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Non-equilibrium thermal behaviour of a main chain thermotropic polymer

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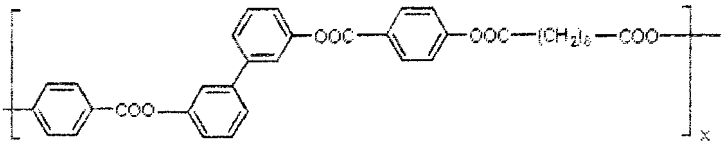
The effect of thermal treatment on the thermodynamic properties and structure of a nematic thermotropic main chain polymer with mesogenic groups containing 3,3′-biphenylene units and octamethylene flexible spacers (BF8) has been studied by DSC and X-ray scattering. We have found that BF8 samples do not crystallize even on very slow cooling from the isotropic state, and possessed a glassy nematic structure at room temperature. The strong influence of the cooling rate on both the enthalpy of the nematic–isotropic transition and the rise of specific heat at the glass transition for BF8 samples was observed. It was attempted to explain this result in terms of the improvement of the nematic structure during cooling.

For polymers with a low clearing temperature non-equilibrium behaviour must be taken into account [1], because at low temperatures the viscosity of the nematic melt is rather high and the time characterizing the process of relaxation of the thermodynamic parameters may be comparable with the time of the thermal experiment. In this case the measured parameters of the transition from the nematic to isotropic (N–I) phase (enthalpy ΔH_{NI} and temperature T_{NI}) will be non-equilibrium.

In this paper we present a calorimetric study of the non-equilibrium thermal behaviour at both N–I and glass transitions for a semi-flexible polyester, containing 3,3′-biphenylene groups and octamethylene spacers:



$\bar{M}_W = 49920$ (BF8), $\bar{M}_W/\bar{M}_n = 2{\cdot}0$, $T_g = 57°C$ and $T_{NI} = 125°C$. The synthesis of BF8 is described in detail elsewhere [2].

We used a DSC (DSM-3 instrument, 'Bioinstrument', Academy of Sciences, Puschino, Russia) connected with a DVC-3 computer. All measurements were made in dry nitrogen. New samples (5–9 mg) were prepared for each measurement. An indium standard was used to determine the enthalpy of the transitions. Two samples of sapphire with different mass were used for the specific heat determinations. Polarizing microscopy observations were made with a hot-stage microscope Boetius (V.E.B. Analitik).

X-ray study of polymer samples was performed on a DRON-3 instrument (Russia) with direct recording of diffractograms at room temperature.

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All samples were heated to $T > T_{\mathrm{NI}}$ (150°C) and held for 15 min in the isotropic state. Samples were then cooled with different rates ($Q = 0{\cdot}2$–$5\,\mathrm{K\,min^{-1}}$) to room temperature.

Figure 1 gives a set of diffractograms obtained at room temperature for BF8 samples, previously cooled from the isotropic melt at different cooling rates. Any crystalline reflections in the diffractograms are absent for samples cooled at $Q > 3\,\mathrm{K\,min^{-1}}$. Small shoulders on the X-ray diffractograms for samples cooled at $Q = 0{\cdot}3$ and $1{\cdot}0\,\mathrm{K\,min^{-1}}$ may be ascribed to the very small amount of crystallites which does not contribute appreciably to the N–I transition parameters [3].

Two halos centred at *c.* $2\theta = 8°$ and 18° were observed for BF8 samples. The halo with $2\theta = 18°$ is related to the interchain distance. The second halo, centred at $2\theta = 8°$, is connected with the layered organization of the mesophase. Similar diffraction patterns were observed by Blumstein [4] for nematic polymers with a high value of the degree of polymerization.

The value of Q strongly affects the transition parameters, as follows from figure 2, which shows thermograms of previously cooled samples. A strong exponential increase of ΔH_{NI} was observed at $Q < 2\,\mathrm{K\,min^{-1}}$ (see figure 3). We fitted the experimental dependence given in figure 3 to the following exponential function:

$$\Delta H_{\mathrm{NI}} = \Delta H_{\mathrm{NI}}(0) + (\Delta H_{\mathrm{NI}}(Q_{\max}) - \Delta H_{\mathrm{NI}}(0)) \exp\left[\frac{1}{k}\left(\frac{1}{Q_{\max}} - \frac{1}{Q}\right)\right]. \tag{1}$$

The fitting parameters were: $\Delta H_{\mathrm{NI}}(0) = 11{\cdot}57 \pm 0{\cdot}61\,\mathrm{kJ\,mol^{-1}}$, $\Delta H_{\mathrm{NI}}(Q_{\max}) = 4{\cdot}4 \pm 0{\cdot}22\,\mathrm{kJ\,mol^{-1}}$ and $k = 2{\cdot}26\,\mathrm{K\,min^{-1}}$. The value of $\Delta H_{\mathrm{NI}}(0)$ corresponding to the cooling rate $Q = 0$ may be considered as an equilibrium value of the N–I transition enthalpy for the defect-free nematic sample. The improvement of the nematic phase is

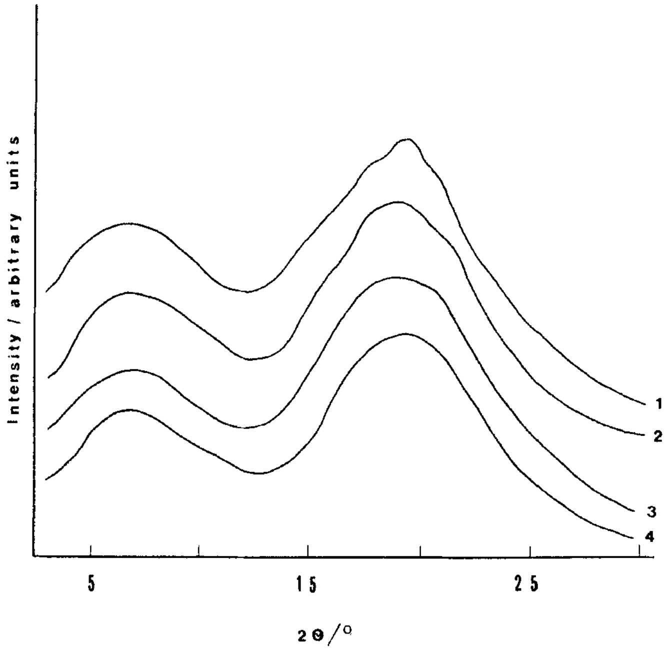

Figure 1. The diffractograms for BF8 samples cooled from the isotropic melt for different cooling rates $Q = 0{\cdot}3$ (1), $1{\cdot}0$ (2), $3{\cdot}0$ (3), and $130\,\mathrm{K\,min^{-1}}$ (4).

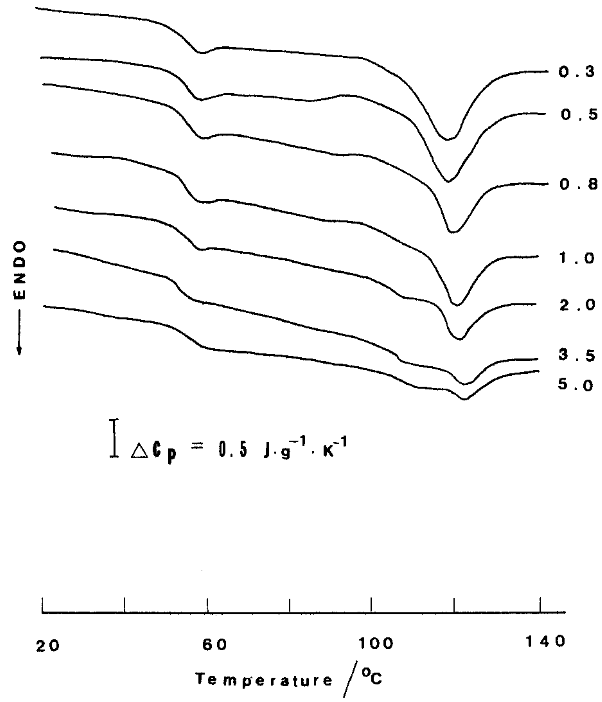

Figure 2. The set of thermograms obtained at a heating rate of 16 K min^{-1} for BF8 samples cooled previously from the isotropic melt for different cooling rates Q in K min^{-1} (the values of Q are indicated on the right hand side of the figure).

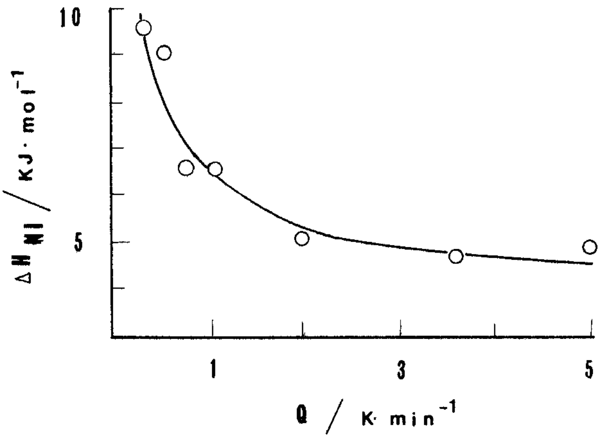

Figure 3. Dependence of the isotropization enthalpy ΔH_{NI} on the cooling rate Q for BF8 samples. The solid line corresponds to the best fit of the experimental points to equation (3).

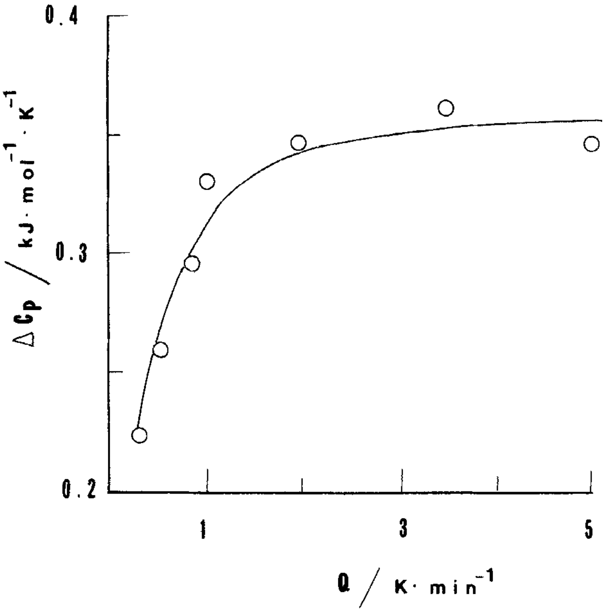

Figure 4. The specific heat rise at the glass transition Δc_p versus the cooling rate Q for BF8 samples. The solid line corresponds to the best fit of the experimental points to equation (4).

evident from DSC data for BF8 samples. The value of $\Delta H_{NI}(Q_{max})$ corresponds to the maximal value of the cooling rate, $Q = 5\,\mathrm{K\,min^{-1}}$, used in our experiment.

Figure 4 presents the dependence of the specific heat change Δc_p at the nematic glass transition on the cooling rate. The value of Δc_p increases strongly with Q.

The dependence of Δc_p on Q for BF8 was fitted to the equation

$$\Delta c_p = \Delta c_p(\infty) + [\Delta c_p(0) - \Delta c_p(\infty)]\exp(-Q/k'), \tag{2}$$

with fitting parameters: $\Delta c_p(\infty) = 0{\cdot}355 \pm 0{\cdot}015\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$, $\Delta c_p(0) = 0{\cdot}130 \pm 0{\cdot}08\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$ and $k' = 0{\cdot}53\,\mathrm{K\,min^{-1}}$ (0 and ∞ correspond to $Q = 0$ and $Q = \infty$). This result can be explained as well as the data for ΔH_{NI} by the improvement of the nematic structure and additional ordering of BF8 samples during slow cooling. The greater this improvement becomes the smaller is the contribution of the defects to the total value of the enthalpy and specific heat of the nematic phase. Therefore the decrease of Δc_p for slowly cooled samples is very consistent with the increase of the isotropization enthalpy (see figure 3). We can estimate the value of the excess enthalpy of a nematic phase connected with such defects

$$\Delta H_{def} = \int_{T_1}^{T_2} (c_p^{\infty}(\mathrm{nem}) - c_p^{0}(\mathrm{nem}))\,dT$$

$$= \int_{T_1}^{T_2} (\Delta c_p(\infty) - c_p(0))\,dT = (\Delta c_p(\infty) - \Delta c_p(0))(T_2 - T_1), \tag{3}$$

where T_1 and T_2 are temperature boundaries of the glass transition, $c_p^0(\mathrm{nem})$ and $c_p^{\infty}(\mathrm{nem})$ are heat capacities of the nematic phase for samples cooled with $Q = 0$ and $Q = \infty$, respectively. The temperature interval of the glass transition $T_2 - T_1$ is about

30–35 K and ΔH_{def} of 6·6–7·7 kJ mol^{-1}. This value of ΔH_{def} is comparable with the difference of $\Delta H_{\mathrm{NI}}(0) - \Delta H_{\mathrm{NI}}(Q_{\mathrm{max}}) = 7{\cdot}17 \pm 0{\cdot}82$ kJ mol^{-1}.

It should be noted that for ordinary glass and amorphous polymers the enthalpy relaxation in the region of the glass transition causes the hysteresis effect [5, 6]. This effect is connected with the relaxation of the number of 'holes' or free volume with temperature. For slowly cooled samples this effect is endothermic because the number of holes increases with temperature. This effect is evident from figure 2.

The endothermic effects for slowly cooled nematic glass samples are also observed. However, for amorphous polymeric glasses the cooling rate does not affect the value of Δc_{p}, whereas for BF8 samples Δc_{p} depends on Q.

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