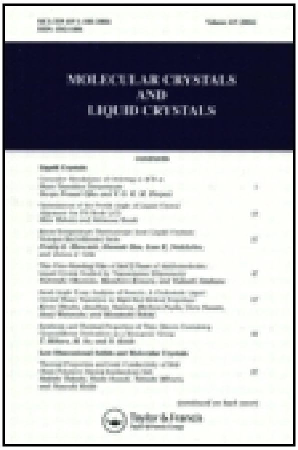

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Superheating of the Nematic Phase in Main Chain Polymers

J. L. Feijoo [a] , G. Ungar [b] & V. Percec [c]

[a] Departamento de Ciencia de los Materiales, Universidad Simón Bolivar, Apdo 89000, Caracas, 1080-A, Venezuela

[b] Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

[c] Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, 44106, USA

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Superheating of the Nematic Phase in Main Chain Polymers

J. L. FEIJOO
Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apdo 89000, Caracas 1080-A, Venezuela

and

G. UNGAR
Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

and

V. PERCEC
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

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Nematic-isotropic transition temperature, T_i, was measured as a function of heating rate for main chain polyethers containing either α-methylstilbene (HMS) or 1-(4-oxyphenyl)-2-(2-methyl-4-oxyphenyl)ethane (MBPE) and flexible aliphatic spacers. At the heating rate of 40°C/minute T_i was found to increase by up to 15°C for HMS polymers, after instrumental correction. Superheating was greatly promoted by increased molecular weight and chain rigidity. The phenomenon is consistent with the previously observed memory effect in the isotropic and nematic phases and is attributed to the diffusion controlled change in overall chain dimensions accompanying the nematic-isotropic transition.

Keywords: liquid crystal polymers, main-chain, nematic phase, isotropic phase, superheating, nematic-isotropic transition

INTRODUCTION

Departures from thermodynamic equilibrium in nematic or isotropic low molar mass liquids are so small that neither the temperature T_i nor the enthalpy ΔH_i of the isotropization transition differ noticeably from their equilibrium values. The situation can be quite different for polymers. A study[1] of the N–I transition in main chain polyethers based on α-methylstilbene and flexible aliphatic spacers, showed an unexpectedly slow attainment of thermodynamic equilibrium. Large deficiency in nematic order, manifested in T_i and ΔH_i depression, could be eliminated only after prolonged annealing below T_i, with the relaxation time τ of the order of several hours. Equally unexpected was the finding that, once above T_i, equilibrium disorder of the isotropic liquid is not achieved instantly but through a comparatively slow diffusion process with $\tau = 2$ minutes at $T = T_i + 10°C$. Memory of the original nematic order that persisted well above T_i was sufficient to significantly affect the *N–I* transition on subsequent reheating.

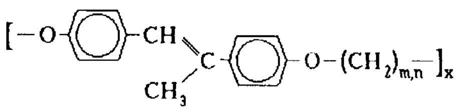
Based on the latter finding of slow loss of nematic order above T_i, it is plausible to expect sizeable superheating effects in main chain polymers. This note describes selected thermal analysis experiments which indeed show that T_i may be raised substantially above the equilibrium value, and that the extent of superheating is greatly influenced by variations in molecular weight and polymer flexibility.

In the present and previous[1,2] studies of the *N–I* transition we employ polyethers rather than the more commonly used polyesters. The former have two advantages for the present purpose[3]: (a) they are synthesised by irreversible polymerization[4] and are thus thermally more stable, and (b) they have a lower T_i.

EXPERIMENTAL

The polymers used were:

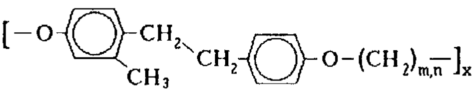
1. Copolyethers based on 4,4′-dihydroxy-α-methylstilbene and two different randomly distributed flexible spacers containing *m* and *n* methylene units in a 1:1 molar ratio (abbreviated HMS-*m*,*n*):



HMS-m,n

and

2. Similar copolymers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (or methylbiphenylethane) as the mesogen (MBPE-*m*,*n*):



MBPE-m,n

Copolymers were used in preference to homopolymers in order to extend the nematic range by suppressing the crystal melting point. The synthesis of HMS and MBPE polymers has been described previously.[3,5]

Thermograms were recorded with a Perkin Elmer DSC-7 instrument. T_i was measured as a function of heating rate. T_i values quoted are peak temperatures duly corrected for instrumental temperature deviation and thermal resistance of the sample holder. The position and slope of the indium melting endotherm at each individual heating rate were employed in these corrections.[6] Specimen size was kept below 2 mg for high heating rate runs to avoid errors due to thermal resistance of the polymer. A fresh specimen was used for each experiment.

In order to ensure a uniform reference state of nematic order prior to the $N-I$ transition, all specimens were first annealed at $T_i^0 - 10°C$ for 4 hours. Here T_i^0 is the extrapolated equilibrium isotropization temperature at zero heating rate. This pre-annealing was carried out under high vacuum to prevent any possible degradation. Next the specimens were rapidly cooled and stored at room temperature under vacuum until immediately before being scanned in the DSC. The temperature was first raised to a starting temperature T_1 sufficiently low to enable the recording of a clear $N-I$ endotherm. T_1 was dependent on the heating rate of the subsequent run, which commenced immediately upon reaching T_1 and equilibrating the instrument.

The DSC sample compartment was purged with oxygen-free nitrogen. A number of samples, particularly those run at low heating rates, were tested after the recording for possible degradation: the specimens were re-annealed under vacuum and re-run at 20°C/minute. In no case was any difference detected between thermograms recorded during an original 20°C/min run and a repeated test run, confirming that the effects described are not the result of irreversible chemical changes.

RESULTS AND DISCUSSION

Figure 1 shows the heating rate dependence of T_i for copolymers HMS-5,7 of two different molecular weights: $M_n = 19{,}000$ ($M_w/M_n = 2.1$), and $M_n = 11{,}000$ ($M_w/M_n = 1.9$). The increase in T_i with increasing dT/dt, though unprecedented, is in direct agreement with the previous results on annealing in the isotropic state.[1]

Here the extent of superheating is expressed as $\Delta T = T_i - T_i^0$, where T_i^0 is obtained by extrapolating T_i to zero heating rate. As Figure 1 shows, values of ΔT of the order of 15°C are obtained at higher heating rates.

As the preceding studies demonstrated, equilibrium disorder is achieved only slowly, on the minute time-scale, upon heating the nematic polymer above T_i. This implies that on reaching the equilibrium isotropization temperature T_i^0, the state of minimum isotropic free enthalpy g_I^0 is not instantly available. Instead, only a non-equilibrium isotropic state can be accessed readily, having a free enthalpy $g_I > g_I^0$. The transition will therefore occur at a temperature $T_i > T_i^0$ at which $g_I = g_N^0$, assuming that the nematic phase is at equilibrium, characterized by g_N^0. However, given sufficient time, states with lower g_I, i.e. closer to g_I^0, become available; hence there is less superheating at lower heating rates.

The results in Figure 1 clearly show that ΔT is significantly affected by the molecular weight of the polymer. In the case of HMS-5,7, ΔT is 13°C for $M_n = 19{,}000$ and only 5°C for $M_n = 11{,}000$ at $dT/dt = 40°C/min$. This limited data

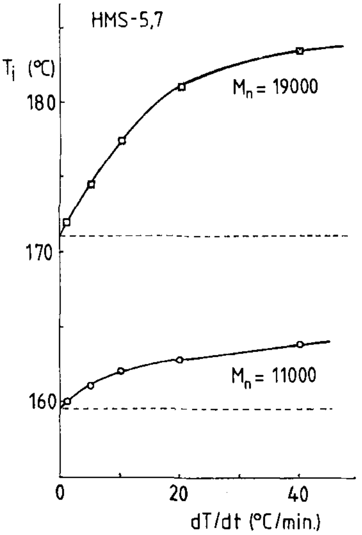


FIGURE 1 Corrected peak nematic-isotropic transition temperatures of HMS-5,7 polymers with M_n = 19,000 and M_n = 11,000 as a function of heating rate.

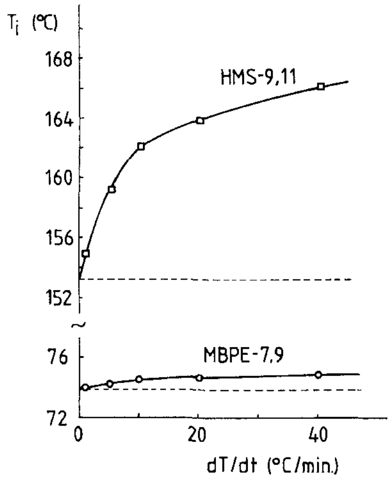


FIGURE 2 Corrected peak nematic-isotropic transition temperatures of polymers HMS-9,11 (M_n = 31,000) and MBPE-7,9 (M_n = 29,100) as a function of heating rate.

indicates a non-linear relationship between M_n and ΔT. Accordingly, the relaxation time involved in achieving equilibrium isotropic disorder appears to be a higher power function of molecular weight.

In Figure 2 superheating behaviour of two different polymer types, HMS and MBPE, is compared. The two polymers have very similar molecular weights (HMS-9,11: M_n = 31,000, M_w/M_n = 2.1; MBPE-7,9: M_n = 29,100, M_w/M_n = 1.9) and similar average spacer lengths. The HMS-9,11 is the same polymer as the one used in the previous annealing study.[1]

TABLE I

Extrapolated equilibrium isotropization temperatures for selected HMS and MBPE polymers

Polymer	**M_n**	**T_i^0 (°C)**	**ΔS_i [a] (mJ K^{-1} g^{-1})**
HMS-5,7	11 000	159.3	
HMS-5,7	19 000	171	19
HMS-5,7	32 000	<u>184</u> [b]	
HMS-9,11	31 000	<u>153</u>	24 (31 [c])
MBPE-7,9	29 100	<u>74</u>	29 (39 [d])

[a]) Measured at 20 °C/min on specimens as-precipitated from solution.

[b]) T_i measured at 0.5 °C/minute.

[c]) Extrapolated equilibrium value from [1].

[d]) After annealing in the nematic state [5].

It can be seen from Figure 2 that, while the extent of superheating in HMS-9,11 is very large and similar to that in HMS-5,7, the MBPE polymer shows almost negligible ΔT. This notable difference must be related to the difference in flexibility of the two polymers. On the one hand α-methylstilbene (HMS) is a typical rigid mesogen. At the same time the two benzyl groups in the methylbiphenylethane (MBPE) mesogen are linked by a single C—C bond around which low barrier rotation can occur between a trans (extended) and two gauche (bent) conformations.[5] MBPE polymers are, in fact, the most flexible of main-chain macromolecules exhibiting a nematic phase, as they do not contain a rigid rod-like mesogen in the conventional sense. Hence the lack of significant T_i superheating in this polymer is probably more an exception than a rule among main chain polymers.

The similarity in the extent of superheating of HMS-5,7 (M_n = 19,000) and HMS-9,11 (M_n = 31,000) may possibly be attributed to a cancellation of the effects of increased molecular weight and increased chain flexibility: a HMS-9,11 chain has a higher proportion of flexible links than HMS-5,7. The differences in chain flexibility are accurately reflected in the values of T_i^0 of the polymers involved. T_i^0 values for the three polymers, having almost identical M_ns of between 29,000 and 32,000, are listed in Table I (underlined). Values for the two other HMS-5,7 polymers used, having lower molecular weights, are also given for completeness.

When comparing the extent of superheating ΔT in different polymers, it has to be remembered that

$$\Delta T = \frac{g_I - g_I^0}{\Delta S_i}$$

where ΔS_i is the N–I transition entropy. Thus the same excess free enthalpy $g_I - g_I^0$ causes more superheating in a polymer with lower ΔS_i than in one with a higher ΔS_i. However, all polymers in this work have ΔS_i values within the factor of 1.5 of each other for the same measurement conditions (see Table I). This justifies the above comparisons of superheating behaviours in terms of the extent of departure from equilibrium and in terms of molecular flexibility.

On the basis of the results of both the present work and the previous study of annealing above T_i,[1] one may also expect a memory effect influencing *supercooling* of the $I \rightarrow N$ transition. A pilot experiment was thus performed with HMS-9,11 (M_n = 31,000). Two identical samples, pre-annealed in the nematic state as in the superheating experiments, were subsequently rapidly heated in the DSC to 190°C, i.e. well into the isotropic range. The first sample was then cooled at 10°C/min immediately, whereas the second sample was held for 2 minutes at 190°C prior to cooling. The latter treatment produces no degradation, as shown in Reference 1. The cooling scans revealed the I–N transition at 144.1°C in the first (immediately cooled) sample and at 141.6°C in the second sample (temperatures corresponding to the maximum leading slope of the exotherm). Less supercooling in the immediately cooled specimen is consistent with the residual non-equilibrium nematic order in the isotropic phase facilitating the I–N transition.

In view of the strong dependence of observed superheating ΔT on molecular weight, we propose that the primary cause of superheating is the slow change in overall chain dimensions which occurs upon the N–I transition. Anisotropy of molecular shape in the nematic phase of main-chain polymers has been predicted[7,8] and observed in polyesters by small angle neutron scattering.[9,10] While in low molar mass liquids rotation of independent mesogens can occur instantly, two extreme situations may be envisaged in the N–I transition of a main-chain polymer:

(i) Randomization of mesogen orientation occurs with the overall backbone conformation unaltered; this leaves spacer links entropically strained resulting in a high g_I state.
(ii) Randomisation of mesogen orientation is accompanied by a change in backbone conformation from ellipsoid to sphere; this leads to the low free enthalpy (g_I^0) state, but can only be reached on a long relaxation time scale, dependent on molecular weight.

For high molecular weights the only isotropic state instantly available may be closer to (i), causing superheating of the nematic phase at high heating rates.

We suggest that the related phenomena, such as "nematic memory" in the isotropic state,[1] and the effects of long annealing in the nematic state on T_i and ΔH_i[1,2] are all primarily caused by the slow attainment of equilibrium backbone conformation.

The reason for low superheating in MBPE polymers may be in the specific flexible nature of the mesogen. The conflict between mesogen director randomization and a nonrandom coil backbone, producing a high g_I state in HMS polymers, may possibly be resolved in MBPE by trans → gauche transition of a fraction of mesogens, effectively removing their rod-like character.

Finally, it is of interest that a time-resolved isothermal neutron scattering experiment on a mixture of a protonated and a deuterated main chain polyester in the biphasic N–I range showed a decay in chain anisotropy on the time-scale of hours.[9] This observation is qualitatively in line with the present results. The difference in time scales may be reconciled by assuming that only the initial (minutes scale) part of the relaxation process is associated with a lowering of free enthalpy significant enough to influence T_i.

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References

1. J. L. Feijoo, G. Ungar, A. Keller and V. Percec, *Polymer*, **31**, 2019 (1990).
2. J. L. Feijoo, G. Ungar, A. J. Owen, A. Keller and V. Percec, *Mol. Cryst. Liq. Cryst.*, **155**, 487 (1988).
3. V. Percec, K. Asami, D. Tomazos, J. L. Feijoo, G. Ungar and A. Keller, *Mol. Cryst. Liq. Cryst.*, **205**, 47 (1991).
4. V. Percec, H. Nava and H. Jonsson, *J. Polyn. Sci., Polym. Chem. Ed.*, **25**, 1943 (1987).
5. V. Percec and R. Yourd, *Macromolecules*, **22**, 524 (1989); idem., *Macromolecules*, **22**, 3229 (1989).
6. M. J. O'Neill, *Anal. Chem.*, **38**, 1331 (1966).
7. P. G. de Gennes, in "*Polymer Liquid Crystals*", (Ed. A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1982.
8. W. Renz and M. Warner, *Phys. Rev. Lett.*, **56**, 1286 (1986).
9. J. F. D'Allest, P. Sixou, A. Blumstein, R. B. Blumstein, J. Teixeira and L. Noirez, *Mol. Cryst. Liq. Cryst.*, **155**, 581 (1988).
10. J. F. D'Allest, P. Maissa, A. Ten Bosch, P. Sixou, A. Blumstein, R. Blumstein, J. Teixeira and L. Noirez, *Phys. Rev. Lett.*, **61**, 2562 (1988).