Kinetics of isotropic-smectic phase transitions in a liquid-crystalline polyether with a methylene spacer of 12 carbons*

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SUMMARY

The isotropic-smectic (s_B or s_G) mesophase transition in a thermotropic main chain polyether based on bis(4-hydroxyphenoxy)-p-xylene with a methylene spacer having 12 carbons has been studied by polarized light microscopy and differential scanning calorimetry. The apparently nucleation-controlled transition followed the general Avrami equation with an exponent value between 2.5 and 3.2. The smectic domains grow more rapidly along the chain axis than in the perpendicular direction. The growth rate exhibited the following temperature (T) dependence: $G = G_0 \exp\left(\dfrac{-K_g}{T(T^\circ_i - T)}\right)$ where G_0 and K_g are constants and T°_i is the equilibrium clearing temperature. A second Arrhenius-activated process was evident at high temperatures. The data presented in this paper are critically compared with data previously reported for similar main-chain polyethers with methylene spacer groups having 9 and 11 carbons in order to reveal possible odd-even effects.

INTRODUCTION

There have been relatively few reports dealing with the kinetics of isotropic-mesomorphic state transitions, e.g. ref. (1-5). This paper is a follow-up paper and presents data for a main-chain polyether of the same class as those studied in ref. (5). The polymers dealt with in ref. (5) were based on bis(4-hydroxyphenoxy)-p-xylene and two different methylene spacer groups with 9 and 11 carbons respectively. This mesogen can adopt different conformational states, i.e. it is semiflexible. The polymers studied in ref. (5) are referred to as HPX-C9 and HPX-C11. Data are here reported for the isotropic-smectic mesophase transition of a thermotropic main-chain polyether (denoted HPX-C12) based on bis(4-hydroxyphenoxy)-p-xylene and a methylene spacer containing 12 carbons. Comparison is made with the earlier data for HPX-C9 and HPX-C11, i.e. with polymers containing spacer groups having an odd number of methylene carbon atoms. In a previous paper (6), it was demonstrated that polymers having spacer groups with an even number of methylene carbon atoms, e.g. HPX-C12, exhibited a higher degree of order than the corresponding polymers with spacer groups having an odd number of carbons. It was also shown that the liquid crystalline phase directly obtained from the isotropic melt was an ordered smectic phase, either s_B or s_G. One of the main tasks of the work reported in the present paper was to see whether

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this difference in order is also reflected in the kinetics of the phase transition from an isotropic to a smectic structure.

The first paper (5) in the series showed that the isotropic - smectic mesophase transition in HPX-C9 and HPX-C11 displayed all the characteristics of a nucleation-controlled process. The process followed the general Avrami equation with an exponent typically between 2.5 and 3.0. The growth rate (G) of the mesomorphic domains was under isothermal conditions constant with time and found to be greater parallel than perpendicular to the chain axis. The linear growth rate in any direction exhibited the temperature (T) dependence:

$$G = G_0 \exp\left(\frac{-K_g}{T(T_i-T)}\right) \qquad \qquad ...(1)$$

where G_0 and K_g are constants, and T_i is the equilibrium clearing temperature. A second process which occurred at a rate almost comparable with the isotropic-smectic phase transition at high temperatures displayed an Arrhenius-type temperature dependence with an activation energy of 400-850 $kJ(mol)^{-1}$. This indicates substantial rearrangement, i.e. perfection of the smectic mesophase, occurring without nucleation. This process followed the Avrami equation with an exponent of 2.0-2.2.

EXPERIMENTAL

A liquid-crystalline polyether based on bis(4-hydroxyphenoxy)-p-xylene and a methylene spacer containing 12 carbons was prepared according to ref. (6). The structure of the polymer here referred to as HPX-C12 is:
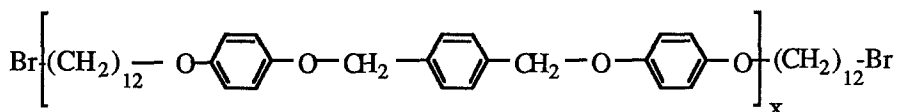
The number average molecular mass, according to end-group analysis, was 7 300. The kinetic studies of the isotropic-smectic mesophase transition were carried out by polarized light microscopy using a Leitz Ortholux POL BK II equipped with a Mettler Hot-stage FP 82 and by differential scanning calorimetry (d.s.c.) using a temperature- and energy-calibrated Perkin-Elmer DSC-7.

Polarized light microscopy was performed in the hot stage by first heating the 10 μm samples to 495 K, holding them at that temperature for 1 min and then cooling them at a rate of 20 $K(min)^{-1}$ to the experimental isothermal temperature (T). The growth of the mesomorphic smectic domains was recorded under the isothermal conditions by taking photos at different times (t). A linear relationship was established between mesomorphic domain size and time (t). The mesophase growth rate (G) was measured for at least 8 different directions from a central point in each domain. Mean values for the linear growth rate (G_{av}) were obtained by considering the growth rates recorded in all possible directions. The directional dependence of G with respect to the director (direction of largest refractive index) was studied by inserting a λ-plate in the

beam. The samples were finally heated at a rate of 1 K(min)$^{-1}$ in the hot stage to obtain the clearing temperature (T_i).

Samples weighing about 5 mg were cooled in the DSC apparatus at a rate of 80 K(min)$^{-1}$ from 495 K to the experimental isothermal temperature (T). The exothermal heat associated with the first-order transition was recorded under the isothermal conditions. The samples were kept at the maximum temperature (495 K) for 1 min. These data were analysed according to the general Avrami equation:

$$1 - \frac{\Delta h}{\Delta h^{\circ}} = e^{(-K(t-\tau)^n)} \qquad \qquad ...(2)$$

where Δh is the integral heat evolved in the process during time t, Δh° is the total heat evolved in the exothermal process, K and n are the parameters to be determined, t is the time and τ is the induction time at which the exothermal process is initiated. The samples were finally heated at a rate of 1 K(min)$^{-1}$ to reveal the clearing temperature (T_i).

RESULTS AND DISCUSSION

Fig. 1 presents a summary of the calorimetric data for HPX-C12. The exothermal heat evolved is clearly associated with two different processes: (a) a rapid process which occurs more slowly at higher temperatures; and (b) a slow process which in the graph is only revealed at 478 K. This process slowed down with decreasing temperature and was in fact not observed at the lower temperatures. The observed behaviour of HPX-C12 is very similar indeed to that of HPX-C9 and HPX-C11 (5), the only difference being that the time lag between the two processes is greater for HPX-C12 than for HPX-C9 and HPX-C11. The total energy evolved in the rapid process (Δh°) decreased in a linear way with increasing temperature from about 50 kJ(kg)$^{-1}$ at 473 K to about 10 kJ(kg)$^{-1}$ at 478 K. The decrease in Δh° demonstrates that the phase transition involves a progressively smaller fraction of the sample at the higher temperatures, i.e. it reflects the multicomponent nature of the polymer. This behaviour was also observed in HPX-C9 and HPX-C11 and can be explained by the chain-length-polydispersity of the polymers. No first order exothermal process occurred for HPX-C12 at temperatures greater than 479 K.

It was shown in the previous paper (5) that the slow process exhibited an Arrhenius-type temperature dependence with an activation energy of 400-800 kJ mol^{-1}. This is indicative of a rearrangement process in the smectic phase. No accurate value of the activation energy could be obtained for the slow process in HPX-C12 due to the fact that it was only recorded within a temperature range of 0.5 K.

Fig. 2 demonstrates that the rapid process in HPX-C12 can be adapted to the Avrami equation (eq. (2)). The slope of the lines, i.e. the Avrami exponent (n), is almost constant at 2.8±0.3. This is again in agreement with earlier data for HPX-C9 and HPX-C11 (5). The slow process was also in agreement with the Avrami equation and the Avrami exponent values recorded (2.0-2.3) are very similar indeed to those earlier reported for HPX-C9 and HPX-C11 (5).
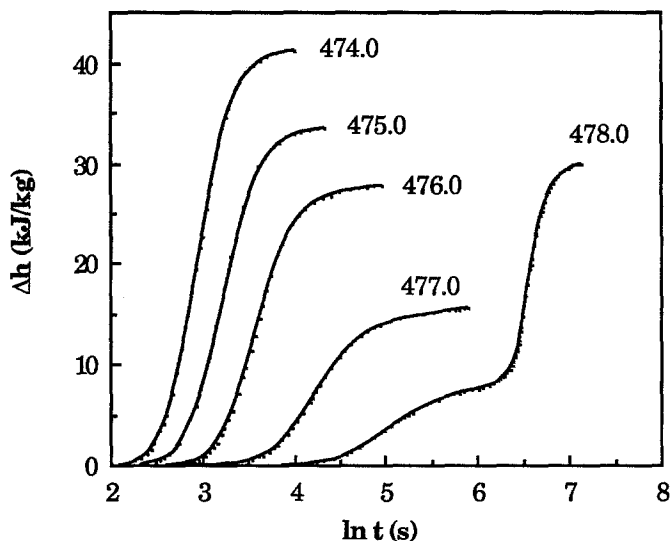
Figure 1. Exothermal heat (Δh) as a function of time (t) at different temperatures.
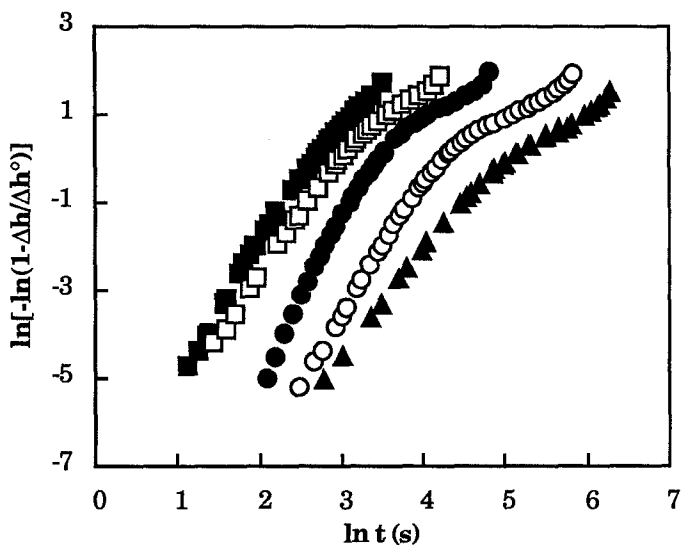

Figure 2. Avrami plots obtained at different temperatures: 474.0 K (■); 475.0 K (□); 476.0 K (●); 477.0 K (○); 478.0 K (▲).

The clearing temperature (T_i) increased only moderately with increasing mesophase formation temperature (T); by 0.5 K in the T range 471-476 K. This was also the case for HPX-C9 and HPX-C11 (5). The equilibrium clearing temperature (T°_i) was determined to 485.9 K by extrapolation of the T-T_i data to T=T_i=T°_i by analogy with the commonly used Hoffman-Weeks plot (8). This

equilibrium clearing temperature should be correct within 2 K according to arguments given in the previous paper (5).
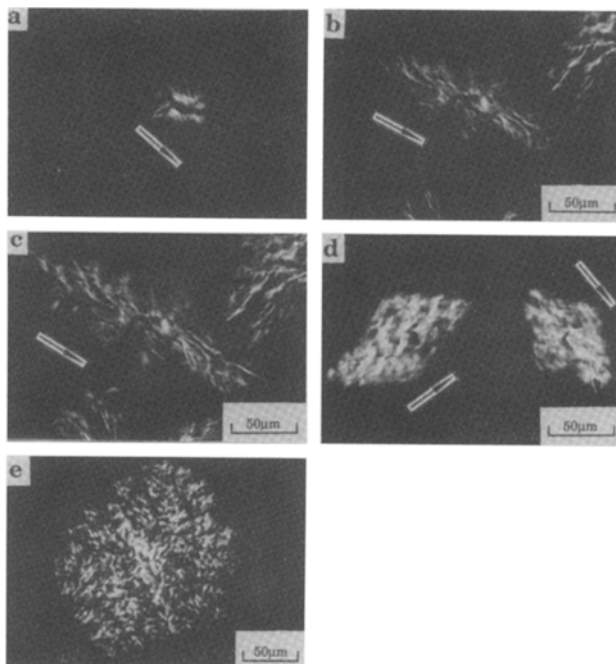

Figure 3. Polarized photomicrograph showing the shape and growth of the mesomorphic domains at (a) 475.1 K, 40 s; (b) 475.1 K, 110 s; (c) 475.1 K, 200 s; (d) 472.1 K; (e) 469.0 K. Arrows indicate the direction of maximum refractive index.

The polarized photomicrographs shown in Fig. 3a-c demonstrate that the growth of the mesophase domains is strongly anisotropic. The mesophase domains have an ordered smectic structure, s_B or s_G (6). The growth rate was more rapid along the direction of maximum refractive index and reaches a minimum perpendicular to this direction. Samples cooled to room temperature exhibited, in each domain, cracks parallel to the direction of maximum refractive index. The structure of the studied polymer indeed suggests that the molecular director should be parallel to the direction of maximum refractive index. Polarized light microscopy also showed that the chain orientation within the domains is almost uniform. Some low-angle reorientation of the molecular director was occasionally found as "kink-bands" within the mesomorphic domains. The growth rate is thus more rapid along than transverse to the molecular director, a result which was also obtained for HPX-C9 and HPX-C11 (5).

The anisotropy of the mesophase growth rate was more pronounced at the higher temperatures. The mesomorphic domains became very elongated in the chain axis direction, often dendritic when growing at the highest temperatures, typically above 473 K (Fig. 3c). The morphology was highly

fibrillar with dendritic structures nucleated on the fibres. The dendrites formed new main fibres which served as new nucleating sites. The different fibrils within a certain domain always exhibited a single domain-unique molecular director.

Intermediate temperatures (470.0 - 473.1 K) resulted in a domain geometry which was more quadratic or rhombic (Fig. 3d). In some cases, preferentially near 473 K, the mesomorphic domains exhibited a dendritic substructure, also in this case with a domain-unique molecular director.

At low temperatures (T=469.0 K), the mesomorphic domains exhibited no preferred growth direction and the structures obtained were almost circular (Fig. 3e). The growth occurred from the centre by the growth of already nucleated mesomorphic sub-domains and new nucleations of mesomorphic sub-domains on the existing mesophase domains. Each sub-domain exhibited a uniform chain orientation. No orientation-correlation was found between adjacent sub-domains. The boundaries between the different sub-domains were clearly seen even when the domains came into contact with each other.
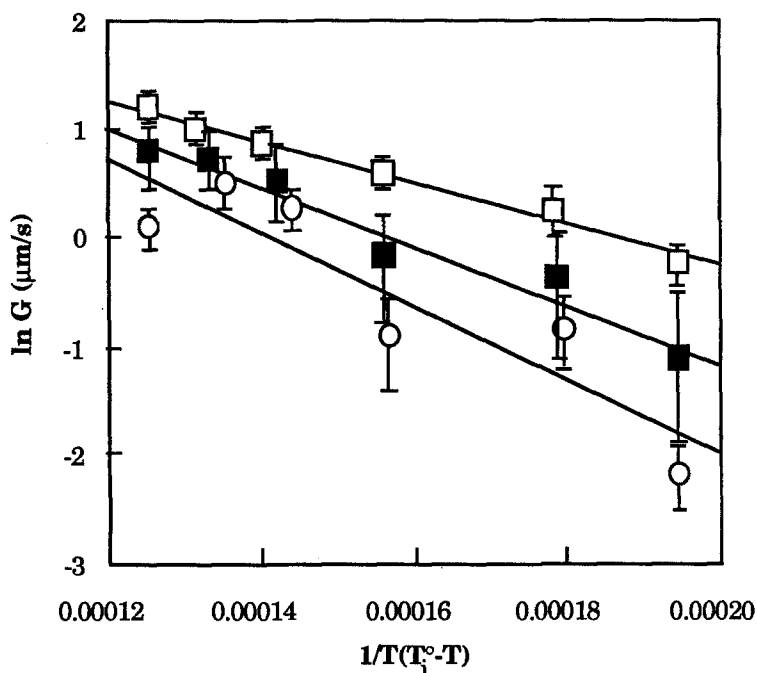
Figure 4. Logarithm of the linear growth rate (G) of the smectic domains plotted as a function of $\frac{1}{T(T^\circ_i - T)}$: mean value (O); parallel to the chain axis direction (●); perpendicular to the chain axis direction (■). The bars indicate standard deviations of single data points.

The mesophase growth rate data are presented in Fig. 4 and Table 1. Regression analysis showed that the linear growth rate data are best described

by eq. (1). This equation was successfully fitted to the rate of growth in the chain axis direction (G_p) and in the transverse direction (G_t), as well as to the average growth rate (G_{av}). The d.s.c. equivalent of the previous equation, eq. (3), was successfully used to fit the calorimetric data and the results are presented in a comparison with K_g values obtained by polarized light microscopy in Table 1.

$$(t_{0.4})^{-1} = C \exp \left(\frac{-K_g}{T(T^\circ_i - T)} \right) \qquad \qquad ...(3)$$

where $t_{0.4}$ is the time to reach 40% conversion by the rapid process and C and K_g are constants. The latter is a constant which depends on the surface free energy (σ_i) and the growth mechanism.

Table 1. Phase transition kinetics

Polymer	$<K_g>$(micr)[a]	$<K_{gc}>$(micr)[b]	$<K_{gp}>$(micr)[c]	K_g(d.s.c.)[d]
HPX-C12	26 900	17 500	36 350	23 700
HPX-C9[e]	23 600	-	-	21 600
HPX-C11[e]	28 400	23 000	33 800	26 000

a) Mean value, from polarized light microscopy according to eq. (1)
b) Growth in main direction, by polarized light microscopy according to eq. (1)
c) Growth in transverse direction, by polarized light microscopy according to eq. (1)
d) From DSC according to eq. (3)
e) Data from ref. (5)

The K_g values presented in Table 1 demonstrate the similarity of the exothermal process recorded by d.s.c. and the growth of the mesomorphic domains as recorded by polarized light microscopy. The directional dependence of K_g is very pronounced: the value associated with chain axis growth is only 50% of the value obtained for transverse growth (Table 1). A very similar directional dependence of the growth rate and of the K_g values was obtained for HPX-C9 and HPX-C11 (5). The absolute values of K_g were also very similar for the different polymers (Table 1).

The calorimetric data agree with the results obtained by polarized light microscopy regarding the Avrami exponent. The latter implied that the growth rate of the mesomorphic domains was constant in time and that growth was not truly three-dimensional. Polarized light microscopy also showed that nucleation was a mixture of thermal and athermal nucleation. The Avrami exponent value recorded (2.8±0.3) is consistent with a mixed thermal/athermal nucleation followed by growth at a constant rate in less than three-dimensions (7).

CONCLUSIONS

The polymer studied, a thermotropic semi-flexible main-chain polyether based on bis(4-hydroxyphenoxy)-p-xylene with a methylene spacer having 12 carbons, exhibited an isotropic-smectic (ordered smectic phase; s_B or s_G) phase transition and at lower temperatures the formation of solid crystals. This class of polymers exhibited a pronounced odd-even dependence of clearing

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temperature/enthalpy/entropy, melting temperature and degree of order regarding number of methylene carbon atoms in the spacer group (6). This study, a follow-up to ref. (5), has shown by differential scanning calorimetry and hot-stage polarized light microscopy that the isotropic-smectic phase transition exhibits an odd-even dependence of the equilibrium transition temperature. The growth rate anisotropy with a pronounced maximum in growth rate in the chain axis direction, the directional dependence and the absolute values of K_g (for definition, see eqs. (1) and (3)) and the Avrami exponent values were however the same for polymers with odd- and even-numbered spacer groups.

A second and slower process occurred at the highest temperatures, above 478 K. A similar process was also observed in HPX-C9 and HPX-C11. The exothermal energy involved in the process seems to be of the same order of magnitude for the different polymers, about 20 kJ(kg)$^{-1}$. The process was however initiated earlier in those polymers which had an odd-numbered spacer. The nature of the slow process remains unknown but a few important facts can be listed: (i) It always follows the initial formation of the smectic phase, i.e. it does not occur from the isotropic melt; (ii) It is Arrhenius-activated and proceeds at a higher rate at higher temperatures. It should thus not be controlled by nucleation. (iii) It involves a considerable enthalpy change, about 20 kJ(kg)$^{-1}$.

ACKNOWLEDGEMENTS

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