

Non-equilibrium excess order in the isotropic state of main-chain liquid-crystal-forming polymers

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A new non-equilibrium phenomenon has been recognized in main-chain liquid-crystal polymers. Persistence of non-equilibrium residual short-range nematic-like order can be detected in the isotropic phase up to several minutes after the nematic-to-isotropic transition has occurred. The effect was observed by differential scanning calorimetry and is closely related to the pronounced non-equilibrium effects in the nematic state. As we reported previously, annealing in the nematic phase, on the timescale of hours, is required to bring the temperature and enthalpy of isotropization up to its equilibrium value. Now we find that even in the isotropic state annealing is required in order to achieve thermodynamic equilibrium; only upon holding above T_i is the residual excess nematic-type order fully removed, and thus all memory of previous annealings in the nematic state erased. The non-equilibrium effects are particularly pronounced for higher-molecular-weight polymers. In the case of the α -methylstilbene polyether with alkylene spacers, $M_n = 31\,000$, the time constant of the exponential approach to equilibrium is found to be 2.1 min at $T = T_i + 10^\circ\text{C}$.

(Keywords: liquid crystal; isotropic state; excess order)

INTRODUCTION

In the case of phase transformations in polymeric systems, such as melting or crystal-crystal transitions, studying the variations in transition temperature and enthalpy has often been useful in learning about non-equilibrium states. Thus the values of lamellar crystal thickness, and energy of chain folds and of other crystal defects could be derived from the variation in melting point. In contrast, little experimental information is available at present about the nematic-to-isotropic (N-I) transition, particularly in thermotropic main-chain polymers. (i) One reason is the common belief that both the nematic and isotropic phases are fluid states very close to thermodynamic equilibrium; accordingly there would be no significant deviation of T_i from the equilibrium value¹. (ii) The second reason is the high temperatures of the N-I transition (T_i) in the commonly studied rigid-rod polymers, with T_i often exceeding the decomposition temperature. Even when flexible spacers are introduced into the chain, T_i often remains comparatively high if mesogens and spacers are connected by ester linkages. (iii) Finally, thermal reactivity of the ester group, usually present in the latter polymers, leads to uncontrolled changes in molecular weight in the T_i region, even if no actual decomposition occurs.

Problems (ii) and (iii) can be largely overcome by resorting to polymers with ether rather than ester linkages in the main chain²: polyethers have a higher

thermal stability and, generally, lower transition temperatures than polyesters. We have thus performed calorimetric and optical studies of the nematic phase and of the N-I transition in polyethers containing rigid α -methylstilbene mesogens linked via flexible alkyl spacers. As reported previously³, the heat and temperature of isotropization, ΔH_i and T_i , were found to be remarkably affected by the preceding thermal treatment: annealing in the nematic state shifts the transition to higher temperatures and produces a significant increase in ΔH_i . These effects correlate with a coarsening of the visible texture. The above thermal evidence of highly non-equilibrium nematic states in polymers is in sharp contrast to the common notion of the nematic phase as an equilibrium fluid at all times, a perception carried through from the field of low-molar-mass liquid crystals. Some new data on the effect of annealing in the nematic phase of PHMS polymers will be presented in the latter part of this article. It will be shown, for example, that nematic ordering upon annealing can lead to a doubling of the isotropization enthalpy.

However, the main thrust of the present paper is on demonstrating the following new phenomenon, which has now been recognized: the memory of such ordering, achieved by annealings in the nematic state, is not erased instantly on reaching the isotropic state; it takes several, possibly ten, minutes of annealing well above T_i to revert the system back to the equilibrium disordered state. Thus, while heat treatment is required for the equilibrium nematic order to develop, annealing in the isotropic state is similarly required for the residual non-equilibrium

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order to be erased and for the short-range molecular correlation to be reduced to its equilibrium isotropic value.

EXPERIMENT AND RESULTS

The material used in this study is a random copolyether containing α -methylstilbene mesogen units separated by flexible $-\text{O}(\text{CH}_2)_9\text{O}-$ or $-\text{O}(\text{CH}_2)_{11}\text{O}-$ units in a 1:1 ratio (abbreviated to PHMS-9,11). Molecular weights were $\bar{M}_n=31\,000$, $\bar{M}_w=65\,500$. The crystal-nematic transition, T_m , of this polymer is at 103°C , and the nematic-isotropic, T_i^∞ , at 172°C . All heat treatments were performed under high vacuum to prevent degradation. In order to study the kinetics of disordering in the isotropic phase, a well ordered nematic reference state had to be used as the starting point. It was found that such a state is best achieved by melting a solution-crystallized mat. The overall procedure was as follows: approximately 10 mg of the mat was weighed and placed in an aluminium d.s.c. pan, without the cover. The pan was inserted in a flat-bottomed thin-walled copper test tube fitted with a ground-glass top for convenient connection to the vacuum line. While under high vacuum, the test tube was first heated briefly in the nematic state for degassing, and then immersed in a thermostated oil bath set at 10°C above the isotropization temperature, i.e. at 190°C , for a defined holding time t_h^* .

The design of the tube ensured good thermal contact between the sample and surrounding bath. After the heat treatment the tube was rapidly cooled to room temperature.

In the first set of experiments (a), where the effect of t_h on the N-I transition was studied, no further heat treatment was applied before the thermal analysis run. The sample pans were taken out of the vacuum, covered and scanned at $10^\circ\text{C min}^{-1}$ heating rate in a Perkin-Elmer DSC-7 calorimeter. The resulting N-I transition endotherms are shown in Figure 1 for different holding times in the isotropic state, t_h . As seen, both the position (T_i) and the area of the peak (ΔH_i) greatly decrease with increasing holding time. The decrease in isotropization temperature, T_i , and enthalpy, ΔH_i , with t_h is plotted in Figures 2 and 3 respectively. The extent of excess order in the as-created non-treated isotropic phase is remarkable; e.g. after $t_h=2$ min of thermal treatment, ΔH_i is reduced to 57% of the initial value.

In the second set of experiments (b) we followed the recovery of T_i and ΔH_i upon annealing in the nematic state subsequent to the thermal treatment in the isotropic phase. Thus the tube with the sample pan, while still under vacuum, was immersed in the oil bath, which was now set to 120°C , i.e. a temperature within the nematic range. The annealing time, t_a , was varied from 0 to 15 h. As before, a fresh specimen was used for each cycle of thermal treatments. After annealing in the nematic state, d.s.c. thermograms were recorded as in (a). The recovery of T_i and ΔH_i with t_a for samples previously held in the isotropic state for $t_h=2$ min is shown in Figures 4 and 5. Compared with the disordering process in the isotropic phase, the rate of achieving equilibrium (reordering) in

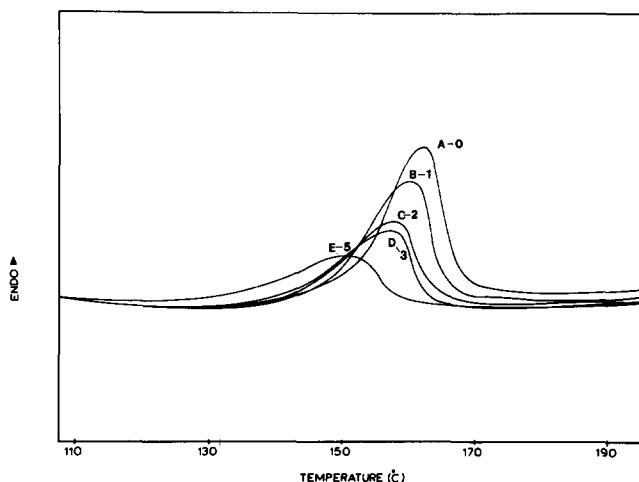


Figure 1 D.s.c. heating thermograms spanning the T_i range for a sample of PHMS-9,11 ($\bar{M}_n=31\,000$, $\bar{M}_w=65\,500$, comonomer ratio 1:1). Prior to the scan the specimens, initially in a well ordered nematic state, were held in the isotropic phase (190°C) for $t_h=0$ (curve A), 1 (B), 2 (C), 3 (D) and 5 min (E)

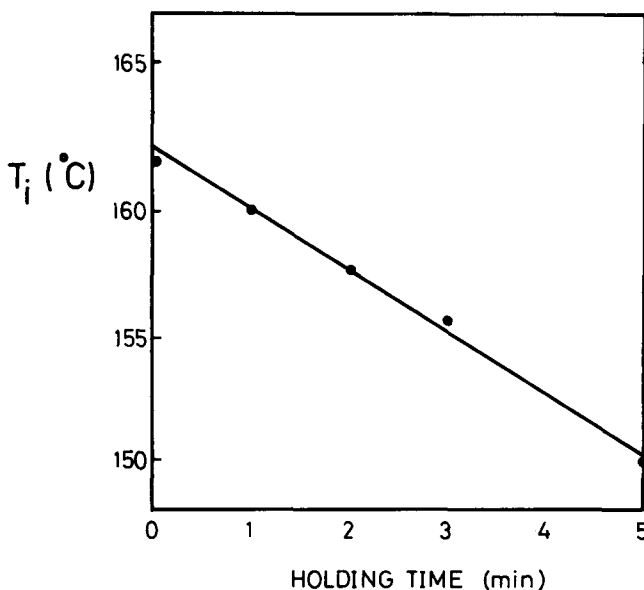


Figure 2 Peak N-I transition temperature (T_i) vs. holding time t_h in the isotropic state (190°C) for PHMS-9,11

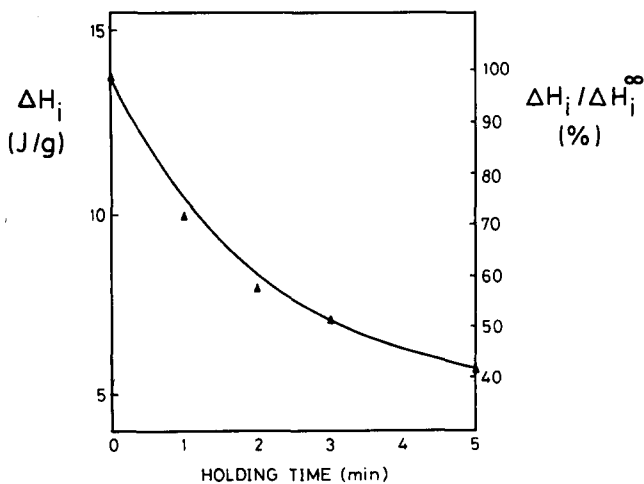


Figure 3 ΔH_i and $\Delta H_i / \Delta H_i^\infty$ vs. holding time t_h in the isotropic state (190°C) for PHMS-9,11

* For clarity heat treatment times are hereafter termed 'holding time' (t_h) and 'annealing time' (t_a), depending on whether the temperature was within the isotropic or nematic range, respectively

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