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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 dodecyloxy 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 dodecyloxy 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 unmelttable and can only be spun from a sulphuric acid solution¹.

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 ways². 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 units³ 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-Parada⁶ the resulting polymers are designated as PTAnHQ, PTAHQn and PTAnHQn (*Scheme 1*).

The flexible side chains will act as a 'bonded solvent' and thus create a meltable polymer. From a practical⁷ as well as a theoretical⁸ point of view, it is well known that increasing the amount of substitution and/or the

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Scheme 1

length of the side chains will result in a lower melting point.

For PTAHQ it is known that a layered mesophase can be formed when the side chains exceed a certain length^{9,10}. 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 CH₂ unit^{9,10}. 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 CH₂ unit respectively¹⁰.

For PTAHQ 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^{9,11}.

For PTA12HQn and PTA16HQn it was shown by Rodriguez-Parada *et al.*⁶ that the phase behaviour of these alkoxy-substituted polymers is significantly affected by the position and length of substituents.

The rheology of a PTAHQ polymer with short side chains, PTA6HQ, as well as that of a polymer with long side chains, PTA16HQ, has been described recently by Schrauwen *et al.*¹². They concluded that, above the isotropization temperature, PTA16HQ behaves like a conventional polymer in the melt. For PTA6HQ with a fairly low molecular weight ($[\eta] = 0.48 \text{ dl g}^{-1}$) they observed the flow-thinning effect typical of liquid-crystalline polymers.

In this paper two polymers with alkoxy substituents of different lengths on the terephthalate moiety, PTA6HQ

and PTA12HQ, will be compared with regard to their phase behaviour. As the molecular weight is known to have a significant influence on the transition temperature of most polymers, this dependence will be investigated as well.

The influence of the position and amount of the substituents on the phase behaviour will be investigated by attaching dodecyloxy side chains on the hydroquinone moiety alone (PTAHQ12), or on both moieties (PTA12HQ12). To gain further insight into the rheological behaviour of the layered mesophase displayed by PTA6HQ and PTA12HQ, as well as the nematic mesophase shown by PTA6HQ, rheological measurements will be performed. Comparisons between the rheological behaviour of these two liquid-crystalline polymers with the two other polymers, PTAHQ12 and PTA12HQ12, will be made.

The complex relations between molecular structure, crystal structure, phase behaviour, processing, relaxation behaviour (dynamic mechanical as well as dielectric) and ultimate mechanical properties of these polymers will be dealt with in detail in following publications.

EXPERIMENTAL

Materials

Diethyl 2,5-dihydroxyterephthalate (Riedel-de Haen, 98%), 1-bromododecane (Aldrich, 98%), 1-bromohexane (Janssen Chimica, >99%), 2,5-dihydroxybenzoquinone (Aldrich, 98%), 1-dodecanol (Aldrich, 98%), sodium dithionite (Aldrich) as well as acetone (Merck, P.A. quality) were used without further purification. Hydroquinone (Merck, Zur Synthese) was purified by sublimation *in vacuo*. Thionyl chloride (Fluka, >99%), pyridine (Merck, P.A.), as well as 1,1,2,2-tetrachloroethane (Merck, Zur Synthese) were distilled *in vacuo* prior to use.

Figure 1 Schematic representation of the layered mesophase; the main chains are separated by the interdigitating side chains at the layer distance d (after Ballauff¹⁰)

Synthesis of monomers

2,5-Dialkoxyterephthaloyl chlorides were synthesized from diethyl 2,5-dihydroxyterephthalate in three steps by a similar, but slightly modified, procedure as described earlier by Ballauff⁷. 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-didodecyloxyterephthalate. Yield 78%; m.p. 62–64°C (lit.⁷ m.p. 57°C). %C 73.36 (calcd. 73.18), %H 10.64 (calcd. 10.58). ¹H n.m.r. (acetone-d₆): δ = 4.32 (q, OCH₂CH₃), 1.35 (t, OCH₂CH₃, *J* = 7.1 Hz), 7.33 (s, H(Ar)), 4.03 (t, OCH₂C₁₁H₂₃), 1.78 (m, OCH₂CH₂C₁₀H₂₁), 1.52 (m, OC₂H₄CH₂C₉H₁₉), 1.25–1.42 (m, OC₃H₆C₈H₁₆CH₃), 0.88 ppm (t, OC₁₁H₂₂CH₃).

Diethyl 2,5-dihexyloxyterephthalate. Yield 79%; m.p. 41–43°C (lit.⁷ 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(Ar)), 3.97 (t, OCH₂C₅H₁₁), 1.67 (m, OCH₂CH₂C₄H₉), 1.42 (m, OC₂H₄CH₂C₃H₇), 1.26–1.32 (m, OC₃H₇C₂H₄CH₃), 0.87 ppm (t, OC₅H₁₀CH₃).

The acids were obtained from the esters as explained in the following example. A solution of 200.8 g (0.475 mol) of diethyl 2,5-dihexyloxyterephthalate 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-Didodecyloxyterephthalic acid. Yield 96%; m.p. 136–138°C (lit.⁷ m.p. 128°C). %C 71.73 (calcd. 71.87), %H 10.16 (calcd. 10.18).

2,5-Dihexyloxyterephthalic acid. Yield 92%; m.p. 144–146°C (lit.⁷ 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(Ar)), 3.98 (t, OCH₂C₅H₁₁), 1.68 (m, OCH₂CH₂C₄H₉), 1.42 (m, OC₂H₄CH₂C₃H₇), 1.26–1.32 (m, OC₃H₇C₂H₄CH₃), 0.87 ppm (t, OC₅H₁₀CH₃).

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-Didodecyloxyterephthalic acid chloride. Yield 88%; m.p. 69–71°C (lit.⁷ m.p. 60°C). %C 67.65 (calcd. 67.23), %H 9.06 (calcd. 9.17), %Cl 12.41 (calcd. 12.40).

2,5-Dihexyloxyterephthalic acid chloride. Yield 92%; m.p. 37–39°C (lit.⁷ 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^{13,14}. In the first step 15 g (0.41 mol) dry HCl gas was passed into 800 ml (3.56 mol) dodecanol at 50°C¹³. 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-didodecyloxy-*p*-benzoquinone were obtained.

2,5-Didodecyloxy-*p*-benzoquinone. Yield 60%; m.p. 125–126°C (lit.⁶ 124°C). ¹H n.m.r. (CDCl₃): δ = 5.71 (s, H(Ar)), 3.81 (t, OCH₂C₁₁H₂₅), 1.73 (m, OCH₂CH₂C₁₀H₂₁), 1.31 (m, OC₂H₄CH₂C₉H₁₉), 1.15–1.21 (m, OC₃H₆C₈H₁₆CH₃), 0.77 ppm (t, OC₁₁H₂₂CH₃).

In the second step¹⁴ 26.7 g (0.056 mol) of 2,5-dodecyloxy-substituted benzoquinone was dissolved in 600 ml chloroform and mixed with a solution of 191 g (1 mol) Na₂S₂O₄ in 1000 ml water. After stirring for 20 h the red-yellow colour of the solution had disappeared and the 2,5-didodecyloxyhydroquinone precipitated. This product was recrystallized from hexane and was obtained as white needles.

2,5-Didodecyloxyhydroquinone. Yield 82%; m.p. 104.7°C (lit.⁶ 102.5°C). ¹H n.m.r. (DMSO-d₆): δ = 6.40 (s, H(Ar)), 3.82 (t, OCH₂C₁₁H₂₅), 1.65 (m, OCH₂CH₂C₁₀H₂₁), 1.39 (m, OC₂H₄CH₂C₉H₁₉), 1.35–1.25 (m, OC₃H₆C₈H₁₆CH₃), 0.86 ppm (t, OC₁₁H₂₂CH₃).

Polymerization

Polymers were synthesized by polycondensation in solution. In a typical example 39.49 g (97.9 mmol) of 2,5-dihexyloxyterephthalic acid chloride and an equivalent amount of hydroquinone (10.78 g) were added to 290 ml of 1,1,2,2-tetrachloroethane, which was already present in a three-necked flask fitted with a dropping funnel, a nitrogen inlet and a stirring unit. The resulting mixture was heated to obtain a homogeneous solution, cooled to room temperature — a small part of the hydroquinone did not dissolve — and a four-fold excess of pyridine (25 ml) was slowly added over 20 min. After the pyridine had been added completely, stirring of the highly viscous and turbid solution was continued for approximately 3 h to complete the reaction. The solution was diluted with approximately twice the volume of solvent and poured into a seven-fold volume excess of methanol (ca. 3.5 litres). The polymer precipitated, and was filtered, washed with methanol and dried to constant weight *in vacuo* at 60°C. Yield was nearly quantitative.

It is worth noting that, in the polymerization process in which the 2,5-didodecyloxy-substituted hydroquinone is one of the monomers, the solution turns red when the pyridine is added. This is probably caused by the formation of a charge-transfer complex and was also noted by others during melt polymerization⁶. After a short while, when the polymerization reaction has actually started, the solution becomes yellow.

The inherent viscosities of the synthesized polymers were between 0.94 and 3.32 dl g⁻¹ for PTA12HQ and between 1.61 and 2.33 dl g⁻¹ for PTA6HQ. For

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^{6,7,10} 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 *T_s*, *T_m* and *T_i* (see Table 1 and Figure 2). The first-order transition at the lowest temperature, *T_s*, is caused by a disordering of the side chains. At this temperature conformational and positional order of the side chains decreases^{10,15}. In the first heating run it is located at 108°C ($\Delta H \approx 50$ J g⁻¹) and in the second heating run at 38°C ($\Delta H \approx 15$ 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 A¹⁰. Irrespective of the polymer's initial crystal form the polymer is in the less ordered structure A' above the side-chain disordering temperature *T_s* (ref. 16). The endotherm at *T_m* has been ascribed to the transition to the layered mesophase, *L_m* (ref. 10). Above this

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

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

Polymer	η_{inh} (dl g ⁻¹)	<i>T_s</i> (°C) ^a	<i>T_m</i> (°C) ^b	<i>T_n</i> (°C) ^c	<i>T_i</i> (°C) ^d
PTA12HQ	2.3	108/38	161/175	—	243/243
PTA6HQ	2.3	—	183/177	233/221	286/282
PTAHQ12	0.7 ^e	118/80	—	—	239/242
PTA12HQ12	1.4	82/87	—	—	189/188

^a Side-chain disordering temperature

^b Main-chain melting temperature, formation of layered mesophase

^c Transition temperature from layered mesophase to nematic mesophase

^d Transition temperature to isotropic melt

^e Measured in *p*-chlorophenol at 50°C

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 *L_m* has a value comparable to that of modification A¹⁰. Throughout this paper this temperature will be referred to as the main-chain melting temperature. The lower value of *T_m* in the first heating run (compared to the second heating run) may be explained by slight differences in the structure of phase A' in first and second heating runs. Eventually the parallel ordering of the main chains is lost at the clearing temperature *T_i* and an isotropic phase is formed. The phase behaviour of PTA12HQ is shown schematically in Figure 3.

Several batches of PTA12HQ were synthesized and

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_i . On cooling from the isotropic melt the layered mesophase L_m is passed (monotropic behaviour)

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_s , an intermediate phase is formed, which transforms to the isotropic melt at the clearing temperature T_i

indeed found by others that PTAHQ12 is in crystal form B at room temperature⁶. 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_i 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.*⁶.

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_s 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.*⁶. They showed that the layer spacing of PTAHQ16, in the temperature region between T_s 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 PTAHQ12²⁰) it seems justifiable to suppose that PTAHQ12 is in a phase resembling phase B between T_s 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 85°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 ($\eta_{inh} = 2.3 \text{ dl g}^{-1}$), PTA12HQ ($\eta_{inh} = 2.8 \text{ dl g}^{-1}$), PTAHQ12 ($\eta_{inh} = 0.7 \text{ dl g}^{-1}$) and PTA12HQ12 ($\eta_{inh} = 1.4 \text{ dl g}^{-1}$) were characterized with a Rheometrics dynamic spectrometer. The complex viscosity η^* 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, 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^{9–11}, 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 9 Complex viscosity η^* at 10 rad s^{-1} as a function of temperature: (a) PTAHQ12 (▼) and PTA12HQ12 (●); (b) PTA12HQ (▲); (c) PTA6HQ (■)

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 ($[\eta] = 0.48 \text{ dl g}^{-1}$) have been published recently by Schrauwen *et al.*¹², 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 melt²¹ and is also observed for lyotropic polymers²². Thus the assignment of this phase by Falk¹¹ 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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Figure 10 Storage and loss moduli of PTA6HQ in the solid phase ($\square$, $\blacksquare$, 150°C), the layered mesophase ($\triangle$, $\blacktriangle$, 200°C), the nematic mesophase (∇ , $\blacktriangledown$, 250°C) and the isotropic phase ($\circ$, $\bullet$, 295°C). Open symbols refer to the storage modulus G' , closed symbols to the loss modulus G'' .