Synthesis and structural studies of poly(tetramethyleneoxypropylene *p*, *p'*-bibenzoate)

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Abstract: A smectic main chain polybibenzoate has been synthesized using a mixture of the branched ether-diols: $\text{HO}(\text{CH}_2)_4\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}$ and $\text{HO}(\text{CH}_2)_4\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$, as flexible spacers. The mesophase has been identified as SmCalt by optical microscopy and X-ray diffraction experiments. The irregular chemical structure of the polymer, due to the asymmetry of the spacers, produce two important effects: the mesophase is stabilized and the liquid crystallization is slowed down, making possible the freezing of the amorphous glass by supercooling the isotropic melt. Therefore, both the amorphous glass and the smectic glass can be obtained and analyzed. By differential scanning calorimetric measurements it was found that the glass transition of the mesophase appears at lower temperature than the glass transition of the amorphous state. Depending on the temperature and rate of deformation, the molecular orientation in the drawn smectic phase can be perpendicular (anomalous orientation) or parallel (normal orientation) to the stretching direction (or a mixture of both orientations). The morphology of these oriented samples has been studied by scanning electron microscopy.

Introduction

Polybibenzoates are suitable model polymers to study the general behaviour of thermotropic liquid crystals. The mesogenic behaviour of these materials hinges on the combination of the inherent anisotropic molecular interaction of the rigid bibenzoate units and the relative position of these units in the macromolecular chain, which is dictated by the chemical structure and the even/odd character of the flexible aliphatic spacers connecting them [1, 2]. Sometimes the study of liquid crystalline polymers is complicated by the existence of a sequence of mesophases with different degree of order (polymesomorphism) or by the transformation of the mesophase into a three-dimensional crystal. Usually it is also observed that the amorphous phase cannot be quenched by supercooling the isotropic melt because the formation of the mesophases is very fast.

It has been proved that the thermal properties of the mesophases and their transformation rates can be controlled with suitable changes in the structure of the flexible spacer [3-9]. A factor that can be managed is the stiffness of the molecular chains, governed by the number of conformations permitted to the chains, which can be modified by inserting side groups and/or ether groups along the spacer. The information from previous works [3-6] indicates that as a result of substituting methylenic groups by ether linkages in the spacer, the thermal transitions of

thermotropic polyesters are shifted to lower temperatures, the thermodynamic behaviour becomes enantiotropic, and the rate of transformation of the mesophase into a more ordered phase is considerably decreased.

These effects are enhanced when the spacer bears a ether and a methyl group both in an asymmetric position [7]. The use of diols with these structural features in the synthesis of polybibenzoates gives rise to random copolymer structures that usually favour the stability of the mesophase, the liquid crystallization is slowed down and sometimes it is possible to obtain the amorphous state when the isotropic melt is cooled at high cooling rates. These systems allow comparing the properties of the amorphous and liquid-crystalline glasses of thermotropic main chain polymers. Moreover the presence of a single mesophase in a wide interval of temperatures makes easy to study the characteristics and properties of the liquid-crystalline state: the phenomena of anomalous orientation [7,8], for instance.

With these structural factors in mind, poly(tetramethylene-oxypropylene *p,p'*-bibenzoate), named as PPO4B, has been synthesized using a mixture of the isomer ether-diols: $\text{HO}(\text{CH}_2)_4\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}$ and $\text{HO}(\text{CH}_2)_4\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$, obtained as products of the addition of 1,4-butanediol to propylene oxide in acid conditions. The mesomorphic characteristics and thermal properties of PPO4B are studied and some features related with the molecular orientation are also shown.

Results and discussion

Synthesis

Propylene oxide (PO) can be opened by acid or basic catalysts. In acid media the process starts with the protonation of the oxirane ring giving an oxonium ion, followed by nucleophilic attack of the oxygen atom of a non-protonated oxirane to the α carbon of the oxonium ion, involving ring-opening. This process continues and the molecule grows to give oligomer or polymer. The mechanism of propagation is known as the active end chain (ACE) mechanism since the active site (oxonium ions) are located at the end of the growing chain. This propagation reaction can be reduced or suppressed if other nucleophiles, like compounds containing hydroxylic groups, are present in the media of reaction in sufficient concentration. The hydroxylic group competes with oxirane in the addition to the protonated monomer. Its addition produces an alcohol molecule and the chain propagation proceeds by the activated monomer (AM) mechanism [10, 11]. The contribution of both mechanisms to the chain growth depends on the polymerization conditions and kinetic studies have revealed that in order to eliminate contributions of ACE mechanism, the instantaneous ratio $[\text{HO-}]/[\text{oxirane}]$ should be kept above a certain level. On the other hand, the presence of an excessive amount of hydroxylic compound reduces the molecular weight of the resulting polymer.

Taking these considerations into account, the polymerization of PO has been limited mainly to the first addition step by using a very big excess of 1,4-butanediol and keeping the instantaneous concentration of the oxirane low. In the experimental procedure, at first place the catalyst (sulphuric acid) was dissolved in the glycol and then a very slow addition of PO over the mixture acid/glycol was carried out in order to keep minimum the concentration of free oxirane in the medium. Consequently, the termination reaction with the glycol molecules is favoured and the first addition products (ether-diols) are mainly obtained. Propylene oxide is an asymmetrically

substituted oxirane and the two pathways of ring opening by addition of 1,4-butanediol shown in Fig. 1a are possible and therefore both isomer ether-diols **I** and **II** can be formed.

Fig. 1. a) The two possible pathways of ring opening of protonated propylene oxide by addition of 1,4-butanediol. b) Pseudo-carbocations that can be postulated for protonated propylene oxide.

The proportion of isomers **I** and **II** was determined (see Experimental part) by gas chromatography (GC) and ¹H NMR analysis: **I**= 46%, **II**= 54%. At the experimental conditions, with excess of glycol, the ratio of the concentrations of the products can be directly related to the ratio of the corresponding rate constants: thus $k_I/k_{II} = 0.85$. These results are in good agreement with those published for the reaction of propylene oxide with 1-propanol [12] and indicate that there is no important preference for any of the two directions of ring opening. The carbon-oxygen bonds are considerably polarized in the protonated oxirane and two pseudo-carbocations can be formulated (see Fig. 1b). Although the reaction with the unsubstituted carbon atom is the more favourable steric situation, the inductive effect of the methyl group stabilizes the partial positive charge on the substituted carbon, counteracting the steric hindrance. Anyway, the steric factors seem to be slightly more important.

The mixture of isomer ether-diols was used in the polymer synthesis, as reported in the experimental part. The polymer composition was determined from its ¹H NMR spectrum, integrating the signals corresponding to the lateral methyl groups (1.27 and 1.38 ppm) and it was found that the proportion of the two possible structural units in the polymer backbone corresponds very well with the composition of the diols mixture used in the polymerization reaction.

Thermal behaviour and mesophase structure

Fig. 2 shows the DSC cooling and heating curves for PPO4B. On cooling from the melt, the curve shows an exothermic peak at 62.7 °C corresponding to the formation of a mesophase, as will be shown below, whereas at lower temperatures, around 16 °C, a change in the specific heat appears, associated with the glass transition. On heating, the glass transition is observed centred at 20 °C, and the curve shows a mesophase-isotropic transition as an endotherm at 85.3 °C with an associated enthalpy of 8.8 J/g (0.74 kcal/mol) and a change of entropy of 2.1 cal/mol K. This low

value implies a great conformational disorder in the mesophase, suggesting the presence of a low-ordered mesophase.

The phase structure was investigated by X-ray diffraction experiments and the observation of birefringent textures with an optical microscope. The MAXS/WAXS synchrotron profiles in a cooling experiment from the melt are presented in Fig. 3. At high temperatures, when the polymer is an isotropic melt, only an amorphous halo in the WAXS region can be observed. On lowering the temperature, the MAXS detector shows the appearance at around 67 °C of a peak centred at 0.55 nm^{-1} (1.81 nm) while the WAXS diffractograms are rather similar to those for the isotropic melt.

Fig. 2. DSC curves for PPO4B on cooling from the isotropic melt (lower) and subsequent heating (upper). Scanning rate: $8 \text{ }^{\circ}\text{C}/\text{min}$.

These features are characteristic of a low-ordered smectic phase, with a smectic layer spacing of 1.81 nm and the molecules packing in an unstructured way into the layer. As usual [5], this smectic spacing is significantly lower than the length of the monomeric units in their all-trans conformation (2.12 nm).

Fig. 3. X-ray diffraction patterns, in the MAXS (left side) and WAXS (right side) regions, for PPO4B in a cooling experiment at $8 \text{ }^{\circ}\text{C}/\text{min}$ starting from the melt.

The variation with temperature of the position and total area of the MAXS peak, and of the maximum of the WAXS broad peak, is shown in Fig. 4. From these results, the isotropic - smectic transition is found to be centred at 62 °C, in perfect agreement with the DSC results.

On the other hand, the isotropic-smectic phase transition produces a slight change in the position of the WAXS halo. It appears at 0.46 nm for the isotropic phase and at 0.44 nm for the smectic one. No change in the MAXS peak and WAXS halo position, besides the expected thermal contraction, is observed in the interval from 60 to 27 °C (see Fig. 4).

Fig. 4. Variation of the position of the WAXS broad peak (lower frame) and of the total area (middle frame) and position (upper frame) of the MAXS peak as a function of temperature for PPO4B in the cooling experiment of Fig. 3.

The inverse phase sequence: low order smectic mesophase - isotropic melt, appeared in the heating experiment.

The microscopic observations show that polymer PPO4B can develop a fan-shape texture (Fig. 5a) when slowly cooled (at 0.5 °C/min) from the isotropic state. This texture is characteristic of smectic mesophases. The smectic mesophases can be homeotropically aligned when a thin sample is sheared and pressed between the slide glass and the cover glass. The observation of schlierens $s = \pm 1/2$ has been proposed as a method for confirming SmC_{alt} mesophases [13-15]. In these mesophases the mesogenic groups are tilted to the layer normal and the tilt directions are opposite between mesogenic groups that are located in neighbouring layers. Fig. 5b shows the optical microscopic texture of PPO4B in homeotropically aligned sandwich cell. This homeotropic texture includes schlierens with four or two dark brushes that correspond to defects $s = \pm 1$, and $s = \pm 1/2$, respectively. The

observation of schlierens with point singularities $\pm 1/2$ in addition to ± 1 confirm the existence of a SmCalt mesophase. The schlieren texture of SmC mesophases are restricted to defects $s = \pm 1$. Disclinations $s = \pm 1/2$ have been observed for SmCalt phases of other semiflexible polybibenzoates [2].

Several annealing experiments in the range of temperatures between the glass transition and the isotropization temperature of PPO4B were performed and in no case a different thermotropic behaviour in the subsequent heating was found by DSC measurements. The isotropization endotherm does not experience significant change in position or shape, showing that for any thermal treatment only the SmCalt mesophase is present. It seems, therefore, that the structural irregularity along the chain due to the simultaneous presence in the spacer of an ether bond and a methyl group in asymmetric positions stabilizes the mesophase and prevents its subsequent crystallization.

Fig. 5. a) Fan-shape texture observed for PPO4B after slow cooling (at 0.5 °C/min) from the isotropic melt. b) Homeotropic texture prepared by shearing between glasses. The texture is birefringent and includes Schlierens with singularities $s=1$ (points with four dark brushes) and $s=1/2$ (points with two dark brushes). Both micrographs were taken at ambient temperature.

Moreover, these structural features along the chain make possible the obtainment, besides the mesomorphic glass, of the amorphous glass when the isotropic melt is cooled using drastic quenching conditions. The amorphous phase of mesomorphic polymers, in general, cannot be frozen due to the high rate of formation of the mesophases, but in some polymers [16,17] the kinetics involving the isotropic-liquid crystal transition have an experimental accessible temperature range. One of the reasons is the proximity between the glass transition and the isotropization temperature, which hampers the molecular motions. In the literature, there are some works describing polymers that present double T_g : one arising from the mesophase and the other one from the amorphous phase [16-23]. The use of an asymmetrical spacer in mesogenic polymers makes possible the observation of this phenomenon. For instance, the polyeterester derived from hydroxybenzoic acid and (*R,S*)-1-methyl-1,3-propanediol possesses this structural characteristics and it has been reported [16] to give amorphous glass and smectic glass with T_g values of 104 °C and 98 °C, respectively. The difference on the glass transitions arises from differences on the fraction of free volumes of both phases, as deduced from measurements of dielectric properties [24].

Concerning PPO4B, the quenching of the amorphous phase cannot be done in the DSC using the maximum rate of cooling (100 °C/min), and the subsequent heating

shows a melting curve rather similar to that for the sample cooled at 10 °C/min (compare upper and middle curves in Fig. 6). However, the amorphous glass can be obtained if a melted sample is dropped directly into liquid nitrogen. The melting curve corresponding to this quenched sample is shown in Fig. 6 (lower curve).

It presents a glass transition at 32.5 °C, an exothermic transition at 48 °C, and an endothermic peak at 88.5 °C, which corresponds to the isotropization of the mesophase. It can be concluded, therefore, that the amorphous glass is obtained by rapid quenching of the isotropic melt in liquid nitrogen, and, at temperatures above the amorphous glass transition, segmental motion occurs and the molecules can be reorganized in the mesophase order.

Fig. 6. DSC heating curves, at 10 °C/min, of PPO4B cooled from the melt under different conditions: Sample cooled at 10 °C/min (upper curve), sample cooled at 100 °C/min (middle curve) and sample quenched in liquid nitrogen (lower curve).

This transformation is reflected in the calorimetric measurements as an exothermic transition, similarly to the cold crystallization observed in some quenched semicrystalline polymers. It is important to note, however, that the T_g of this quenched sample, 32.5 °C, is significantly higher than that corresponding to the liquid-crystallized one: 26 °C. These differences are similar to those commented above for other polymer systems.

The thermodynamic parameters of PPO4B are compared to those of poly(heptamethylene *p,p'*-bibenzoate) (P7MB) [5] and poly(oxybis(trimethylene) *p,p'*-bibenzoate) (PDTMB) [3,5] in Table 1, which permits to establish some conclusions. The three polymers have an odd number of groups in the spacer, seven in all the cases, and they all form SmCalt mesophases. The data show that the higher T_g corresponds to P7MB, with all methylenic groups in the spacer. The presence of an ether group and a methyl substituent in asymmetric position hardly decreases the glass transition of PPO4B, probably because the structural irregularity is partially compensated by the restricted conformational versatility that introduces the simultaneous presence of an ether group, shortening the bond distances in relation to the methylenic groups, and the steric interactions arisen from the methyl groups. However, the effect of the structural irregularity of the spacer is really reflected in the

thermodynamic parameters of isotropization. The packing disorder that introduces this kind of spacer decreases both the enthalpy and the entropy of isotropization. The percent of decrease is a little higher in the former, resulting in lowering the isotropization temperature. Consequently, the “temperatures window” ($T_i - T_g$) of PPO4B is small enough (~ 65 °C) so that upon cooling from the isotropic melt the molecular movements could be restricted by the proximity of the glass transition, making easier the obtainment of the amorphous glass.

Tab. 1. Glass transition temperature, T_g , isotropization temperature, T_i , and enthalpy, ΔH_i , and entropy, ΔS_i , of isotropization for the polybibenzoates PPO4B, P7MB [5], PDTMB [3,5], PTMTB [7] and PTPB [7].

Polymer	Spacer	n^a	Mesophase	T_g (K)	T_i (K)	ΔH_i (kcal/mol)	ΔS_i (cal/mol K)
P7MB	$(CH_2)_7$	7	SmCalt	314	433	1.50	3.5
PDTMB	$(CH_2)_3O(CH_2)_3$	7	SmCalt	290	445	1.55	3.5
PPO4B	$(CH_2)_4OCH(CH_3)CH_2$ (46%)	7	SmCalt	293	358	0.74	2.1
	$(CH_2)_4OCH_2CH(CH_3)$ (54%)						
PTMTB	$(CH_2)_3OCH_2CH(CH_3)CH_2$	7	SmCalt	293	378	1.02	2.7
PTPB	$(CH_2)_3OCH(CH_3)CH_2$ (40%)	6	SmA	306	416	1.17	2.8
	$(CH_2)_3OCH_2CH(CH_3)$ (60%)						

^a Sum of CH_2 and O groups in the spacer.

The polymer PPO4B can also be compared with other semiflexible polybibenzoates with asymmetric oxymethylene spacers containing a lateral methyl group, synthesized and analyzed previously in our laboratory [7] (see rows 5th and 6th of Table 1). As observed, the transition temperatures of PPO4B are rather similar to those of PTMTB, the polymer with a spacer of similar length. However, PTPB, with only six groups in the spacer, exhibits considerably higher transition temperatures (and a different kind of mesophase).

Thus, all the odd polymers develop a single mesophase: SmCalt, but it is of the type SmA in the case of the even polymer PTPB. Moreover, the even/odd oscillation is also observed in the enthalpies and entropies of isotropization: the values for PTPB are higher than those for the polymers with odd numbered spacers (PPO4B and PTMTB). In the case of polybibenzoates with linear methylenic spacers, these effects have been explained as a consequence of the conformation of the spacer in the mesophase, which confines the arrangement of the mesogenic groups in the smectic layers [1, 2].

Molecular orientation

Interesting structural information can be obtained from the flat-pattern X-ray diffractograms of oriented thermotropic polymers. X-ray diffraction experiments of drawn PPO4B samples have been performed. The photograph obtained for a sample

stretched at 35 °C at a rate of deformation of 0.55 s^{-1} is given in Fig. 7. This pattern can be attributed to a smectic mesophase. The sharp inner reflection appears like a spot on the meridian and consequently the smectic planes are perpendicular to the polymer chain axis (stretching direction). The diffuse outer reflection shows a minimum of intensity on the equatorial line and two intense maxima lying above and below the equator. This pattern is similar to those observed for the odd members of the methylenic series, BB-n, that develop SmCalt mesophases [2, 25]. As illustrated in the right part of Fig. 8, the mesogenic groups are tilted to the layer normal and the tilt directions are opposite between mesogenic groups located in neighbouring layers.

Fig. 7. X-ray diffractogram of PPO4B stretched with a strain rate of 0.55 s^{-1} at 35 °C, and schematic of the SmCalt structure. The fiber axis is placed in the vertical direction.

Polymer PPO4B, like other polybibenzoates [7, 8, 26], has a peculiar behaviour concerning to the direction in which the smectic planes are oriented. It has been established that the smectic planes can be oriented perpendicular or parallel to the draw direction depending on the rate of deformation and temperature. The mechanical properties of the corresponding drawn polymer have also been reported [27]. This particular behaviour of molecular orientation displayed by PPO4B is observed in Fig. 8.

Fig. 8. X-ray fiber photograph corresponding to specimens of PPO4B stretched at 35 °C and different strain rates: a) $2.1 \cdot 10^{-1} \text{ s}^{-1}$; b) $2.1 \cdot 10^{-2} \text{ s}^{-1}$; c) $2.1 \cdot 10^{-4} \text{ s}^{-1}$.

It can be seen that the fiber stretched at the lower drawing rate presents a similar diffraction pattern than the stretched at the higher rate, though its orientation is rotated 90° . This implies that the normal to the smectic layers is perpendicular to the direction of the fiber. In other words, the macromolecular axes are aligned perpendicularly to the stretching direction ("anomalous" orientation). On the contrary, the pattern of the fiber stretched at the highest strain rate is characteristic of a normal deformation, with the molecular axes aligned parallel to the deformation direction, while the one for the intermediate strain deformation indicates the coexistence of both orientations.

Fig. 9. SEM images of fracture surfaces for drawn PPO4B specimens. Sample identification code: *n*: normal orientation, *a*: anomalous orientation, and *m*: mixed orientation. The fracture direction is indicated with 0 or 90 at the end of the sample's code.

The differences in the arrangement of the macromolecules with the type of orientation makes that the best mechanical properties of a fiber not always coincide with the fiber direction. Thus, when the macromolecules are transverse to the fiber,

this direction presents the best mechanical properties and the fiber direction shows the worst properties [27]. Since the proportion of macromolecules disposed along the stretching direction or in the transverse direction depends on the rate of deformation and temperature, therefore a fiber with similar mechanical properties in both directions could be prepared using the adequate stretching conditions.

There are several works in the literature dealing with the phenomenon of perpendicular orientation (anomalous orientation) in polymers. Most of them are concerned with low-ordered mesophases and discuss orientation either by shearing [28-33] or by drawing [7, 8, 26, 27, 34-37]. This interesting phenomenon has been explained [27, 35] by assuming that the macromolecules are disposed in domains that can move rather independently, what means that the macromolecular interconnection between domains is scarce. These domains must have one dimension much larger than the other two, being the macromolecules settled transverse to the longer dimension. At low rates of deformation, or high temperatures, the domains are moved without breaking, getting aligned with its greater dimension in the direction of the flow, and consequently with the macromolecules placed in the transverse direction. High rates of deformation prompted the breaking of the domains prevailing in the macromolecular flow and, consequently, the macromolecules result oriented in the fiber direction. Intermediate rates of deformation give both types of orientation.

To gain information about the morphology of drawn smectic polymers, scanning electron microscopy experiments were carried out. Oriented samples of PPO4B were fractured along two directions: perpendicular (90°) and parallel (0°) to the drawing direction. Scanning electron micrographs of the two fracture surfaces associated with each sample are shown in Fig. 9. The fracture surfaces of the sample stretched at high rate of deformation, $2.1 \cdot 10^{-1} \text{ s}^{-1}$, and with the macromolecules parallel to the drawing direction (normal orientation) show a well oriented lamellar-like structure. Quite different is the fracture surface of the sample stretched to low rates of deformation, $2.1 \cdot 10^{-4} \text{ s}^{-1}$, exhibiting anomalous orientation. In this case, quite rough textures without any signal of oriented structures appear. The behaviour is more or less intermediate in the case of mixed orientations.

Conclusions

Poly(tetramethylene-oxypropylene *p,p'*-bibenzoate) (PPO4B) forms a mesophase that has been identified as SmCalt by optical microscopy and X-ray diffraction experiments. This mesophase is quite stable and no transformation into a more ordered state has been found by annealing. The asymmetry of the spacer and, consequently, the irregular chemical structure of PPO4B, together with the vicinity of T_i and T_g , allows to freeze the amorphous phase by quenching from the isotropic melt. Therefore, both the amorphous glass and the smectic glass can be obtained and analyzed. The glass transition of the amorphous phase appears a few degrees higher than that of the mesophase, which is explained in terms of free volume, as in other similar liquid crystal polymers. Depending on the temperature and rate of deformation, the molecular orientation in the drawn smectic phase of PPO4B can be perpendicular or parallel to the stretching direction, or a mixture of both orientations. The morphology of these oriented samples has been studied by SEM. The surface fracture of the sample with orientation along the fiber shows microstructures like stacked lamellae, while no clear texture was found in the transversal orientation.

Experimental part

Materials

Propylene oxide (Fluka) was stirred for 48 hours over KOH pellets and distilled in a vacuum line prior to use. 1,4-Butanediol (Fluka) was purified by distillation at reduced pressure. Diethyl 1,1'-biphenyl-4,4'-dicarboxylate was synthesized as previously reported [7] and titanium (IV) isopropoxide from Aldrich Co. was used as received.

Diol synthesis and characterization

The ether-diols used as flexible spacer were synthesized by ring opening reaction of propylene oxide with 1,4-butanediol, initiated by sulphuric acid. The following procedure was applied: 26.37 g (0.45 mol) of propylene oxide was added dropwise to a solution of sulphuric acid (5.52 g, 0.056 mol) in 1,4-butanediol (133 g, 1.47 mol). This solution was degassed prior to the addition. The reaction mixture was stirred under vacuum at room temperature during 24 h. The mixture was poured into water, neutralized with aqueous sodium bicarbonate and filtered. The product was extracted with chloroform and purified by consecutive distillations under vacuum. A pure fraction, free of unreacted alcohol and higher oligomers (formed in small quantities) was finally obtained (boiling range: 142-144 °C at 12 mmHg). This fraction is composed by a mixture of the isomer ether-diols: $\text{HO}(\text{CH}_2)_4\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}$ and $\text{HO}(\text{CH}_2)_4\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$. Their chemical structures were characterized by NMR in deuterated chloroform. The ^1H NMR and ^{13}C NMR signals were assigned using COSY, HMQC and DEPT experiments:

^1H NMR (400 MHz, CDCl_3): δ = 1.08 (d, $\text{HOCH}_2\text{CH}(\text{CH}_3)\text{O}$), 1.10 (d, $\text{HOCH}(\text{CH}_3)\text{CH}_2\text{O}$), 1.57-1.70 (m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2.4-2.7 (OH), 3.18-3.40 (ABX, $\text{HOCH}(\text{CH}_3)\text{CH}_2\text{O}$), 3.40-3.57 (m, $\text{HOCH}_2\text{CH}(\text{CH}_3)\text{OCH}_2$, $\text{HOCH}(\text{CH}_3)\text{CH}_2\text{OCH}_2$), 3.57-3.65 (m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.92 (m, $\text{HOCH}(\text{CH}_3)\text{CH}_2\text{O}$) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 15.8 ($\text{HOCH}_2\text{CH}(\text{CH}_3)\text{O}$), 18.7 ($\text{HOCH}(\text{CH}_3)\text{CH}_2\text{O}$), 26.4 and 26.9 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 29.8 and 30.0 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 62.5 and 62.4 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 66.1 ($\text{HOCH}_2\text{CH}(\text{CH}_3)\text{OCH}_2$), 66.3 ($\text{HOCH}(\text{CH}_3)\text{CH}_2\text{O}$), 68.8 ($\text{HOCH}_2\text{CH}(\text{CH}_3)\text{O}$), 71.2 ($\text{HOCH}(\text{CH}_3)\text{CH}_2\text{OCH}_2$), 76.2 ($\text{HOCH}_2\text{CH}(\text{CH}_3)\text{O}$), 76.4 ($\text{HOCH}(\text{CH}_3)\text{CH}_2\text{O}$) ppm.

This mixture of diols was used in the polymer synthesis, since it was not possible to separate the two components by fractional distillation. The composition of the diols mixture was determined by gas chromatography (GC) and ^1H NMR analysis.

GC analysis was performed by using an Agilent Technologies 6890N Gas Chromatograph equipped with a 5973 quadrupole mass selective detector (Agilent Technologies). A HP-5ms fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness of 5% phenyl methylpolysiloxane) was employed for diol separation. Helium was the carrier gas, with a gas flow velocity of 0.8 mL/min. The split ratio was 42:1. Injector temperature was 250 °C. Oven temperature programming consisted of an initial temperature of 80 °C held for 2 min, an increase in temperature of 6 °C/min until 130 °C, and a hold time of 4 min at 130 °C. The mass spectrometer detector was tuned by maximum sensitive autotune. The composition **I**= 46% and **II**= 54% was found, with an estimated uncertainty of $\pm 3\%$.

The composition was also analysed integrating the ^1H NMR signals corresponding to the lateral methyl groups. The integration values were 0.57 and 0.73, so that **I**= 44% and **II**= 56%, with an estimated uncertainty of $\pm 5\%$.

Polymer synthesis and structural characterization

Fig. 10. ^1H NMR and ^{13}C NMR spectra of polymer PPO4B.

Poly(tetramethylene-oxypropylene *p,p'*-bibenzoate), PPO4B, was prepared by melt transesterification of diethyl 1,1'-biphenyl-4,4'-dicarboxylate and the mixture of the isomer ether-diols, using titanium (IV) isopropoxide as catalyst.

The chemical structure of the polymer was ascertained by solution ^{13}C and ^1H -NMR measurements, carried out in a Varian 400 spectrometer, in deuterated chloroform at 40 °C (see Fig. 10). The ^1H and ^{13}C NMR signals were assigned using complementary two-dimensional experiments such as COSY and HMQC:

^1H NMR (400 MHz, CDCl_3 , 40 °C): δ = 1.27 (d, 3H, Hc), 1.38 (d, 3H, Hc'), 1.74 (m, 4H, He, He'), 1.86 (m, 4H, Hf, Hf'), 3.49-3.70 (m, 6H, Hd, Hd', Hb') 3.80 (m, 1H, Hb), 4.33 (m, 6H, Ha, Hg, Hg'), 5.35 (m, 1H, Ha'), 7.55-8.15 (m, 16H, Harom.) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 40 °C): δ = 16.8 (Cc'), 17.1 (Cc), 25.6 y 25.7 (Cf, Cf'), 26.3 y 26.7 (Ce, Ce'), 64.9 (Cg, Cg'), 67.8 (Ca), 68.7 (Cd), 70.2 (Ca'), 70.9 (Cd'), 73.3 (Cb'), 73.5 (Cb), 127.1 and 127.2 (Ck, Ck', Cn, Cn'), 129.8 and 130.0 (Ci, Ci', Cp, Cp'), 130.1 and 130.2 (Cj, Cj', Co, Co'), 144.2-144.4 (Cl, Cl', Cm, Cm'), 165.7 and 166.1 (Cq, Cq'), 166.2 (Ch, Ch') ppm.

The polymer composition was determined by integrating the ^1H NMR signals corresponding to the lateral methyl groups (protons Hc at 1.27 ppm and protons Hc' at 1.38 ppm). The integration values were 1.28 and 1.39, so that the proportion of the two possible structural units in the polymer backbone corresponds very well, inside the experimental error with the composition of the diols mixture used in the polymerization reaction.

Size-exclusion chromatography data were obtained using a Waters Alliance GPCV 2000, equipped with two detectors: the conventional refractive index concentration detector and a viscometer. The dual detection allows to achieve a universal calibration (obtained from measurements in different polystyrene standards, using chloroform as eluent at 35 °C), and to determine absolute molecular weight and viscosity values. The different obtained values are: M_n = 16700; M_w = 29100; M_p = 25400 and the intrinsic viscosity is 0.345 dL/g.

A film of the polymer was prepared by compression moulding in a Collin press between hot plates (100 °C) and subsequently cooling to room temperature. Parts of this film were used for the different experiments.

Thermotropic characterization

Differential scanning calorimetric measurements were carried out with a Perkin-Elmer DSC7 calorimeter, connected to a cooling system.

X-ray scattering experiments were performed by employing synchrotron radiation at the soft-condensed matter beam line at Hasylab (DESY, Hamburg). The beam was monochromatized (0.15 nm) by Bragg reflection through a germanium single crystal. Wide- (WAXS) and Middle-angle scattering (MAXS) profiles were acquired simultaneously while the sample is subjected to a temperature program. The scattering patterns were collected in time frames of 15 s for the rate of 8 °C/min, so that we have a temperature resolution of 2 °C between frames. Crystalline PET and silver behenate samples were used for the calibration of the WAXS and MAXS detectors, respectively. Further details concerning the instrument were given elsewhere [9].

Fiber WAXS patterns were obtained at room temperature using a flat-plate camera attached to a Phillips 2 kW tube X-ray generator. The fibers were obtained by uniaxial stretching to 6:1 ratio at 35 °C and at different strain rates in a Minimat 2000 dynamometer.

Optical microscope observations of the mesophase textures of PPO4B were carried out using a Carl Zeiss polarized optical microscope equipped with a Linkam TMS92 hot stage thermal controller. The samples were prepared by melting the polymer between a glass slide and a coverslip to obtain thin films. For the obtainment of the fan-shape texture, the sample was melted in the Linkam hot stage at 120 °C for 5 min in order to eliminate any previous thermal history and then it was slowly cooled at 0.5 °C/min. The homeotropic texture was prepared by shearing and pressing the melted sample between the slide glass and the cover glass. The micrographs were taken at ambient temperature.

Scanning electron microscopy

Scanning electron microscopy (SEM) experiments were performed with a XL30 ESEM PHILIPS equipment.

Samples of PPO4B stretched at 35 °C and different strain rates were quenched in liquid nitrogen and fractured along two directions: perpendicular (90°) and parallel (0°) to the drawing direction. Scanning electron micrographs of the two fracture surfaces were taken.

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