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Solubility of thermotropic polybibenzoates with oxyethylene spacers

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Summary

Three polybibenzoates with two, three and four oxyethylene units in the spacer have been synthesized in order to analyze the influence of the length of the spacer on the stability of the mesophase and on the solubility behaviour. It was found that the thermal stability of the mesophase decreases as the length of the spacer increases, in such a manner that an amorphous polymer is obtained when four oxyethylene units are involved. On the other hand, although the value of the solubility parameter is little affected by the spacer, the solubility range is significantly widened by an increase in the number of oxyethylene units. Optimal characteristics are displayed by the polyester with three such units in the spacer.

Introduction

One of the problems derived from the inherent rigidity of mesogen groups is the reduced solubility (and high transition temperatures) exhibited by main-chain liquid crystalline polymers. Many studies (1) have been performed showing the reduction of transition temperatures by the lengthening of the spacer, the use of more flexible oxyalkylene structures and the presence of lateral substituents. However, very little information on the corresponding changes in solubility has been reported.

We have recently studied (2) some of these aspects in several polyesters derived from p,p'-bibenzoic acid (4,4'-biphenyldicarboxylic acid), finding a specially important effect of the substituents on the solubility range of these polyesters, although the value of the solubility parameter, δ , remains almost unchanged.

This work is part of a general project dedicated to analyze the influence of the nature of the spacer on the phase diagrams and on the final properties of thermotropic polyesters. We present here a study about the solubility of three polybibenzoates with varying number of oxyethylene units in the spacer, and a parallel investigation of the phase behaviour of these polyesters.

Experimental

Three polybibenzoates with different spacers have been synthesized by melt transesterification of the diethyl ester of p,p'-bibenzoic acid and the corresponding glycol, using isopropyl titanate as catalyst. These polymers are poly|oxybis(ethylene oxide) p,p'-bibenzoate|, PDEB, poly|oxytris(ethylene oxide) p,p'-bibenzoate|, PTEB, and poly|oxytetraquis(ethylene oxide) p,p'-bibenzoate|, PTTEB, with spacers of two, three and four oxyethylene units, respectively.

A Mettler TA3000 differential scanning calorimeter was used for the determination of the transition temperatures of the polymers, at a heating rate of 20°C/min. The DSC curves presented in figure 1 have been obtained in a second heating cycle, after quenching from the melt to low temperature at the inherent rate of the calorimeter. Complete reproducibility is obtained in subsequent runs under the same thermal history. X-ray diffraction and optical microscopy were employed in the identification of the mesophase.

The solubility of the three polyesters was tested in several common solvents (see Table 1) by using about 15 mg of polymer in 10 ml of solvent. Three degrees of solubility are considered: good solubility (+), solubility only in the hot solvent (+-) and null solubility (-). Intrinsic viscosities, $|\eta|$, were measured at 25°C in an Ubbelohde viscometer.

Results and Discussion

The number of oxyethylene units in the spacer is clearly affecting to the phase behaviour of these polybibenzoates. Thus, figure 1 shows the DSC heating curves of the three polymers crystallized from the isotropic melt, i.e. the second heating cycle. Two transitions can be observed for PDEB and PTEB, while only the glass transition is obtained for PTTEB. The temperatures of these transitions are presented in Table 2 and compared with those of poly(ethylene p,p'-bibenzoate), PEB (3). The first order transition has been assigned to a smectic-isotropic transition, in analogy with other polybibenzoates (4-6). Thus, X-ray analysis of the samples crystallized from the melt shows the abscence of 3-dimensional order and only the diffractions corresponding to the length of the smectic layer and to the disordered lateral arrangement are obtained. Texture observations by means of optical microscopy were not useful because the presumably high molecular weight of these polymers seems to preclude the obtention of revealing textures and only very small birefringent spheres are observed (4). Regarding the case of PTTEB, this polymer was found to be amorphous and we were unable to produce any ordered phase in this polyester (at least in a reasonable time).

Therefore, the effect of the number of oxyethylene units in the spacer is of capital importance for the thermal stability of the mesophase. Table 2 shows the great decrease of the isotropization temperature as the length of the spacer increases, passing from 350°C for PEB to only 114°C for PTEB and ending with PTTEB where the mesophase is not obtained. A parallel decrease in the glass transition temperature seems to be produced.

The influence of the number of oxyethylene units on the solubility of polybibenzoates was analyzed by determining the solubility parameter from intrinsic viscosity measurements. According to the results of the preliminary solubility test presented in Table 1, chlorinated compounds are the best solvents for these polyesters, as it has been previously reported for other polybibenzoates (2). Therefore, the intrinsic viscosity determinations were carried out in this kind of solvents. Following the usual procedure (7), the solubility parameter is equated to that of the solvent where the intrinsic viscosity is maximum. The values of the intrinsic viscosity are plotted in figure 2 against the solubility parameter of the solvent. The determination of the corresponding maxima is not completely reliable due to the reduced number of solvents. For example, only four good solvents were found for PDEB (see Table 1). Among these good solvents, acetophenone was not considered in the same series than the chloro-aliphatic solvents, since the nature of its specific

Table 1: Solubility of polybibenzoates

Solvent	δ (cal/cm^3)$^{1/2}$	PDEB	PTEB	PTTEB
Heptane	7.5	-	-	-
Cyclohexane	8.2	-	-	-
Benzene	9.2	-	+	+
Chlorobenzene	9.6	+-	+	+
o-dichlorobenzene	10.0	+-	+	+
Carbon tetrachloride	8.6	-	-	+-
Trichloroethylene	9.2	+-	+	+
Chloroform	9.3	+	+	+
Tetrachloroethane	9.7	+	+	+
Methylene chloride	9.9	+	+	+
Ethyl acetate	9.1	-	-	-
Tetrahydrofuran	9.5	-	+	+
Acetophenone	9.7	+	+	+
Cyclohexanone	9.9	-	+	+
Acetone	9.8	-	-	-
Ethanol	12.9	-	-	-
Methanol	14.3	-	-	-

Table 2: Glass transition temperature, Tg, and isotropization temperature, Ti, of polybibenzoates with different number of oxyethylene units, n.

Polymer	n	Tg(°C)	Ti(°C)
PEB	1	40 (3)	350 (3)
PDEB	2	43	192
PTEB	3	20	114
PTTEB	4	4	-

interactions with the polymer can be very different, judging from the components of the respective solubility parameters (8). Furthermore, polybibenzoates have been found to be very sensitive to subtle changes in these components (2) and the aromatic solvents were also disregarded for the determination of the solubility parameter, performed only with the chloro-aliphatic family.

Taking into account these considerations, the solubility parameters were determined from the maxima of the smooth curves drawn in figure 2, obtaining very similar values for the three polybibenzoates. These numbers are compared in Table 3 with the calculations from tabulated group contributions (9-11) and the density, d, of the polymers. The calculated values are somewhat higher than the experimental ones for the three polyesters.

The values in Table 3 indicate that the solubility parameters of the

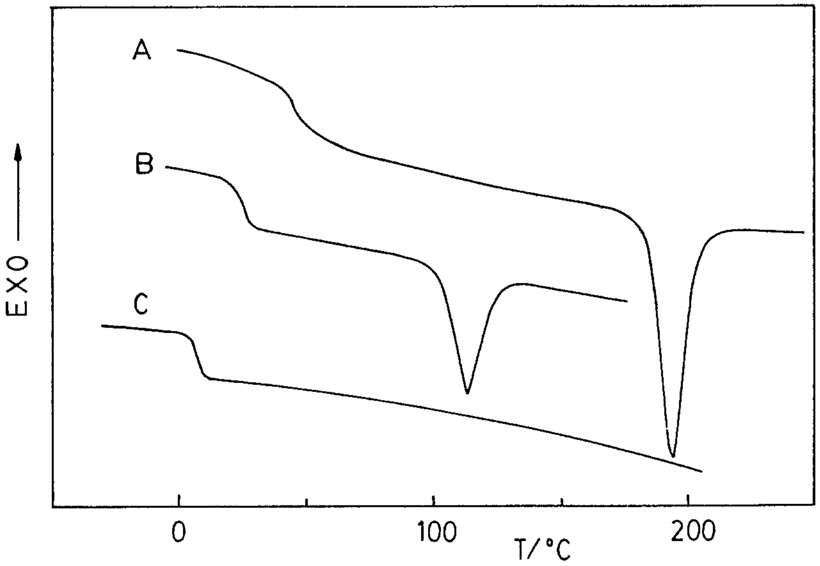

Fig. 1. DSC heating curves of polybibenzoates crystallized from the isotropic melt. A: PDEB; B: PTEB; C: PTTEB.

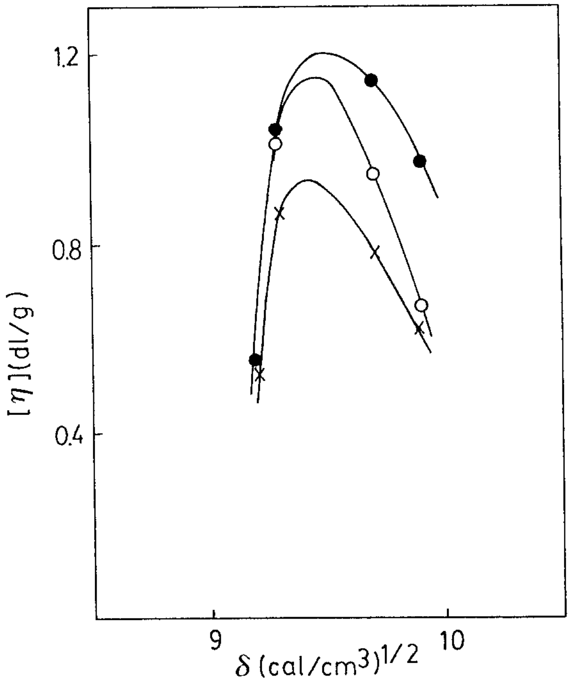

Fig. 2. Determination of solubility parameters of polybibenzoates.
o PDEB; ● PTEB; x PTTEB.

Table 3: Experimental and calculated solubility parameters of polybibenzoates

Polymer	$\delta(\mathrm{cal/cm^3})^{1/2}$ exptl.	Small (9)	Hoy (10)	VKH (11)	d $(\mathrm{g/cm^3})$
PDEB	9.5	10.5	10.8	10.0	1.31
PTEB	9.5	10.2	10.7	10.0	1.30
PTTEB	9.4	9.9	10.4	9.8	1.25

three polybibenzoates are practically the same. A similar behaviour has been already pointed out for other polybibenzoates (2), with solubility parameters in the interval 9.4-9.6 $(\mathrm{cal/cm^3})^{1/2}$. Despite this constancy, the increasing number of oxyethylene units in the spacer is clearly reflected on a widening of the solubility range. Thus, PTEB and PTTEB are also soluble in aromatic liquids, tetrahydrofuran and some ketones, with the exception of acetone, what can be explained by the high polar component of this solvent (8). On the contrary, only PTTEB is partially soluble in carbon tetrachloride, with reduced polar and hydrogen bonding capabilities of interaction (8). Previous estimations (2), confirmed in this work, show that the components of the 3-dimensional solubility parameter of polybibenzoates are of the order of 8.7, 2.5 and 3 $(\mathrm{cal/cm^3})^{1/2}$ for the dispersive, polar and hydrogen bonding interactions, respectively. A liquid would be a good solvent for polybibenzoates only if its three components are in a region close to that of the polymer. The magnitude of this region (but not the solubility parameter value) is dependent on the number of ethylene oxide units in the spacer, as well as on the presence of lateral substituents (2).

Conclusions

The effect of the number of oxyethylene units in the spacer of thermotropic polybibenzoates is reflected both in the thermal stability of the mesophase and in the solubility behaviour of these polymers. The thermal stability of the mesophase decreases as the length of the spacer increases, in such a manner that an amorphous polymer is obtained when four oxyethylene units are involved. On the other hand, although the value of the solubility parameter is little affected by the spacer, the solubility range is significantly widened by an increase in the number of ethylene oxide units. Thus, PTEB is a polymer which displays very good characteristics: it presents a mesophase with an isotropization temperature very easily accessible (114°C) and its solubility is more than satisfactory for liquid crystalline polyesters.

Acknowledgment

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