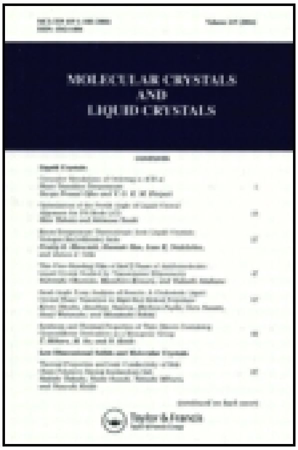

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Effects of Thermal Treatment on the Temperature and Heat of Isotropization in a Nematic Polyether

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EFFECTS OF THERMAL TREATMENT ON THE TEMPERATURE AND HEAT OF ISOTROPIZATION IN A NEMATIC POLYETHER.

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Abstract A new family of liquid crystal forming compounds, polyethers constituted of a mesogen (α-methylstilbene) and flexible aliphatic spacers provides a ready realization of isotropic-liquid crystal-true crystal regimes in one and the same material in a convenient temperature range without degradation problems. Within the thermotropic range the isotropization temperature was found to be variable, affected by preceding thermal treatment: heat treatment shifts the transition to higher temperatures with correspondingly higher heat of isotropization. The effect was found to correlate with coarsening of visible texture.

INTRODUCTION

The findings here presented form part of a wider programme on main chain mesogenic polymers first introduced by Roviello and Sirigu (1) and since more recently by Percec and collaborators (2).

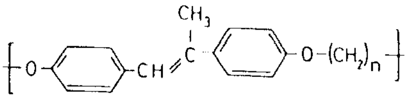
In these materials mesogenic and flexible spacer units are joined through ether linkages, which, from the point of view of the present works, has the advantage over the more extensively studied and used polyesters of greater chain flexibility and higher thermal stability. The combined effect of these two properties enables the isotropic state to be readily attained at convenient temperatures without the risk of thermal degradation. In addition, the materials are soluble to varying extents through which they can be obtained in the lyotropic state with the concommitant possibility of mapping the full lyotropic - thermotropic phase diagram (3).

In the work here reported we are confining ourselves to the thermotropic range and shall use the opportunity offered by these materials to explore the nematic - isotropic transition in some depth. In the course of it we find that the isotropization temperature (T_i) cannot be uniquely identified by just any temperature scan because, as in the case of crystal melting in crystalline polymers, it is affected by the thermal history of the sample. The latter has visible manifestations in the microstructure observed in the form of coarsening of the disinclination networks. These findings open up future possibilities of quantitative correlations with disinclination content and of determining the disinclination free enthalpy.

EXPERIMENTAL

Materials and Methods

The materials used in this study were main chain random copolyethers of 4,4'-Dihydroxy-α-methylstilbene (HMS) and 1:1 molar mixtures of 1,5-dibromopentane and 1,7-dibromoheptane. These were synthesised by phase transfer catalyzed polyetherification (2). The random copolymers studied were with 1:1 mole ratios of 5 and 7 $-CH_2-$ units, and they have the general formula:



PHMS-5/7 (50:50)

A Perkin-Elmer DSC-2 calorimeter was used to measure the thermal properties of random copolymer samples as a function of temperature. Various heat treatments (annealings) were also carried out in the calorimeter when the need for these arose. The heating rates used were 10°K/min. The D.S.C. instrument was calibrated according to recommended procedures.

Solvent-cast films were prepared on microscope cover glasses and used as test specimens for optical microscopy. Isothermal heat treatment of the films was performed by placing the specimens in the D.S.C. sample holders. Selected samples were examined under the polarising microscope.

RESULTS AND DISCUSSION

Figure 1 displays three transition temperatures, glass transition (T_g), crystal melting (T_m^{max}) and isotropization (T_i) as a function of molecular weight ($\bar{M}_n$). Here T_m^{max} represents the maximum melting temperature of the most stable crystal form obtainable by heat annealing at small supercoolings. As anticipated all three transitions first increase and then level off with $\bar{M}_n$. T_i, the principal subject of our investigation, initially increases sharply with $\bar{M}_n$ until $\bar{M}_n \sim 12000$. From thereon, while broadly levelling off, the data points are multivalued. It did turn out that this variability is affected by heat treatment both below and above the crystal melting point T_m prior to isotropization. In view of the fact that the as-measured T_i is generally thought to be an equilibrium quantity this behaviour is unexpected and was examined further.

Fig. 2 shows DSC thermograms corresponding to the isotropization transition as a function of heat treatment time for $\bar{M}_n$ = 17700, in this case below T_m^{max}. As seen,

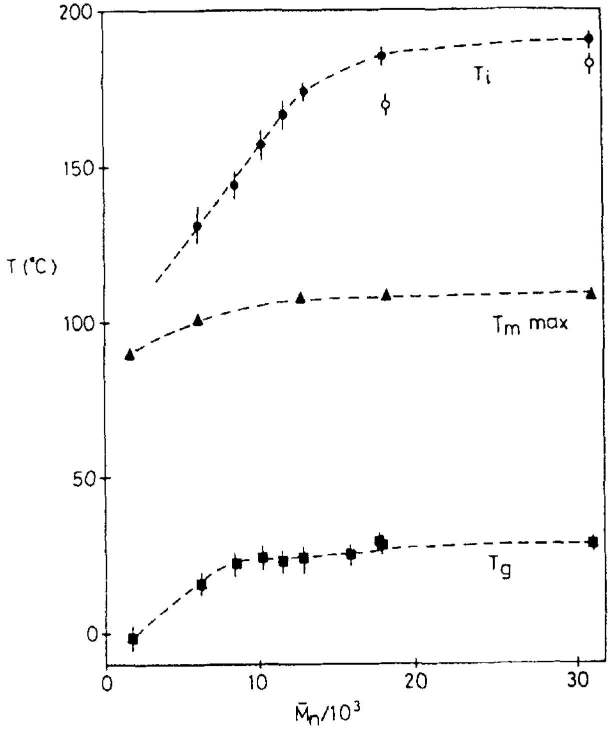


FIGURE 1. Transition temperatures of PHHS - 5/7 (50:50) copolymer as a function of molecular weight as determined by DSC: T_g = glass transition temperature; T_m^{max} = maximum melting point of the most stable crystal form, achieved by annealing at low supercooling; T_i = nematic-isotropic transition temperature (ϕ= some as-prepared samples which were transformed into the corresponding samples ● on heat treatment).

both the transition temperature T_i and the heat of isotropization (ΔH_i), as assessed from the endotherm peak area, are increasing with annealing time. It follows therefore that T_i and ΔH_i, simply as measured, may not correspond to equilibrium values beyond a certain molecular weight, M_n^c, and it is necessary to anneal the sample for the equilibrium to be approached.

Beyond M_n^c, the molecular weight dependence would then reflect the lowered mobility of the chains, and in particular, that of the mesogenic units.

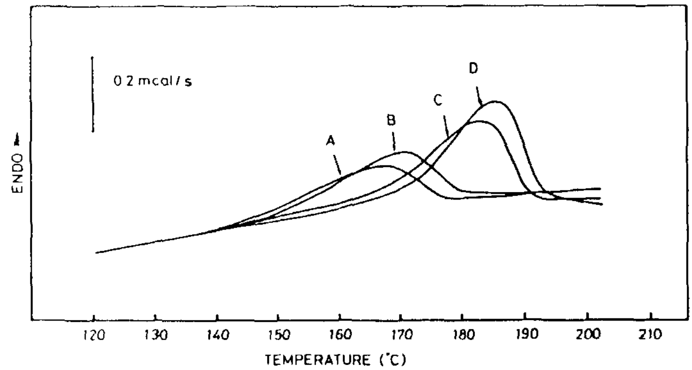


FIGURE 2 DSC thermograms of PHMS-5/7 (50:50), $\bar{M}_n$ = 17700, samples annealed at 100°C: A(2.0h),B(6.4h), C(13.5h) and D(16.6h).

Fig. 3 displays the polarising optical images for the same samples as in Fig. 2. The dark lines, are most likely to be disinclinations circumscribing, what appears as "domains". The size of the "domains" increases with annealing time, the texture coarsening and the number of disinclinations reducing accordingly. The latter in itself would entail a reduction of net enthalpy and free enthalpy of the nematic phase thus, at least in a qualitative sense, correlating with the trend in the thermograms of Fig. 2.

The above findings allow a sample which is in an imperfect nonequilibrium state to be characterized using the measured heat and temperature of isotropization, ΔH_i and T_i, in relation to the corresponding equilibrium values ΔH_i^∞ and T_i^∞.

We assume an exponential approach of ΔH_i to ΔH_i^∞ and find the latter parameter by linearizing $\ell_n(\Delta H_i^\infty - \Delta H_i(t))$ versus annealing time t (fig. 4). This then provides $\Delta H_i^\infty = 12.5$ J/g for the heat of isotropization in the equilibrium state. With this value we can then characterise a sample by considering $\Delta H_i(t)/\Delta H_i^\infty$ a quantity which, risking some objections to the term, may, in analogy with crystalline polymers, be termed degree of liquid crystallinity.

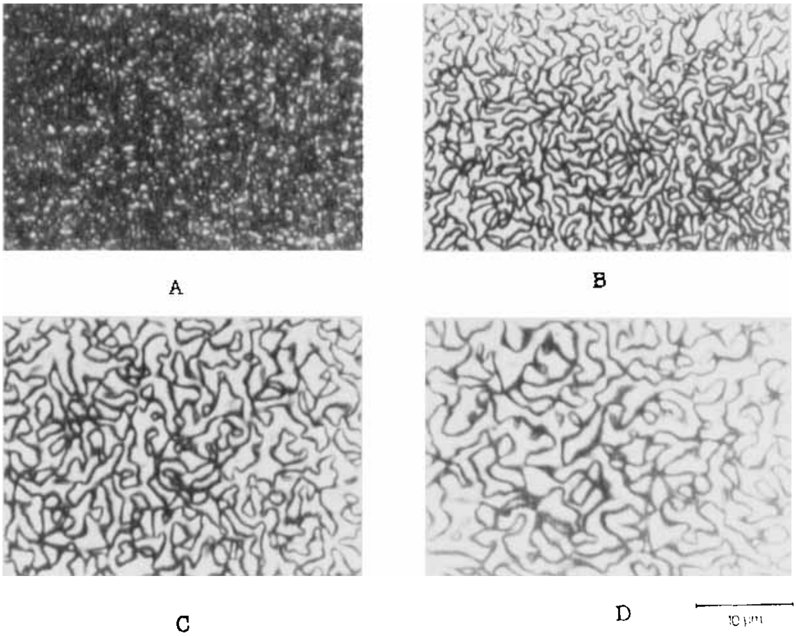


FIGURE 3. Sequence of optical micrographs for PHMS 5/7 (50:50), $\bar{M}_n$ = 17700, taken at different time intervals during annealing at 100°C. A(Unannealed), B(6.4h), C(13.5h) and D(16.6h).

Values of $(\Delta H_i(t)/\Delta H_i^\infty).100$ together with the actual ΔH_i values as a function of annealing time are plotted in Fig. 5. As seen the $(\Delta H_i(t)/\Delta H_i^\infty)100$ values range from 39% to 72% representing the perfection of liquid crystallinity as a percentage of its equilibrium value.

The reason that in the experimental series presented here the heat treatment was conducted below T_m^{max} is that some oxidation of the polymer was detected during prolonged annealings in air above T_m^{max}. Currently, vacuum annealings are being performed above T_m^{max}, i.e. while in the nematic state. In the latter case shorter annealing times are required to obtain the same ΔH_i value than for heating below T_m.

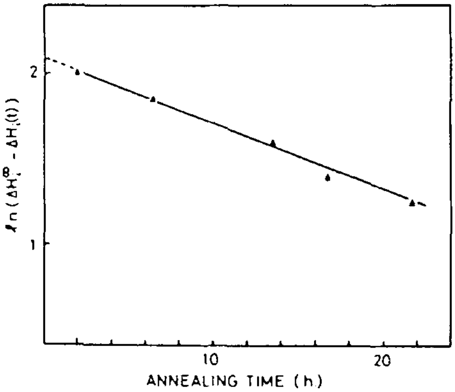


FIGURE 4. $\ell_n\,(\Delta H_i^\infty - \Delta H_i(t))$vs annealing time as derived from the thermograms of PHMS - 5/7 (50:50) $(\bar{M}_n = 17700)$, with $\Delta H_i^\infty = 12.5$ J/g.

The preliminary results here presented contain, in our view, an essential recognition: namely that in high molecular weight material there can exist non-equilibrium states of liquid crystallinity, where departures from the equilibrium states can be quantified calorimetrically and also correlated (even if so far only qualitatively) with

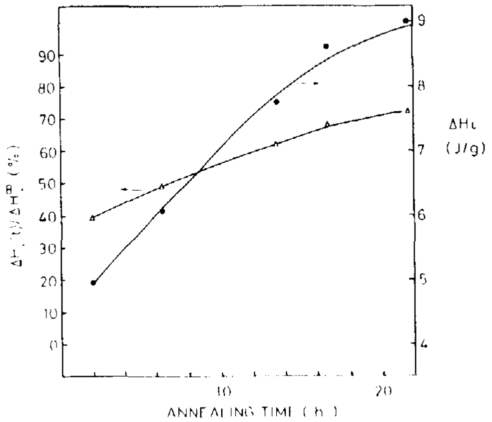


FIGURE 5 ΔH_i and $\Delta H_i(t)/\Delta H_i^{\infty}$ vs annealing time as derived from the thermograms of PHMS-5/7 (50:50) samples (M_n = 17700).

the scale of the disinclination texture as observed visually under the polarising microscope. Above all, this recognition is essential for the correct identification of isotropization temperatures (T_i). The observed effect also presents an opportunity for experimental determination of the free enthalpy of disinclinations. The work on this issue is currently in progress.

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