

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

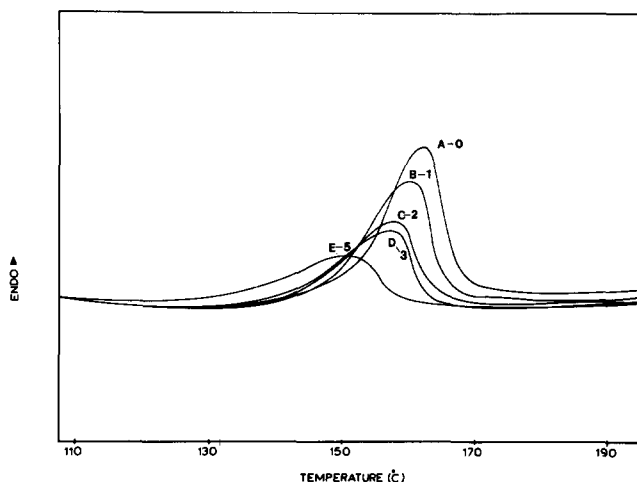


Figure 1 D.s.c. heating thermograms spanning the T_i range for a sample of PHMS-9,11 ($\bar{M}_n=31\,000$, $\bar{M}_w=65\,500$, comonomer ratio 1:1). Prior to the scan the specimens, initially in a well ordered nematic state, were held in the isotropic phase (190°C) for $t_h=0$ (curve A), 1 (B), 2 (C),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

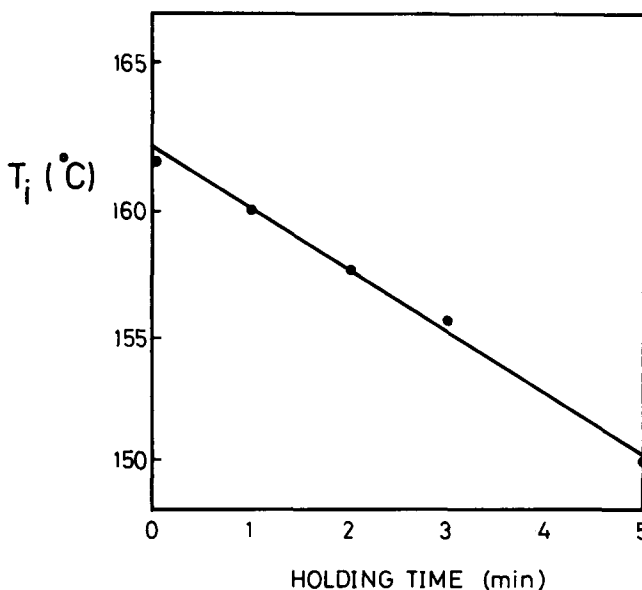


Figure 2 Peak N-I transition temperature (T_i) vs. holding time t_h in the isotropic state (190°C) for PHMS-9,11

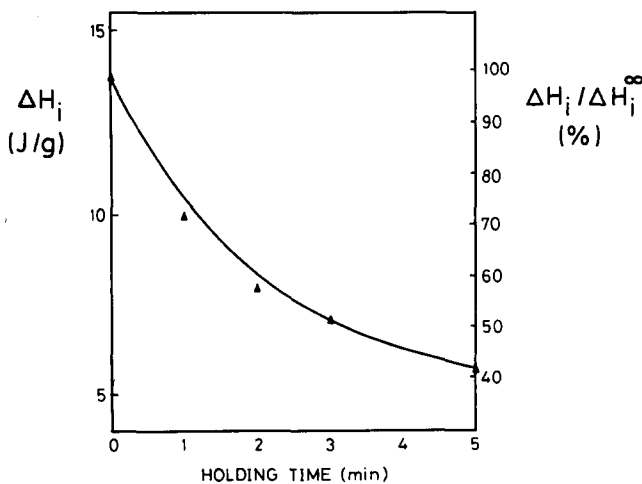


Figure 3 ΔH_i and $\Delta H_i/\Delta H_i^\infty$ vs. holding time t_h in the isotropic state (190°C) for PHMS-9,11

* 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

the nematic state is very slow. It should be noted that, up to $t_h = 5$ min holding time in the isotropic phase, the initial highest T_i and ΔH_i , i.e. the values corresponding to $t_h = 0$, were fully recoverable by prolonged annealing in the nematic phase. For longer t_h irreversible reduction in ΔH_i occurred, which was attributed to degradation. Thus only experiments with $t_h < 5$ min are considered in this work.

The respective dependences of ΔH_i and T_i on treatment time, shown in Figures 3–5, were fitted to exponential functions of the form:

$$\Delta H_i(t) = \Delta H_i^\infty + (\Delta H_i^0 - \Delta H_i^\infty) \exp(-t/\tau) \quad (1a)$$

$$T_i(t) = T_i^\infty + (T_i^0 - T_i^\infty) \exp(-t/\tau) \quad (1b)$$

Here the superscripts 0 and ∞ refer to ΔH_i and T_i values for $t=0$ and $t=\infty$, respectively. The resulting best-fit parameters are listed in Table 1. The time constant τ for the disordering process in the isotropic state at 190°C was 2 min, while that for the reordering process in the nematic state at 120°C was 4 h, the ratio of the two being 10^{-2} .

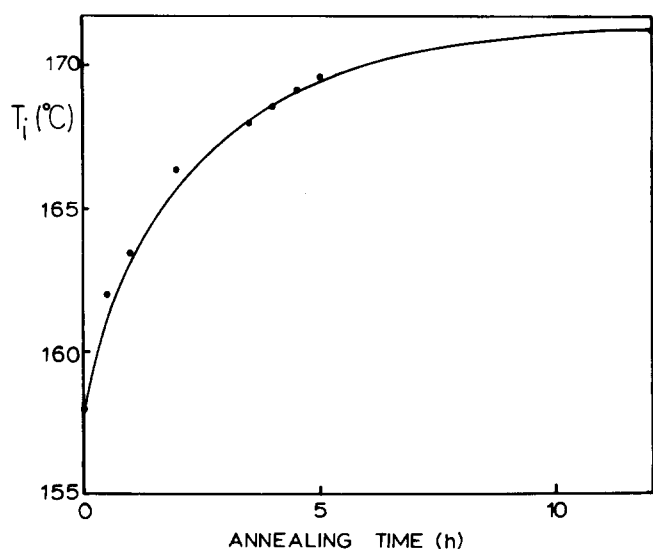


Figure 4 Peak N–I transition temperature (T_i) vs. annealing time t_a in the nematic state (120°C). The samples had been held in the isotropic state for $t_h = 2$ min preceding the annealings at 120°C

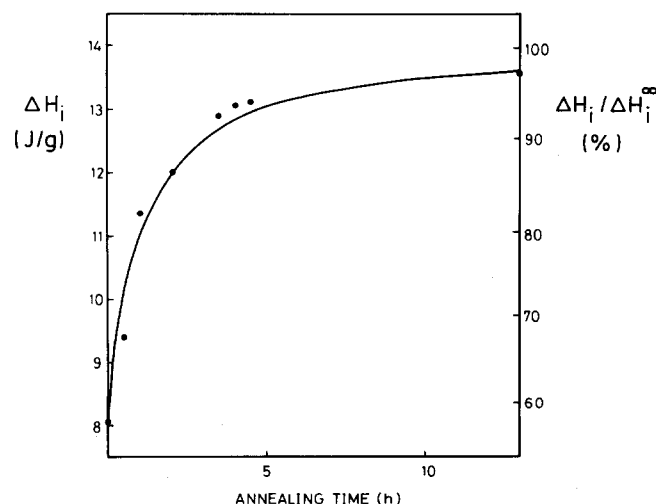


Figure 5 ΔH_i and $\Delta H_i/\Delta H_i^\infty$ for PHMS-9,11 vs. annealing time t_a in the nematic state (120°C, cf. Figure 4)

Table 1 Best-fit parameters for the dependence of heat and temperature of isotropization on thermal treatment time (equations (1))

Thermal treatment at:	$T = 190^\circ\text{C}$ (isotropic)	$T = 120^\circ\text{C}$ (nematic)
T_i	–	172.0°C
τ	–	4.0 h
ΔH_i	4.95 J g ⁻¹ (4.9 kJ mol ⁻¹)	13.9 J g ⁻¹ (5.1 kJ mol ⁻¹)
τ	2.13 min	4.1 h

DISCUSSION

It is only thanks to the slow ordering process in the nematic phase³ that the differences in the preceding isotropic state are reflected in the N–I endotherm on subsequent heating (see Figure 1). If thermodynamic equilibrium in the nematic phase was quick to establish, as has been generally assumed until recently, the memory of any differences in the precursor isotropic state would have been erased in the nematic phase in the course of the d.s.c. heating scan. Thus, owing to its sluggishness, the nematic phase is preserved in its as-formed state; hence the N–I endotherm recorded on subsequent heating indirectly mirrors the state of local order in the precursor isotropic liquid.

The effect of thermal treatment in the isotropic state on the subsequent N–I transition, shown in Figures 1–3, is a new, previously unrecognized phenomenon. It shows two particularly interesting features: (a) the nematic phase can be influenced by the state of the isotropic precursor to an unexpectedly high extent (e.g. ΔH_i varies by a factor of more than 2; see Figure 3), and (b) the rate with which nematic memory is erased in the isotropic state is unexpectedly low. The implications for measurements of thermodynamic parameters (temperature, heat, entropy) of the N–I transition in main-chain polymers are self-evident. It is clear from the current results that great care must be exerted in properly annealing the nematic polymer before a d.s.c. scan, and slow heating, preferably with extrapolation to zero heating rate, is recommended.

The form in which memory of the preceding nematic order is stored in the isotropic state is a matter for speculation. Similarly, we can only guess as to the mechanism by which such memory is passed back on to the re-formed nematic phase during the subsequent I–N transition. However, this much is certain: in contrast to low-molecular-weight liquid crystals, the equilibrium nematic order and isotropic disorder in main-chain polymers are attained very slowly. Even on the short-range scale, detectable calorimetrically, the approach to equilibrium is surprisingly slow indeed.

Concerning the isotropization transition, while any long-range orientational order is clearly lost, it would appear that a significant degree of local order is preserved after the transition and it decays to its equilibrium level only upon subsequent thermal treatment. It is possible then that localized regions of such residual short-range order serve as nuclei for nematic domain formation on subsequent cooling. As such ‘seeds’ would largely preserve their original mutually parallel orientation, the resultant adjacent nematic domains may have their directors aligned parallel or almost parallel to each other, and may possibly coalesce. On the other hand, if the

residual seeds in the isotropic phase are allowed to disappear, the director axes in the adjacent nematic domains formed on subsequent N–I transition would be randomly oriented and uncorrelated. Thus a higher density of defects (disclinations) may be expected in the latter case, resulting in lower T_i and ΔH_i .

An additional factor to consider is chain conformation. While longer extended-chain portions normally exist in an equilibrium nematic, and a more coiled conformation prevails in the isotropic state^{4,5}, the required conformational change may be too slow for the equilibrium path to be followed during the N–I or I–N transitions. Both the orientational and conformational non-equilibria may qualitatively account for the observed memory effects and the variations in T_i and ΔH_i , and we cannot comment presently on which of the two effects might be dominant.

CONCLUSIONS

Immediately following the N–I transition, the isotropic phase of a thermotropic main-chain polymer is in a non-equilibrium state of considerable excess short-range order. The equilibrium disorder is achieved only on subsequent heat treatment which, in the present case, is on the timescale of several minutes. Upon the subsequent I–N transition a largely non-equilibrium nematic is formed, with excess frozen-in disorder. The latter anneals out at a rate 100 times lower than the rate of equilibration of the isotropic phase, i.e. in a matter of hours. In connection with these unsuspected findings precautions are called for in performing measurements and interpreting thermal data on the N–I transition in main-chain polymers.

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ADDENDUM

Comparison with the crystalline state

This addendum is in response to a query by the referee. While not intended as an integral part of the paper, it may help to provide distinction between the nematic and crystalline states coupled with some clarification.

It might appear that an analogy exists between the non-equilibrium defect state of polymer nematics and the well known case of non-equilibrium polymer crystals. Generally speaking, in both cases, increasing perfection and a reduction in excess enthalpy and free enthalpy is achieved on annealing. One might thus argue that large deviations from thermodynamic equilibrium, such as are observed in the semicrystalline polymeric state, are naturally to be expected also in the nematic and indeed also in the isotropic state. Thus, by such an argument, the present findings would not come as a surprise. It should be noted, however, that such a generalization has, to our knowledge, never actually been proposed. On the contrary, the belief that the nematic polymeric state is a near-equilibrium one is illustrated by the fact that the numerous reported values for temperatures and heats of isotropization (for reviews see refs. 1 and 6) are all straight

measured values. This is in stark contrast to the reported polymer melting temperatures and heats of fusion, where the concepts of an extrapolated 'equilibrium melting temperature' and a 'heat of fusion of a 100% crystalline phase' are firmly established and routinely used.

More fundamentally, there are crucial differences between the semicrystalline and the nematic states in polymers, which would cast doubt on *a priori* generalizations, suggesting that both states are equally liable to large deviations from equilibrium. First, the main reason for the excessive free enthalpy of polymeric crystals is their thinness (usually of the order of 10–30 nm) and the high end surface free energy. In contrast, even the finest nematic texture in polymers is on the scale of a micrometre. Secondly, a nematic material is still a liquid, and the viscosity component along the director is actually lower than that in the isotropic liquid state. Thirdly, low-molecular-weight nematics never show a depression in T_i or ΔH_i due to defects, whereas T_m of unannealed crystals of low-molecular-weight non-mesogenic molecules is often depressed by tens of degrees^{7,8}.

Within the present discussion, a comment is also due on the occasional reports that the state of polymeric melt may influence subsequent crystallization. Most of these reports refer to the effect of 'self-seeding'⁹, and are thus irrelevant to the present observation of the memory effect in the isotropic state. The seeding temperature T_s , while being above the melting point of the bulk of the small metastable crystals in the sample, is still below the equilibrium melting temperature of the polymer. The seed crystals are larger than average and are stable at T_s . They will provide crystal growth upon cooling, but they will not disappear at T_s . In contrast, the 'seeds' of the nematic order above T_i , as implied by the present observations, are unstable and they disappear with time. It might be mentioned that certain indications of possible transient effects of melt memory on subsequent polymer crystallization have been reported in the past, mainly in the older literature¹⁰. Such effects were complicated by possible partial fractionation during solution crystallization and, possibly, by oxidation of high processing temperatures. Because of these complications and a lack of systematic studies of the effect, we cannot comment further on possible parallels with our present observations of transient nematic memory in the isotropic melt. Under these conditions the main thrust of our paper of drawing attention to non-equilibrium excess order in the isotropic state of liquid-crystal-forming polymeric materials remains pertinent.

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