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Liquid-crystalline main-chain polymers with a poly(p-phenylene terephthalate) backbone: 1. Synthesis, characterization and rheology of polyesters with alkoxy side chains

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The influence of the position and length of alkoxy substituents on the phase behaviour of poly(p-phenylene terephthalate)s was investigated by differential scanning calorimetry and rheological measurements. The two polymers with respectively dodecyl and hexyloxy side chains on the terephthalate moiety (PTA12HQ and PTA6HQ) both showed stable liquid-crystalline phases. For these two polymers the location of the transition temperatures as a function of the molecular weight (inherent viscosity) was shown to level off above an inherent viscosity of 2 dl g⁻¹. From rheological measurements it is concluded that the layered mesophase, shown by PTA6HQ and PTA12HQ, behaves more like a solid than a liquid. For the nematic mesophase, only shown by PTA6HQ, a minimum in the viscosity-temperature curve was found. The polymer with dodecylx substituents on the hydroquinone moiety (PTAHQ12) only shows mesomorphic behaviour on cooling, while the polymer with double the amount of substituents (PTA12HQ12) does not show any liquid-crystalline behaviour.

(Keywords: rigid-rod polymer; thermotropic; synthesis; phase behaviour; rheology; poly(p-phenylene terephthalate))

INTRODUCTION

Rigid-rod polymers form a separate class of polymers because of their ability to form a liquid-crystalline phase. This creates the possibility to form highly oriented structures in a simple way. A typical example is poly(p-phenylene terephthalamide), from which the high-modulus, high-strength Twaron (Akzo) and Kevlar (Du Pont) fibres are spun. This polymer is unmeltable and can only be spun from a sulphuric acid solution 1.

Obviously the development of melt-processable liquid-crystalline polymers (LCPs) has received a great deal of attention over the past years. Melt processability can be obtained in several ways 2. A well known method is to disrupt the regular structure of the main chain by random copolymerization and/or the introduction of "crankshafts" in the chain. Both methods are employed in the Vectra (Hoechst–Celanese) polymer. It results in a frustrated chain packing in the solid state, thus lowering the melting point. In another approach the chain stiffness is lowered to obtain a meltable LCP (poly(ethylene terephthalate) (PET)) modified with rigid p-hydroxybenzoic acid (pHBA) units, also known as X7G from Eastman–Kodak.

However, a decrease in chain stiffness will eventually lead to a loss of the ability to form liquid-crystalline phases. Though there has been considerable progress in studying the structure and properties of these polymers, full understanding is hampered by some inherent disadvantages. Especially in the case of random copolymers the unknown and probably unstable (due to transesterification) sequence distribution of the building units 3 gives rise to a complicated solid-state behaviour 4,5. Furthermore the insolubility in common organic solvents obstructs easy characterization on a molecular level.

The difficulties encountered in investigating the above-mentioned systems emphasize the need for additional research on LCPs of non-random copolymeric nature. Thus the polymers described in this study are based on a rigid poly(p-phenylene terephthalate) backbone (abbreviated as PPT). In order to obtain meltability (and solubility), flexible aliphatic side chains are attached to this backbone. Following the abbreviations used by Rodriguez-Parada 6 the resulting polymers are designated as PTAxHQ, PTAxHQn and PTAnHQn (Scheme 1).

The flexible side chains will act as a "bonded solvent" and thus create a meltable polymer. From a practical 7 as well as a theoretical 8 point of view, it is well known that increasing the amount of substitution and/or the
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length of the side chains will result in a lower melting point. For PTAnHQ it is known that a layered mesophase can be formed when the side chains exceed a certain length. In this layered mesophase the side chains interdigitate and the main chains form layers (see Figure 1). The distance between these layers is proportional to the length of the side chains, and increases by 1.25 Å for each added CH$_2$ unit. At room temperature two crystal modifications A and B are found in which the characteristic layer distance increases by 1.25 and 0.82 Å per CH$_2$ unit respectively.

For PTAnHQ polymers with long side chains (n $\geq$ 12) three disordering transitions can be seen upon heating both modifications. These transitions are associated with the side chains, the main chains (formation of the layered mesophase) and the transformation to the isotropic melt. For a polymer with shorter side chains a nematic mesophase is observed in addition.

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Synthesis of monomers

2,5-Dialkoxyterephthaloyl chlorides were synthesized from diethyldihydroxyterephthalate in three steps by a similar, but slightly modified, procedure as described earlier by Ballauff. In the first step 152.5 g (0.6 mol) of diethyl 2,5-dihydroxyterephthalate, 165.8 g (1.2 mol) of potassium carbonate and 3.0 mol of 1-bromoalkane were refluxed in 3.6 litres of acetone until the yellow-orange colour had disappeared. After nearly complete reaction, as indicated by 1H n.m.r., the solid potassium bromide was filtered off and the acetone was removed in vacuo. The resulting alkoxy-substituted diethyl terephthalate was recrystallized twice from ethanol.

Diethyl 2,5-dialkoxyterephthalate. Yield 78%; m.p. 62–64°C (lit. m.p. 57°C). %C 73.36 (calcd. 73.18), %H 10.64 (calcd. 10.58). 1H n.m.r. (acetonat-d6): δ = 4.32 (q, OCH2CH3), 1.35 (t, OCH2CH3, J = 7.1 Hz), 7.33 (s, H(2Ar)), 4.03 (t, OCH2C12H25), 1.78 (m, OCH2CH2C12H25), 1.52 (m, OCH2CHCH2CH3), 1.25–1.42 (m, OCH2CH2C12H25), 0.88 ppm (t, OCH3).

Diethyl 2,5-diethoxyterephthalate. Yield 79%; m.p. 41–43°C (lit. m.p. 39°C). %C 68.20 (calcd. 68.22), %H 8.69 (calcd. 9.06). 1H n.m.r. (DMSO-d6): δ = 4.27 (q, OCH2CH3), 1.30 (t, OCH2CH3, J = 7.0 Hz), 7.28 (s, H(2Ar)), 3.97 (t, OCH2C12H25), 1.67 (m, OCH2CH2C12H25), 1.42 (m, OCH2CH2CH2CH3), 1.26–1.32 (m, OCH2CH2C12H25), 0.87 ppm (t, OCH3).

Diethyl 2,5-dimethoxyterephthalate. Yield 82%; m.p. 136–138°C (lit. m.p. 128°C). %C 71.73 (calcd. 71.87), %H 10.16 (calcd. 10.18).

The acids were obtained from the esters as explained in the following example. A solution of 200.8 g (0.47 mol) of diethyl 2,5-dihydroxyterephthalate in 0.5 litres of ethanol was treated, under reflux conditions, with a solution of 266.8 g (4.76 mol) potassium hydroxide in 0.62 litres of water (30 wt% aqueous solution, 10-fold amount of excess) for approximately 45 min. In order to maintain a clear solution, 150 ml of ethanol was added, and reflux was continued, under vigorous stirring, for 3–4 h. After cooling to 0°C, the solution was neutralized with a small excess of concentrated HCl from which the acid precipitated. Recrystallization from a mixture of ethanol/H2O (4/1, v/v) afforded white needles in nearly quantitative yield.

2,5-Diacetoxyterephthalic acid. Yield 96%; m.p. 136–138°C (lit. m.p. 128°C). %C 71.73 (calcd. 71.87), %H 10.16 (calcd. 10.18).

2,5-Diacetoxyterephthalic acid. Yield 92%; m.p. 144–146°C (lit. m.p. 138°C). %C 65.56 (calcd. 65.55), %H 8.05 (calcd. 8.25). 1H n.m.r. (DMSO-d6), δ = 12.85 (s, COOH), 7.27 (s, H(2Ar)), 3.98 (t, OCH2CH3), 1.68 (m, OCH2CH2CH3), 1.42 (m, OCH2CHCH2CH3), 1.26–1.32 (m, OCH2CH2CH3), 0.87 ppm (t, OCH3).

In the third and last step the acid was refluxed with a 10-fold excess of thionyl chloride for approximately 4 h. To avoid contact with air the excess of thionyl chloride was removed by distillation, and the acid chloride was isolated from the crude product by extraction with n-hexane in a Soxhlet apparatus, followed by crystallization from the same solvent.

2,5-Diacetoxyterephthalic acid chloride. Yield 88%; m.p. 68–71°C (lit. m.p. 60°C). %C 67.65 (calcd. 67.23), %H 9.06 (calcd. 9.17), %Cl 12.41 (calcd. 12.40).

2,5-Diacetoxyterephthalic acid chloride. Yield 92%; m.p. 37–39°C (lit. m.p. 63°C, apparently a printing error). %C 59.79 (calcd. 59.56), %H 7.06 (calcd. 7.00), %Cl 17.38 (calcd. 17.58).

The dodecyloxy-substituted hydroquinone was prepared from 2,5-dihydroxybenzoquinone in two steps following modified literature procedures. In the first step 15 g (0.41 mol) dry HCl gas was passed into 800 ml (3.56 mol) dodecane at 50°C. To this solution 17.0 g (0.12 mol) of dihydroxybenzoquinone was added and a highly viscous and turbid solution was formed. The temperature of the solution was raised to 100°C and maintained at this temperature for 3 h, while continuously stirring. By then the solution had turned clear dark-brown and was cooled to room temperature. Approximately 1.5 litres of ether was added to the cooled solution and the yellow product was filtered off and washed twice with ether. After recrystallization from ethanol, yellow crystals of 2,5-didecyloxy-p-benzoquinone were obtained.

2,5-Didecyloxyterephthalic acid. Yield 60%; m.p. 125–126°C (lit. 124°C). %C 59.79 (calcd. 59.56), %H 7.06 (calcd. 7.00), %Cl 12.41 (calcd. 12.40).
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PTAHQ12 and PTA12HQ12 inherent viscosities of 0.70 and 1.39 dl g⁻¹ were obtained.

Characterization methods

D.s.c. measurements were performed on a DuPont 9900 DSC and on a Perkin–Elmer DSC7. The heating rate was 20°C min⁻¹. The peak of the melting endotherm was taken as the melting point.

N.m.r. spectra were recorded at 30°C on a Varian VXR400 spectrometer (¹H resonance frequency 400 MHz) using a 5 mm switchable probe and a VXR data system. Tetramethylsilane (TMS) was used as internal reference for the proton spectra.

Inherent viscosities were determined at 25°C with solutions of the polymers in CHCl₃ (2 g l⁻¹) using an Ubbelohde capillary viscosimeter.

Dynamic rheological measurements were performed on a Rheometrics RDS-2 mechanical spectrometer in the parallel-plate arrangement using 25 mm plates. The parallel-plate gap spacing was 1–1.5 mm and the dynamic strain amplitude was 1%. Samples were prepared on a press by compressing dried powders to 25 mm diameter plaques at 50°C (PTAHQ12), 190°C (PTA12HQ12) and 260°C (PTA6HQ, PTA12HQ). The rheological measurements were performed under a nitrogen atmosphere. As checked by g.p.c. no significant sample degradation occurred.

RESULTS AND DISCUSSION

Thermal behaviour

In Figure 2 the d.s.c. thermograms of the four polymers are shown. In agreement with observations made by others, the existence of a glass transition could not be determined unambiguously by this technique for any of the polymers.

PTA12HQ shows three endotherms, which are denoted as θ, Tm and Tc (see Table 1 and Figure 2). The first-order transition at the lowest temperature, θ, is caused by a disordering of the side chains. At this temperature conformational and positional order of the side chains decreases. In the first heating run it is located at 108°C (ΔH ≈ 50 J g⁻¹) and in the second heating run at 38°C (ΔH ≈ 15 J g⁻¹). This difference is caused by a change in crystal structure; solution-precipitated powder is in crystal form B, while once molten powder is in crystal form A. Irrespective of the polymer’s initial crystal form the polymer is in the less ordered structure A’ above the side-chain disordering temperature θ. The endotherm at Tm has been ascribed to the transition to the layered mesophase, Lₘ (ref. 16). Above this temperature the main chains are still aligned parallel in a layered structure, but their position/distance relative to each other is not well defined. The layer distance d in phase Lₘ has a value comparable to that of modification A. Throughout this paper this temperature will be referred to as the main-chain melting temperature.

Table 1 Transition temperatures (first/second heating runs) of the d.s.c. thermograms shown in Figure 2

<table>
<thead>
<tr>
<th>Polymer</th>
<th>θ (°C)²</th>
<th>Tm (°C)²</th>
<th>Tc (°C)²</th>
<th>Tc (°C)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTA12HQ 2.3</td>
<td>108/38</td>
<td>161/175</td>
<td>243/243</td>
<td></td>
</tr>
<tr>
<td>PTA6HQ 2.3</td>
<td>183/177</td>
<td>233/221</td>
<td>286/282</td>
<td></td>
</tr>
<tr>
<td>PTAHQ12 0.7</td>
<td>118/80</td>
<td>239/242</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTA12HQ12 1.4</td>
<td>82/87</td>
<td>183/188</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

²Side-chain disordering temperature
³Main-chain melting temperature, formation of layered mesophase
⁴Transition temperature from layered mesophase to nematic mesophase
⁵Transition temperature to isotropic melt
⁶Measured in p-chlorophenol at 50°C

Figure 2  D.s.c. thermograms of the PTA12HQ, PTA6HQ, PTAHQ12 and PTA12HQ12 powders: (a) first heating run, (b) second heating run

Several batches of PTA12HQ were synthesized and...
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The effect of the molecular weight on the transition temperatures is shown in Figure 4. The side-chain disordering temperature of both modifications A and B remains almost constant for all molecular weights. The main-chain melting and especially the clearing temperature show a considerable molecular-weight dependence; the region between $T_m$ and $T_i$, in which the liquid-crystalline phase exists, extends with molecular weight. Similar to the poly(2-n-alkyl-1,4-phenylene terephthalate)s described by Majnusz et al.\textsuperscript{17,18}, the molecular-weight dependence is very strong below an inherent viscosity of 1 dl g\textsuperscript{-1}. Above this value a small, continuous increase in transition temperatures exists, which starts to level off at an inherent viscosity of 2 dl g\textsuperscript{-1}.

In the d.s.c. thermograms of the polymer with hexyloxy side chains, PTA6HQ, no separate disordering transition of the side chains is observed (Figure 2). The fact that the ability of the side chains to order (or crystallize) depends on the side-chain length is well known for comb-like polymers with a flexible backbone; in general, a minimum length of about 10 to 12 CH\textsubscript{2} units is required for the side chains to crystallize.\textsuperscript{19} Above 100°C three endotherms are detected in the first heating run, which are denoted as $T_m$, $T_n$ and $T_i$, respectively. The endotherm at the lowest temperature, $T_m$, is the main-chain melting temperature. At this temperature the layered mesophase $L_m$ is formed. At a higher temperature $T_n$ the layered ordering that is present in this mesophase is lost and a nematic mesophase N is formed.\textsuperscript{11} The parallel ordering of the main chains that is present in this mesophase finally disappears at the clearing temperature $T_i$. Upon reheating a once molten material (Figure 2b) the transitions are located at somewhat lower temperatures. This is probably caused by some degradation, as well as undercooling effects. The phase behaviour of PTA6HQ is shown schematically in Figure 5. At room temperature two layered modifications A and B can exist. At respectively $T_m$ and $T_i$, the layered and nematic mesophases are formed, while the isotropic melt is reached at $T_i$. It was reported earlier by Falk et al.\textsuperscript{11} that the transition at $T_i$ is very molecular-weight-sensitive; for a polymer with an inherent viscosity of 0.2 dl g\textsuperscript{-1}, this transition is shifted to lower temperatures and overlaps with $T_m$. This is illustrated in Figure 6, in which the molecular-weight dependence of the transition temperatures is shown and the data from Falk can be compared with our data points. It can be seen that the temperature range in which the layered mesophase exists broadens with increasing molecular weight. Similar to PTA12HQ a plateau region is reached at an inherent viscosity of 2 dl g\textsuperscript{-1}.

The PTAHQ12 polymer was used to investigate the effect of the place of the substituents on the thermal behaviour. For this polymer the low-temperature disordering $T_s$ of the side chains is located around 100°C in the first and second d.s.c. runs (Figure 2). This corresponds to the side-chain disordering temperature of PTA12HQ in modification B. By X-ray diffraction it was
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PTA12HQ12 shows a decrease in viscosity at the respective transition temperatures to the isotropic melt. These temperatures compare well with the transitions observed by d.s.c. Because of their low molecular weight, the viscosity in the isotropic melt is very low compared to PTA6HQ and PTA12HQ.

From the d.s.c. measurements as well as publications by others, we concluded that PTA12HQ shows a layered mesophase between ~170 and 240°C. From Figure 9b it can be concluded that the layered mesophase has a viscosity resembling that of the intermediate phase A'.

Figure 7 Scheme of the phase behaviour in PTAHQ12 powders. Upon heating modification B the intermediate phase B' is obtained, which transforms to the isotropic melt I at the clearing temperature $T_c$. On cooling from the isotropic melt the layered mesophase $L_m$ is passed (monotropic behaviour).

$B \leftrightarrow T_{c}^{(B)} \leftrightarrow T_i \leftrightarrow L_m \leftrightarrow T_c \leftrightarrow I$

Figure 8 Scheme of the phase behaviour in PTA12HQ12 powders. Upon heating the solid room-temperature phase to above the side-chain melting temperature $T_m$, an intermediate phase is formed, which transforms to the isotropic melt at the clearing temperature $T_c$. Indeed found by others that PTAHQ12 is in crystal form B at room temperature. The melting transition of the main chains is located at a higher temperature compared to PTA12HQ and overlaps with the transition to the isotropic phase at $T_i$. In the cooling run, however, $T_c$ and $T_m$ are clearly separated and a liquid-crystalline phase can be detected. This monotropic behaviour was reported earlier by Rodriguez-Parada et al.

In Figure 7 the phase behaviour of PTAHQ12 is shown schematically. The higher main-chain melting temperature as compared to PTA12HQ and the insolubility of this polymer in chloroform suggest a better crystal packing in the case of substitution on the hydroquinone moiety. From the cooling runs it is indeed apparent that the heat of crystallization (when going from $L_m$ to the intermediate phase B') is much higher than in PTA12HQ ($\Delta H_c \approx 33 \text{ J g}^{-1}$ for PTAHQ12, compared to $\Delta H \approx 8 \text{ J g}^{-1}$ for PTA12HQ). This could mean that above $T_c$ the main chains are better ordered in PTAHQ12 compared to PTA12HQ. More information regarding this point is gained from results obtained by Rodriguez-Parada et al. They showed that the layer spacing of PTAHQ16, in the temperature region between $T_c$ and $T_m$, resembles that of modification B. For PTA16HQ the layer spacing in this temperature region resembles that of modification A. If we combine these results with our own findings (high-temperature X-ray diffraction on PTAHQ12) it seems justifiable to suppose that PTAHQ12 is in a phase resembling phase B between $T_c$ and $T_m$. This is why this phase is denoted as B'.

In PTA12HQ12, which is substituted on both moieties, the high amount of side chains prevents the formation of a mesophase; no liquid-crystalline behaviour is detected. After disordering of the side chains at about 100°C the main-chain structure melts at 190°C and an isotropic melt is formed (Figure 2). This is shown schematically in Figure 8.

Rheology

PTA6HQ ($\eta_m = 2.3 \text{ dl g}^{-1}$), PTA12HQ ($\eta_m = 2.8 \text{ dl g}^{-1}$), PTAHQ12 ($\eta_m = 0.7 \text{ dl g}^{-1}$) and PTA12HQ12 ($\eta_m = 1.4 \text{ dl g}^{-1}$) were characterized with a Rheometrics dynamic spectrometer. The complex viscosity $\eta^*$ is shown as a function of temperature in Figure 9.

The two polymers that do not exhibit a liquid-crystalline phase upon heating, PTAHQ12 and PTA12HQ12, were characterized with a Rheometrics dynamic spectrometer. The complex viscosity $\eta^*$ is shown as a function of temperature in Figure 9.
For PTA12HQ it can be seen that the viscosity shows a small stepwise decrease on entering the layered mesophase at the main-chain melting temperature (170°C), followed by a plateau region. At about 210°C, corresponding to the start of the broad d.s.c. transition to the isotropic melt (Figure 2), the melt viscosity starts to decrease and reaches a new plateau at about 260°C (the end of the d.s.c. endotherm).

Though rheological data on PTA6HQ ([η] = 0.48 dl g⁻¹) have been published recently by Schrauwen et al., the higher molecular weight of the polymer (which was shown to have a significant effect on the transition temperatures) used by us makes it useful to present our rheological data. The viscosity-temperature curve of PTA6HQ, shown in Figure 9c, reveals that the plateau region for the layered mesophase cannot be discerned as clearly as for PTA12HQ. Already at 200°C the viscosity starts to decrease, and at about 230°C, corresponding to the transition to the nematic melt as found by d.s.c., a drastic decrease in the melt viscosity is observed. Such a very low melt viscosity, followed by an increase in viscosity on entering the isotropic phase, is typical for a nematic melt and is also observed for lyotropic polymers. Thus the assignment of this phase by Falk is affirmed by the present rheological measurements. In the isotropic phase the viscosities of PTA6HQ and PTA12HQ are of the same order of magnitude.

To illustrate the rheological behaviour in the layered and nematic mesophases, the storage and loss moduli G' and G'' of PTA6HQ are shown as a function of frequency in Figure 10. Data at four different temperatures, corresponding to the four different phases that can exist in this polymer, are shown. In the solid phase as well as in the layered mesophase an elasticity-dominated state exists; the storage modulus exceeds the loss modulus. In the nematic mesophase a viscosity-dominated state is found (G'' > G'), while G' and G'' almost equal each other in the isotropic phase. This leads to the conclusion that the layered mesophase resembles a solid phase, while the nematic mesophase behaves like a liquid.

CONCLUSIONS

The phase behaviour of substituted PPTs was shown to be strongly dependent on the position and length of substituents. Only the two polymers with substituents on the terephthalate moiety show stable liquid-crystalline phases.

For both PTA6HQ and PTA12HQ the transition temperatures are strongly dependent on the molecular weight below an inherent viscosity of 1.5 dl g⁻¹. Above an inherent viscosity of 2 dl g⁻¹ this dependence levels off.

From rheological measurements it is concluded that the layered mesophase, shown by PTA6HQ and PTA12HQ, behaves more like a solid than a liquid. The nematic mesophase shown by PTA6HQ has a very low melt viscosity and, similar to other nematic polymers, the viscosity of this polymer increases at the transition from nematic to isotropic melt.

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