) units connected through alkylene segments of different length (C_m) and regularly sequenced by a sulphur-containing chiral segment, (S_6^*). We have studied their thermotropic behaviour and chiroptical properties in dilute solution.

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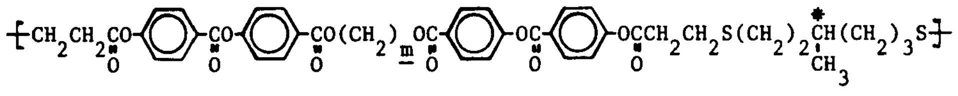

m = 6,7,8,9,10,12

The bis(*p*-oxybenzoate) group is a mesogenic core scarcely used in segmented polyesters [8], even though it was previously obtained in structurally disordered *p*-oxybenzoate modified poly(terephthalate)s [9, 10] and employed in oligomer model compounds [11]. (*R*)-3-methyl-1,6-hexanedithiol, derived from the well-known carboxylic diacid precursor, is a new versatile chiral component for optically active thermotropic polymers. Within the homologous series of poly(esters-β-sulphide)s investigated, the incidence and persistence of the mesophases depend in an unusual manner on the polymer structure and further demonstrate the necessity of taking into account the fine structural details in the design of liquid-crystalline polymers with predictable thermal responses.

2. Results and discussion

The polymer samples were prepared from different α,ω-alkylene bis[4-(4-acryloyloxybenzoyloxy)benzoate]s (m = 6–10, 12) and (*R*)-3-methyl-1,6-hexanedithiol by a polymerization reaction involving a base-catalyzed Michael-type nucleophilic addition of the bisthiol to the corresponding bisacrylic ester. This reaction is very general [12] and has been used by us to produce functional polyesters comprising a variety of mesogenic units [8, 13, 14].

Table 1. Physicochemical characteristics of chiral poly(ester-β-sulphide)s $C_mS_6^*$ containing two bis(*p*-oxybenzoate) units.

						C.D.	
Sample	m	$[\eta]$(*a*)/dl/g	$\bar{M}_w$(*b*)	MWD(*b*)	$[\Phi]_D^{25}$(*c*)/deg	$\Delta\varepsilon$(*d*)/cm^{-1}M^{-1}	λ/nm
$C_6S_6^*$	6	0·35	14000	1·35	−26·1	+0·78	255
$C_7S_6^*$	7	0·24	9500	1·32	−15·9	+0·60	259
$C_8S_6^*$	8	0·27	11500	1·34	−18·0	+0·72	259
$C_9S_6^*$	9	0·26	13500	1·38	−15·5	+0·68	256
$C_{10}S_6^*$	10	0·28	13500	1·35	−13·0	+0·70	255
$C_{12}S_6^*$	12	0·21	9000	1·20	−16·2	+0·55	257

(*a*) Intrinsic viscosity, in chloroform at 30°C.
(*b*) By gel permeation chromatography.
(*c*) Molar optical rotation, in chloroform.
(*d*) Maximum molar dichroic absorption coefficient, referred to one repeating unit.

In table 1 we report some physicochemical characteristics of the prepared polymers. The poly(ester-β-sulphide)s are characterized by relatively high molecular weights $\bar{M}_w$ = 9000–14000 ($[\eta]$ = 0·21–0·35 dl/g in chloroform at 30°C) and narrow molecular weight distributions of between 1·20 to 1·38. All the polymers were optically active and the molar optical rotation was consistently negative and little affected by the number, m, of methylene groups within the flexible spacer. All the samples were characterized by ultraviolet (U.V.) and circular dichroism (C.D.) absorption measurements in dilute dioxane solution. A typical representation of the U.V. and C.D.

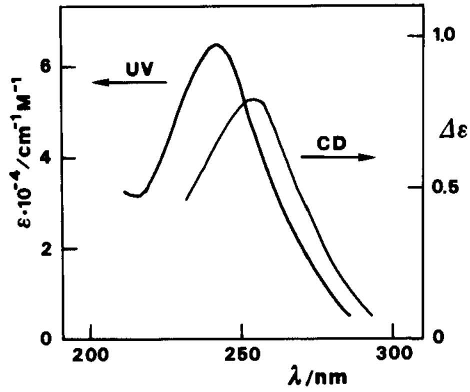

Figure 1. Ultraviolet (U.V.) and circular dichroism (C.D.) spectra in dioxane solution of poly(ester-β-sulphide) $C_6S_6^*$ (m = 6).

profiles is given in figure 1. The C.D. spectra showed rather intense absorption bands with a positive maximum at 255–260 nm which corresponds to the $\pi \rightarrow \pi^*$ electronic transitions of the complex aromatic chromophores [15, 16] (ε_{max} = 6·0–6·4 × 10^4 cm^{-1} l (mol r.u.)$^{-1}$; λ_{max} = 240–243 nm). The maximum C.D. absorption, whose intensity is insensitive to the structure of the polymer repeating unit ($\Delta\varepsilon$ = 0·55–0·78 cm^{-1} l (mol r.u.)$^{-1}$), was 10–15 nm shifted towards longer wavelengths than the corresponding U.V. peak. The observed behaviour suggests the presence of intramolecular electronic interactions among different mesogens, somewhat similar to those already detected in semiflexible liquid-crystalline polyesters based on a more extended aromatic triad and shorter chiral diol residues [7, 17]. These results indicate that the aromatic units experience a chirally homogeneous environment whose effects apparently propagate in the same manner and are independent of the length of the alkylene spacers.

All of the polymers were investigated for their liquid-crystalline behaviour by differential scanning calorimetry (D.S.C.) and polarizing microscopy. A detailed X-ray diffraction analysis will be described elsewhere [18]. Based on these studies the smectic phases encountered were found to be disordered (A or C), but unequivocal assignments are not yet possible [18]. The values of the melting temperature (T_m), isotropization temperature (T_i), cholesteric-to-smectic temperature (T_{ChS}) and crystallization temperature (T_c) together with the relevant enthalpies were determined on samples annealed by cooling (10 K/min) from the isotropic melt (cf. table 2). The liquid-crystalline behaviour of the poly(ester-β-sulphide)s prepared, show dramatic differences within the series, which could not have been anticipated by simple consideration of the polymer structure (cf. figure 2). For the sake of completeness and clarity the thermal behaviour of the polymer samples is now described separately.

2.1. *Polymer $C_6S_6^*$*

The poly(ester-β-sulphide) with six methylene units in the central alkylene segment (m = 6) showed on heating a cholesteric phase with a thermal range of 31 K (ΔS_i = 16·3 J (mol r.u.)$^{-1}$ K^{-1}). On cooling, the crystallization process was highly supercooled and the mesophasic range was enlarged to 86 K. Such a degree of supercooling allowed us to observe the onset of a monotropic smectic phase at 370 K. The cholesteric phase was characterized by a homogeneous planar texture with

Table 2. Thermal and liquid-crystalline properties of chiral poly(ester-*β*-sulphide)s $C_mS_6^*$ containing two bis(*p*-oxybenzoate) units (*a*).

Sample	[*η*]/dl/g	T_m/K	ΔH_m (*b*)/kJ mol^{-1}	T_i/K	ΔH_i (*b*)/kJ mol^{-1}	ΔS_i (*b*)/J mol^{-1} K^{-1}	T_c/K
$C_6S_6^*$	0·35	390 (*c*)	12·1	421	6·7	16·3	335
$C_7S_6^*$	0·24	363	nd (*d*)	371	5·4	15·1	< 300
$C_8S_6^*$	0·27	399	24·3	(396)	(8·4)	(21·3)	370
$C_9S_6^*$	0·26	342 (*e*)	4·6	408	~0·2	~0·4	330
$C_{10}S_6^*$	0·28	404	32·2	(396)	(9·2)	(23·4)	385
$C_{12}S_6^*$	0·21	399	49·8	(380)	nd (*f*)	nd (*f*)	379

(*a*) By D.S.C.; monotropic transitions in parentheses.
(*b*) Referred to one repeating unit (r.u.).
(*c*) Cholesteric-to-smectic monotropic transition at 370 K, $\Delta H_{ChS} < 0{\cdot}2$ kJ (mol r.u.)$^{-1}$.
(*d*) No melting endotherm.
(*e*) Smectic-to-cholesteric transition at 376 K, $\Delta H_{SCh} = 5{\cdot}0$ kJ (mol r.u.)$^{-1}$.
(*f*) Obscured by crystallization.

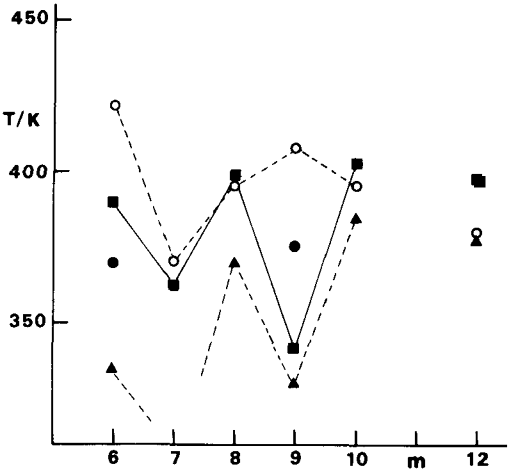

Figure 2. Variations of transition temperatures in poly(ester-β-sulphide)s $C_mS_6^*$ as a function of the methylene number *m* in the alkylene segment: (■) melting, (○) isotropization, (●) cholesteric-to-smectic, (▲) crystallization.

practically no defects; this changed to a smectic phase with a fine schlieren texture. The relevant entropy was very low ($\Delta S_{\mathrm{ChS}} < 0{\cdot}5\,\mathrm{J\,(mol\ r.u.)^{-1}\,K^{-1}}$) and the phase transition seemed to be second order in character. Second order smectic-to-nematic transitions have been predicted for low molar mass mesogens [19] and found experimentally in some cases [20, 21]. Evidence for this was also provided by the examination of an oligomer $C_6S_6^*$ sample ($[\eta] = 0{\cdot}14\,\mathrm{dl/g}$). In this case, the isotropization temperature was somewhat depressed ($T_i = 410\,\mathrm{K}$; $\Delta S_i = 9{\cdot}6\,\mathrm{J\,(mol\ r.u.)^{-1}\,K^{-1}}$) and the mesophasic range was slightly narrower (24 K). The monotropic cholesteric-to-smectic transition was located at 368 K by observation of a sharp transformation from a focal–conic texture into a schlieren pattern. Only a weak variation of heat capacity was detected by D.S.C. in the same temperature region. These results also suggest that in this class of poly(ester-β-sulphide)s increase of molecular weight causes cooperative effects to create mesophases characterized by progressively increasing thermal stability and degree of order up to a saturation value [22]. In structurally analogous poly(ester-β-sulphide) samples a critical value of $[\eta] = 0{\cdot}15$–$0{\cdot}20\,\mathrm{dl/g}$ has been evaluated [23], and this should guarantee that in the present polymer series the liquid-crystalline properties are no longer appreciably affected by the molecular weight.

2.2. *Polymer $C_7S_6^*$*

This polymer ($m = 7$) showed one enantiotropic cholesteric phase of very low thermal persistence (8 K) and a relatively narrow biphasic gap (14 K). The degree of supercooling of the isotropization transition was limited to 7 K, while no crystallization exotherm was observed on cooling and, consequently, the mesophase remained frozen-in down to room temperature with a blurred schlieren texture.

2.3. *Polymer $C_9S_6^*$*

Poly(ester-β-sulphide) $C_9S_6^*$ ($m = 9$) exhibited two enantiotropic phases of almost equal extension: 34 K for the smectic phase and 32 K for the cholesteric phase

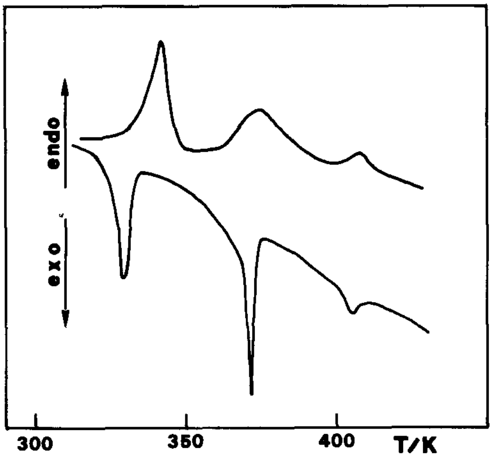

Figure 3. D.S.C. heating and cooling curves (10 K/min) for poly(ester-β-sulphide) $C_9S_6^*$ (m = 9), after first cooling from the isotropic melt.

on heating. Both isotropic to cholesteric and cholesteric-to-smectic transitions underwent practically no supercooling (3 and 4 K respectively), while the biphasic region was 8 K for the former and 19 K for the latter transformation (cf. figure 3). The isotropization entropy (ΔS_i = 0·4 J (mol r.u.)$^{-1}$K^{-1}) was considerably lower than for the other homologues, probably because of the occurrence of the intermediate smectic phase with a fairly high entropy of transition (ΔS_{ChS} = 13·4 J (mol r.u.)$^{-1}$K^{-1}). This polymer offers one clear example of liquid crystal polymorphism in thermotropic polymers.

2.4. *Polymers* $C_8S_6^*$ *and* $C_{10}S_6^*$

The poly(ester-β-sulphide)s with m = 8 and m = 10 did not show any distinct mesophase on heating. However, while the latter melted directly to an isotropic liquid, the former displayed liquid-crystalline regions coexisting with the isotropic melt in a range of about 20 K above the quoted melting temperature. On cooling, both samples exhibited a monotropic phase between the isotropization and crystallization temperatures. The liquid crystal range was 26 K for the former homologue, and 11 K for the latter. This behaviour is in contrast with that observed for the corresponding diacrylate precursors that showed enantiotropic nematic phases of high thermal stability with T_i = 436 K (m = 8) and 416 K (m = 10) [24].

2.5. *Polymer* $C_{12}S_6^*$

The polymer with m = 12 did not show any indication of liquid-crystalline behaviour on heating or cooling at 10 K/min. On cooling at 40 K/min, the crystallization exotherm was much supercooled and split into two components, the high temperature peak being assigned to the onset of a metastable mesophase ($T_i \simeq$ 380 K). An additional exotherm was present at 361 K, probably due to the transformation to another crystalline form. These results indicate that there is a competition between crystallization and mesophase formation, which may be suppressed because of dilution effects by the alkylene segment of excessive length. We have previously observed that poly(ester-β-sulphide)s $C_{12}Sn$ derived from the same mesogenic diacrylate (m = 12) and various dithiols exhibit in all cases monotropic nematic phases independent of the nature and length of the dithiol spacer S*n* [8].

3. Concluding remarks

In the series of polymers investigated it is interesting to note that the isotropization temperatures of the even homologues decreased progressively on increasing the length of the alkylene segment, while the odd members appeared to follow a rising trend. This dual behaviour is very unusual in polymers although it occurs for low molar mass mesogens with intermediate nematic-to-isotropic transition temperatures [24, 25]. The melting temperatures change in the opposite direction, which results in a most frequent incidence of thermotropic enantiotropism in odd homologues, a comparatively very broad mesophasic range occurring for polymer $C_9S_6^*$. These peculiar odd–even effects demonstrate that in poly(ester-β-sulphide)s the onset of liquid-crystalline properties, either smectic or nematic (cholesteric), may be restricted to odd values of the length of the flexible segments [26], which would be forced to adopt predominant conformations especially favourable to mesomorphic ordering. Extensive investigations by deuterium N.M.R. of nematic order of semiflexible polyesters have recently highlighted that conformational order in polymers depends greatly on the details of their geometrical and configurational characteristics, but the strong preference of highly extended spacer segments in the liquid crystal phase is expected to be a general feature [27, 28]. On the other hand, the occurrence in the present polymer system of examples of liquid crystal dimorphism is also noteworthy, despite the complex chemical structure of the poly(ester-β-sulphide)s prepared, comprising two different flexible segments per repeat unit. Within this framework, it may be finally remarked that bis(*p*-oxybenzoate)-containing diacrylates and (*R*)-3-methyl-1,6-hexanedithiol are suitable precursors for thermotropic polyesters characterized by prevalent chirality in solution and in bulk.

4. Experimental part

4.1. *Monomeric precursors*

The α,ω-alkylene bis[4-(4-acryloyloxybenzoyloxy)benzoate]s (m = 6–10, 12) were prepared as described previously [24]. (*R*)-3-methyl-1,6-hexanedithiol was prepared from (*R*)-3-methyl-1,6-hexanediol [24] according to the procedure described for 1,2-ethanedithiol [29].

(*R*)-3-methyl-1,6-hexanedibromide: A solution of 31·4 g (151 mmol) of thionyl bromide in 20 ml of dichloroethane was added at room temperature to a solution of 10·0 g (76 mmol) of (*R*)-3-methyl-1,6-hexanediol in 150 ml dichloroethane. The reaction mixture was refluxed for 2 hours and then washed with 1 M $NaHCO_3$. The organic layer, after drying over sodium sulphate, was evaporated under vacuum and the oily residue was distilled: b.p. 125–135°C/25 mm. Yield: 13·7 g (70 per cent) {$[\alpha]_D^{25}$ + 2·7 (chloroform)}. ^1H–N.M.R. ($CDCl_3$): δ (in p.p.m. from TMS) = 1·0 (*d*, 3H, CH_3); 1·1–2·2 (*m*, 7H, aliphatic); 3·45 (*t*, 2H, CH_2Br); 3·55 (*t*, 2H, CH_2Br).

(*R*)-3-methyl-1,6-hexanedithiol: A solution containing 6·0 g (79 mmol) of thiourea in 60 ml of 95 per cent ethanol was refluxed in a steam bath and, when the solution became clear, 10·0 g (39 mmol) of (*R*)-3-methyl-1,6-hexanedibromide were added. After 1 hour the solution was cooled and 200 ml of diethylether were added. The isothiuronium salt was collected by filtration and dried: m.p. 179–180°C (dec.). Yield: 15·7 g (98 per cent). A mixture of 12 g (29 mmol) of (*R*)-3-methyl-1,6-hexanediisothiuronium dibromide and 4·9 g (88 mmol) of potassium hydroxide in 60 ml of water was refluxed for 1 hour. The mercaptan, which separated as a pink oil, was extracted with diethylether. The aqueous layer, acidified with dilute sulphuric acid, was extracted with diethylether and the combined extracts were washed with water and dried over sodium sulphate. The solvent was removed and the residual oil distilled: b.p. 120–125°C/20 mm. Yield: 3·5 g (55 per cent) $\{[\alpha]^{25}_{D}$ + 2·5 (chloroform)$\}$. ^{1}H–N.M.R. ($CDCl_3$): δ (in p.p.m. from TMS) = 0·9 (*d*, 3H, CH_3); 1·2–1·9 (*m*, 9H, aliphatic + SH); 2·5 (broad *s*, 4H, CH_2S).

4.2. *Polymers*

The polymers were prepared by the same experimental procedure that is reported for polymer $C_6S^*_6$, as a typical example. 2·00 g (2·8 mmol) of hexamethylene bis[4-(4-acryloyloxybenzoyloxy)benzoate] and 0·48 g (2·8 mmol) of (*R*)-3-methyl-1,6-hexanedithiol were dissolved in 60 ml of anhydrous dioxane with 1 ml of triethylamine and 0·2 g of 2,6-di-tertbutyl-4-methylphenol. The polymerization mixture was stirred vigorously for 2 days at room temperature and finally the precipitated polymeric product was filtered and purified by repeated precipitations from chloroform solution into diethylether. Yield: 2·0 g (81 per cent). ^{1}H–N.M.R. ($CDCl_3$): δ (in p.p.m. from TMS) = 0·9 (*d*, 3H, CH_3); 1·2–2·0 (broad *s*, 15H, aliphatic); 2·5–2·9 (*m*, 4H, CH_2S); 3·0 (*s*, 8H, $COCH_2CH_2S$); 4·4 (*t*, 4H, OCH_2); 7·4 (*d*, 8H, aromatic); 8·2 (*d*, 4H aromatic); 8·4 (*d*, 4H, aromatic).

4.3. *Physicochemical characterizations*

^{1}H–N.M.R. spectra were recorded on a Varian XL-100 spectrometer. Average molecular weights of the polymers were determined by gel permeation chromatography with a Perkin-Elmer 2/2 liquid chromatograph equipped with Shodex A802/S and A803/S columns. Monodisperse polystyrene standard samples were used for calibration.

Optical rotatory power measurements were performed with a Perkin-Elmer 141 spectropolarimeter (path length 1 dm). Molar optical rotation was calculated from the relation $[\Phi] = [\alpha]M/100$, in which M is the molecular weight of the repeating unit (r.u.).

Ultraviolet and circular dichroism spectra were recorded in the region 350–210 nm on solutions ($c \simeq 10^{-4}$(mol r.u.)/l] of spectral grade dioxane (path length 0·1 cm) with a Varian DMS-80 and a Jasco J500C spectrophotometer, respectively. Molar differential absorption coefficients ($\Delta\varepsilon$) referred to a monomeric unit were calculated from the equation $[\theta] = 3300\Delta\varepsilon$, where $[\theta]$ is the molar ellipticity. Differential scanning calorimetry analyses were performed under dry nitrogen flow on polymer samples (8–12 mg) by a Perkin-Elmer DSC-2 calorimeter. The transition temperatures were taken as corresponding to the maximum in the enthalpic peaks obtained with heating/cooling rate of 10 K/min. Indium and tin standards were employed for temperature calibration, while indium samples were used for enthalpy evaluation.

Texture observations were performed on polymer films between glass slides, without any previous treatment, by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 K/min.

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References

[1] Vilasagar, S., and Blumstein, A., 1980, *Molec. Crystals liq. Crystals*, **56**, 203.

[2] Krigbaum, W. R., Ciferri, A., Asrar, J., Toriumi, H., and Preston, J., 1981, *Molec. Crystals liq. Crystals*, **76**, 79.

[3] Watanabe, J., and Krigbaum, W. R., 1985, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 565.

[4] Park, H. J., Jin, J. I., and Lenz, R. W., 1985, *Polymer*, **26**, 1301.

[5] Chiellini, E., Galli, G., Malanga, C., and Spassky, N., 1983, *Polym. Bull.*, **9**, 336.

[6] Chiellini, E., Nieri, P., and Galli, G., 1984, *Molec. Crystals liq. Crystals*, **113**, 213.

[7] Chiellini, E., and Galli, G., 1985, *Macromolecules*, **18**, 1652.

[8] Angeloni, A. S., Laus, M., Burgin, E., Galli, G., and Chiellini, E., 1985, *Polym. Bull.*, **13**, 131.

[9] Jackson, W. J., Jr., and Kuhfuss, H. F., 1976, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2043.

[10] Chiellini, E., Lenz, R. W., and Ober, C., 1980, *Polymer Blends*, edited by E. Martuscelli, R. Palumbo and M. Kryszewski (Plenum Press), p. 373.

[11] Ballauff, M., Wu, D., Flory, P. J., and Barrall, E. M., II, 1984, *Ber. Bunsenges. phys. Chem.*, **88**, 524.

[12] Danusso, F., and Ferruti, P., 1970, *Polymer*, **11**, 88.

[13] Angeloni, A. S., Laus, M., Castellari, C., Galli, G., Ferruti, P., and Chiellini, E., 1985, *Makromolek. Chem.*, **186**, 977.

[14] Galli, G., Angeloni, A. S., Laus, M., Ferruti, P., and Chiellini, E., 1985, *Eur. Polym. J.*, **21**, 727.

[15] Cilento, G., 1953, *J. Am. chem. Soc.*, **75**, 3748.

[16] Martin, R., and Coton, G., 1973, *Bull. Soc. chim. Fr.*, p. 1442.

[17] Chiellini, E., and Galli, G., 1983, *Makromolek. Chem., Rapid Commun.*, **4**, 285.

[18] Torquati, G., Angeloni, A. S., Laus, M., Chiellini, E., and Galli, G. (in preparation).

[19] McMillan, W. L., 1971, *Phys. Rev.* A, **4**, 1238.

[20] Thoen, J., Marynissen, H., and van Dael, W., 1984, *Phys. Rev. Lett.*, **52**, 204.

[21] Navard, P., and Cox, R., 1984, *Molec. Crystals liq. Crystals*, **102**, 261.

[22] Blumstein, R. B., Stickles, E. M., and Blumstein, A., 1983, *Molec. Crystals liq. Crystals Lett.*, **82**, 205.

[23] Angeloni, A. S., Laus, M., Chiellini, E., and Galli, G. (in preparation).

[24] Galli, G., Angeloni, A. S., and Laus, M., 1986, *Makromolek. Chem.*, **187**, 289.

[25] Gray, G. W., Hartley, J. B., Ibbotson, A., and Marson, F., 1955, *J. chem. Soc.*, p. 4359.

[26] Gray, G. W., 1975, *J. Phys., Paris*, **36**, 337.

[27] Bruckner, S., Scott, J. C., Yoon, D. Y., and Griffin, A. C., 1985, *Macromolecules*, **18**, 2709.

[28] Samulski, E. T., Gauthier, M. M., Blumstein, R. B., and Blumstein, A., 1984, *Macromolecules*, **17**, 479.

[29] Urquhard, G. G., Gates, J. W., Jr., and Conner, R., 1955, *Org. Synth., Coll.*, **3**, 364.