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Phase Transitions in Poly(heptane-1,7-diyl biphenyl-4,4'-dicarboxylate). SAXS, WAXS and DSC Study

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Summary: The main-chain thermotropic liquid-crystalline poly(heptane-1,7-diyl biphenyl-4,4'-dicarboxylate) (P7MB) was investigated by time-resolved small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), and differential scanning calorimerty (DSC). Nonisothermal crystallisation with different rates of cooling and heating was used. On cooling, two phase transitions are observed, isotropic melt - smectic (I-Sm) and Sm- three-dimensional crystalline structure (Sm-Cr), whereas on heating only one transition is observed, Cr-I transition. The transition enthalpies were calculated. Temperature dependences of d-spacings of all crystalline peaks and of the peak observed at high values of scattering vector in the SAXS region were derived. The temperature dependence of the degree of crystallinity was established, based on the integrated intensities of the crystalline peaks and amorphous halo in WAXS.

Keywords: DSC; liquid crystalline polymers; phase transitions; polyesters; WAXS

Introduction

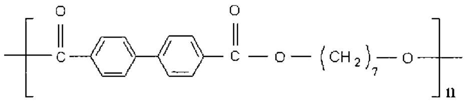
In the last decades, liquid crystals (LC) attract great attention because of their broad spectrum of applications. A deep understanding of their structure formation and processes under different conditions as well as the nature of phase transitions will show the way to creating materials with predictable and desired properties.

P7MB belongs to the class of main-chain liquid-crystalline polyesters. It consists of biphenyl group as mesogen, and seven methylene groups as flexible spacer. So far, several publications have been devoted to investigations of polymeric dibenzoate series with all-methylene[1-4] and oxymethylene spacers[5], as well as blends[6] and statistic copolymers[7], composed of monomers with spacers of different lengths.

Since P7MB is known to be thermotropic LC[1-4], we focus our attention on the investigation of phase transitions, observed during nonisothermal processes.

Experimental

The chemical structure of P7MB is:



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P7MB was synthesized by melt transesterification of the diethyl ester of biphenyl-4,4'-dicarboxylic acid and the corresponding diol, using isopropyl titanate as catalyst. The details of the preparation have been described elsewhere[3]. It inherent viscosity is 1.03 dL/g, measured in chloroform at 25 °C.

Time-resolved SAXS and WAXS measurement were carried out at synchrotron DESY, Hamburg, Germany. Cooling (v_c) and heating (v_h) rates were 2 °C/min and 12 °C/min, respectively. Data treatment was performed using Bragg's law ($d = \lambda/2\sin\theta = 1/s$), where λ is the X-ray beam wavelength, θ is the scattering angle, and s is the scattering vector. Degree of crystallinity was calculated from the equation: $X_{cr} = \dfrac{\Sigma I_i}{I_{tot}}$, where ΣI_i is the sum of integrated intensity of crystalline reflections and I_{tot} is the total integrated intensity under the WAXS pattern.

Differential scanning calorimetry was applied to identify the number and temperature intervals of the observed phase transitions. Measurements were carried out on a Perkin-Elmer DSC7 apparatus under nitrogen atmosphere. A heating rate of 10 °C/min cooling rates were used, 2, 4, 6, 10, 20 °C/min.

Results and discussion

On cooling, P7MB undergoes two phase transitions, whereas during heating, only one transition is observed (Fig. 1a). The first exotherm is single for all cooling rates, whereas the second transition is split into two exotherms.

The high-temperature transition is attributed to I-Sm phase transformation[1,2]. Upon cooling from isotropic state (Fig. 1a, curve at 167.5 °C), the transition to smectic phase manifests itself by the growth of a diffraction peak at $s \approx 0.587$ nm^{-1} (1.705 nm), originating from the smectic layer periodicity, d_s, and a liquid-like diffuse scattering in WAXS pattern, centered at $s \approx 2.164$ nm^{-1} (0.462 nm), which is characteristic of interchain packing correlation (Fig. 2a, curve at 138.5 °C). The smectic layers are formed by the mesogens and one and the same macromolecule passes through many layers. Watanabe and Hayashi[1,2] elucidated the smectic type as S_{CA}, where the average macromolecular axis is normal to the smectic layer surface and the mesogen axes are tilted with respect to the layer normal in such a way that the consecutive mesogens form an angle of about 60° - i.e. the mesogens in every neighboring layers are tilted with respect to the layer normal at the same angle but in the opposite directions.

The maximum of the transition exotherm shows a linear dependence on v_c (see Fig.1b - upper plot). The shift of the transition with v_c is due to the undercooling effect. The enthalpy for all the used cooling rates is constant, $\Delta H_{\text{I-S}} \approx 15.8$ J.g^{-1}, suggesting that the quantity of the material, which is transformed into a smectic phase, is independent of v_c. The temperature interval, in which Sm phase is stable, varies from 5.22 °C (at $v_c = 4$ °C/min) to 14.79 °C (at $v_c = 20$ °C/min). The general tendency is expansion of the interval with increasing cooling rate, which could be explained by the conditions of crystallization onset. At high cooling rates, the crystallization is hindered and it starts at lower temperatures.

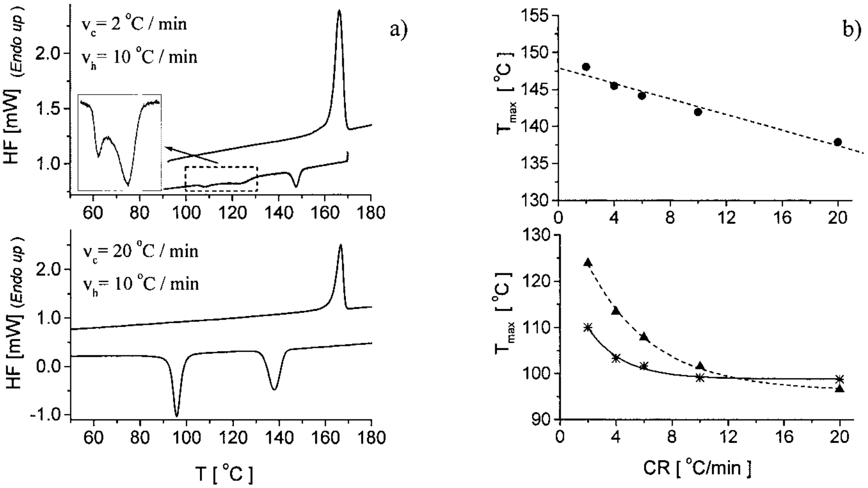

Figure 1. a) DSC curves of P7MB, starting with cooling from isotropic melt a subsequent heating: cooling rate 2 °C/min (upper plot) and 20 °C/min (bottom plot), heating rate 10 °C/min. HF is the heat flow; b) Dependence of transition temperatures on cooling rate, presented by the exotherm maxima: I-Sm transition (upper plot) Sm-Cr transition with double exotherm (lower plot).

Second transition interval of the DSC cooling runs corresponds to transformation to the Cr phase. When v_c is low (2 °C/min), two different exotherms are well seen (Fig.1a - upper curve), while for 10 °C/min the peaks merge and only the peak shape asymmetry is a hint for the existence of two exotherms. Once the high cooling rate is used, the shape is even almost symmetric (Fig.1a - lower curve). The results for the cooling rate dependence of the two exotherm maxima are plotted in Figure 1b (lower graph). They follow an exponential law. T_{max} of the first DSC peak component decreases faster than the second one. The enthalpies of the exotherms vary in a different way (see Table I). $\Delta H_{\text{Sm-1-Cr}}$ decreases with v_c, whereas

$\Delta H_{\mathrm{Sm\text{-}2\text{-}cr}}$ increases. It is worth noting that the sum of both enthalpies is constant ($H_{\mathrm{Sm\text{-}Cr}} \approx 19.4$ J.g^{-1}). The fact could be explained as a competition between two kinetics dependent processes. At low v_c, the prevailing mechanism is associated with the first exotherm component, whereas at high v_c the mechanism connected with the second exotherm component is dominant. It could be speculated that there exists polymorphism, similar to the case discussed by Bae et al.[8], and the structure transformation goes through different metastable phases under different crystallization conditions, but since we do not have any unambiguous proof, we will not concern the problem here.

Table I. Transition enthalpies, calculated from DSC curves at different cooling rates and a heating rate of 10 °C/min. $\Delta H_{\mathrm{Sm\text{-}1\text{-}Cr}}$ and $\Delta H_{\mathrm{Sm\text{-}2\text{-}Cr}}$ are enthalpies for first and second component of the double exotherm, observed at Sm-Cr transition and $\Delta H_{\mathrm{Cr\text{-}I}}$ is the enthalpy of fusion.

		Cooling rate (°C/min)				
		2	4	6	10	20
$\Delta H_{\mathrm{Sm\text{-}1\text{-}Cr}}$	(J.g^{-1})	13.96	13.15	10.91	7.60	4.59
$\Delta H_{\mathrm{Sm\text{-}2\text{-}Cr}}$	(J.g^{-1})	5.54	6.49	8.50	12.01	14.48
		Subsequent heating at 10 °C/min				
$\Delta H_{\mathrm{Cr\text{-}I}}$	(J.g^{-1})	31.2	31.2	31.9	32.1	32.6

In the case of v_c=2 °C/min, at the beginning of this interval, six crystalline peaks overlapping the amorphous halo are seen on WAXS patterns (see Fig.2a, the curve at 67.5 °C and the inset). Their intensities gradually increase with decreasing temperature. It seems that the smectic layer spacing, d_s, gradually decreases from the beginning to the end of the transitional area, and the peak is preserved in the crystalline phase (Fig. 2b). Its value in Cr phase is $d_s \approx$ 1.672 nm. In fact, the smectic peak probably disappears and a crystalline peak, with d-spacing very close to that of the smectic periodicity, grows[3,9] but, because of the difficulties originating from the deconvolution procedure, we were not able to distinguish them.

In Fig. 2c, index of crystallinity, X_{Cr}, deduced from WAXS, is shown. Since some of the crystalline peaks are very weak and, after the deconvolution procedure, they were estimated with comparatively high levels of errors, we used only the integrated areas under the highest two peaks (p.1 and p.3 in the inset of Fig 2a) in calculations of crystallinity. We believe that the degree of crystallinity is proportional to these values since we assume only one crystalline structure on the basis of some previous results. On cooling, X_{Cr} grows stepwise during transformation from the Sm into Cr phase.

The final crystalline structure is stable in the low-temperature region with an upper limit of ca. 112 °C (derived from X-ray experiments) and the peaks depend very slightly on temperature. The particular values for the temperature expansion coefficients (β_T) of all Cr peaks are shown in Table II.

On heating, the crystalline structure obtained on cooling is preserved up to the isotropisation temperature. This fact is supported by the presence of all crystalline peaks. The temperature dependences are the same as those for cooling at temperatures below 112 °C (see Table II). The degree of crystallinity gradually decreases (from values of ca. 20 % to 10 %) up to the melting interval, in which it reaches zero.

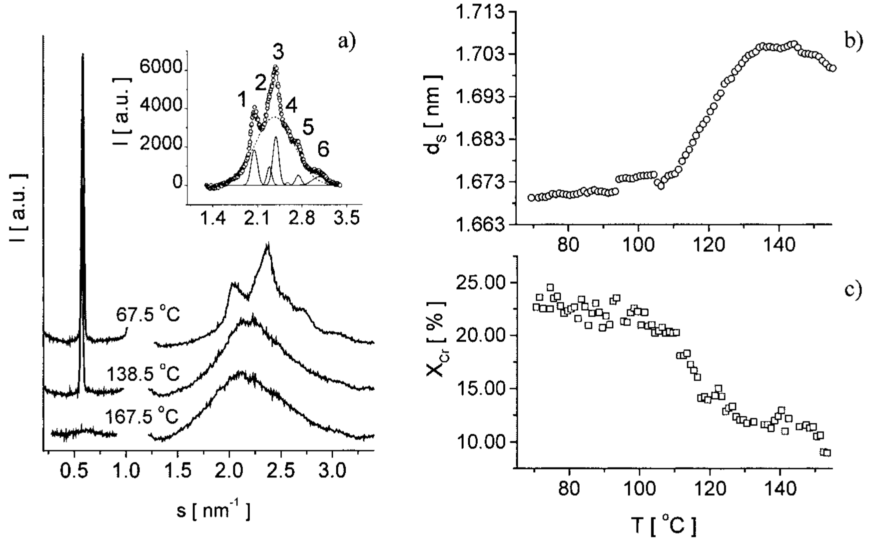

Figure 2. a) X-ray diffractograms at different temperatures: 167.5 °C - I melt, 138.5 °C - Sm LC phase, 67.5 °C - Cr structure. The inset shows assignment of the crystalline peaks (for details, see the text); b) smectic or crystalline d-spacing, d_s, versus temperature; c) index of crystallinity, X_{Cr}, versus temperature.

The transition temperature during heating is constant (≈166.7 °C), showing that the final structure, formed in the solid state, is the same for all cooling rates. One could make a conclusion that despite of possible different ways of reaching the final structure, it is the same and independent of the cooling rate. The enthalpies of fusion are shown in Table I (last row). Their values slightly increase with the rising cooling rate and constant heating rate.

Unfortunately, because of the low degree of crystallinity, we were not able to calculate the parameters of crystal unit cell and the type of symmetry. We only assumed monoclinic or triclinic system of symmetry, similarly to the conclusion made by Osada et al.[10] for P5MB. The direction of the d-spacing between consecutive mesogens is collinear with crystallographic *c*-axis; because of the zig-zag mesogen arrangement, the length of the unit cell along (001) is around 3.344 nm - i.e., twice d_S.

Table II. d-spacings of crystalline peaks in the Cr phase (at 41 °C) and their temperature dependences, described by temperature expansion coefficients, β_T. Cooling rate – 2 °C/min and heating rate – 12 °C/min. The cooling values are valid below 112°C.

Peak	1	2	3	4	5	6
d^{cool} (nm)	0.489	0.438	0.419	0.390	0.365	0.326
$\beta_T^{\text{cool}} = \delta d/\delta T$ (nm/°C)10^{-5}	4.2 ± 0.2	8.7 ± 0.6	11.8 ± 2	80 ± 4	3.0 ± 0.2	8.2 ± 0.5
d^{heat} (nm)	0.489	0.437	0.419	0.389	0.364	0.326
$\beta_T^{\text{heat}} = \delta d/\delta T$ (nm/°C)10^{-5}	4.6 ± 0.4	8 ± 0.9	11.5 ± 0.7	93 ± 8	3.25 ± 0.04	9.2 ± 0.9

Conclusion

P7MB shows enantiotropic behavior on cooling and monotropic on heating for all the used cooling and heating rates. Smectic structure is formed for all cooling rates on cooling and the temperature interval of its stability increases with rising cooling rate. The quantity of the material, which is transformed into smectic phase, is independent of the cooling rate. The smectic layer spacing slightly increases with decreasing temperature. The crystalline structure, formed at the end of structure transformation during cooling, is the same for all the used cooling rates. The structure is stable below 112 °C on cooling and up to the melting interval on heating. Cr structure has low symmetry, with plausible monoclinic or triclinic symmetry of the unit cell.

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