

SMALL ANGLE LIGHT SCATTERING MEASUREMENT OF THE ISOTROPIC TO NEMATIC TRANSITION OF A SIDE CHAIN NEMATIC POLYMETHACRYLATE*

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Abstract The kinetics of I→N transition of a side chain nematic polymethacrylate has been studied by small angle depolarized light scattering intensity measurements using a charge coupled device linear image sensor. The polymer shows the transition temperatures K52N79I in °C. The H_v scattering intensity $\mathcal{I}(q, t)$ during the transition I (at 80.2°C)→N (at 75.8°C) shows that $\mathcal{I}(q)$ is independent of q for all t , and during the initial stage (in 6 s) $\mathcal{I}(t)$ increases exponentially with t . In the later stage of the transition $\mathcal{I}(t)$ approaches a saturation value in 2 min. This experimental result indicates that the I→N transition of a liquid crystalline polymer is a spinodal type of phase transition mediated by orientation fluctuation.

Keywords Side chain nematic polymer, Isotropic-nematic transition, Small angle depolarized light scattering

INTRODUCTION

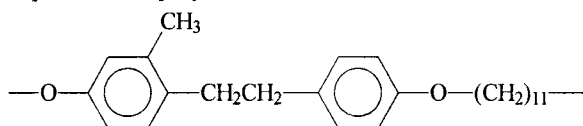
The phase transition from isotropic to nematic states of a liquid crystalline polymer is a molecular condensation and orientation alignment process. It is a first order phase transition with enthalpy change $\Delta H_{I \rightarrow N}$ and volume change $\Delta V_{I \rightarrow N}$, which are both small as compared to $\Delta H_{N \rightarrow K}$ and $\Delta V_{N \rightarrow K}$, and both changes are negative, where I, N and K designate isotropic, nematic and crystalline phases respectively. The transition I→N has been found to be rapid and reversible, and apparently with no or very slight undercooling^[1]. Liquid crystalline polymers are usually not in the form of totally rigid rods but with some degree of chain flexibility. In this case for a lyotropic nematic polymer there is a temperature region, from the transition temperature $T_{I \rightarrow N}$ to some (10–30)°C below it, in which the polymer solution is a two phase system, containing both isotropic and nematic phases. Because of the existence of orientation defects or disclinations in the nematic phase the latter is made of nematic domains. Within each nematic domain the mesogens are aligned along a preferential direction with statistical fluctuations, but the preferentially aligned director directions of different domains are in random orientation. In a thermotropic nematic polymer at temperatures not too far below $T_{I \rightarrow N}$ there is also the possibility of being present both isotropic melt and nematic domains. It is not entirely clear, if it is a true co-existence of (N+I) phases of thermodynamic origin from molar mass polydispersity of the sample, as $T_{I \rightarrow N}$ is usually molar mass dependent, or of kinetic origin due to long relaxation time of long chain molecules to attain thermodynamic equilibrium, the latter being analogous to the coexistence of amorphous and crystalline regions in a partially crystallized polymer. Experimentally it is almost impossible to prepare an ideally monodisperse polymer as well as to realize true thermodynamic equilibrium, so the question remains open. In this temperature region of co-existence of nematic and isotropic regions the nematic domains could have their degree of mesogen alignment and the number and

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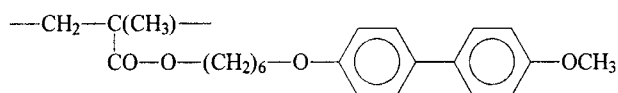
size of nematic domains changing with temperature and time, after I→N transition on cooling, or before N→I transition on heating or by annealing in the nematic state. This is manifested in the effect of thermal history of the sample in the nematic state on the values of $T_{N\rightarrow I}$, $\Delta H_{N\rightarrow I}$, $\Delta S_{N\rightarrow I}$ ^[2, 3] and even the density of melt^[4]. More direct evidence for the coexistent isotropic-nematic regions at temperatures of a few °C below $T_{I\rightarrow N}$ was observed in the case of a thermotropic monotropic nematic polyether of the structure^[5]



which was partially crystalline and showed $T_{N\rightarrow I} = 77.5^\circ\text{C} < T_m$ (the melting point). The isothermal DSC measurements for the crystallization of this polymer from the melt at 75.5°C or 76.5°C showed first a fast I→N transition followed by a crystallization process from nematic state with no induction period for crystallization and by another crystallization process from isotropic state with an induction period. This means that when the melt is cooled to $T_{I\rightarrow N}$, the nematic and isotropic regions undergo crystallization independently.

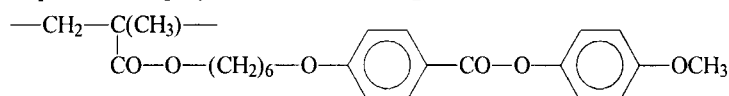
On recognizing the coexistent isotropic and nematic regions below $T_{I\rightarrow N}$ it is natural to apply Avrami type kinetics to the process of I→N transition^[6]. Experimental results seem to indicate that, in almost all cases reported, the I→N transition kinetics shows an Avrami index $n = 1$, for both lyotropic^[7–10] and thermotropic systems^[11–13]. The transition is very rapid so that it is practically impossible to follow by isothermal differential scanning calorimetric (DSC) measurements. Most kinetic experiments were done by non-isothermal DSC with temperature scanning or by depolarized light intensity (DLI) measurement. Both methods have complications in the interpretation of experimental results. The effect of rate of thermal conduction between the sample and DSC capsule for non-isothermal DSC and the true relation between depolarized light intensity and the extent of nematic order for the DLI method are not precisely explored. Besides, it should be pointed out here that a satisfactory plot of kinetic data according to the Avrami equation does not imply that the process is of Avrami mechanism (thermally nucleated), especially when the Avrami index $n = 1$. It may be just simple exponential kinetics.

For side chain nematic polymers with mesogens connected to the main chain through flexible spacers the transitions N→I or S→I (here S stands for smectic liquid crystalline phase) show no thermal history effect^[4, 14]. The flexible main chain and the flexible spacer render the mesogens to have better mobility for orientation ordering, thus the thermal behavior is analogous to the case of a low molar mass nematic compound dispersed in a highly viscous medium. A good example of kinetic study of I→N transition was done on the thermotropic nematic polymer:



by dilatometry^[15], the result of which should be more reliable than that of non-isothermal DSC and DLI methods. It was found that I→N transition of this polymer followed simple exponential kinetics, Avrami index $n = 1$, and $\Delta V_{N\rightarrow I} = 0.4\%$ as compared to $\Delta V_{K\rightarrow N} = 1.07\%$.

The fact that I→N transition is rapid with no or slight undercooling suggests that formation of nematic phase does not need a nucleation step. Doi *et al.* gave a theory of I→N transition as a spinodal type of phase transition mediated by orientation fluctuation^[16]. So far as the present authors are aware, no experimental verification of this interesting idea has been carried out. In this paper the results of an experimental study of the I→N transition of a side chain thermotropic nematic polymer of the following chemical structure:



are presented. The transition was followed by small angle light scattering (SALS) intensity measurements using a CCD (charge coupled device) linear image sensor. The purpose of this study is aimed at two objectives: (1) To

see if the physical nature of I→N transition is a spinodal type of phase transition can be confirmed as a result of fast growth of orientation fluctuations. (2) In view of the recent developments in our understanding of the polymer crystallization from its melt, the induction period of crystallization has been attributed to the formation of nematic nanodomains^[17–19]. The experimental study of I→N transition by SALS can offer a solid foundation for the above-mentioned mechanism of induction period of polymer melt crystallization.

EXPERIMENTAL

The monomer for the side chain nematic polymethacrylate was prepared according to the literature^[20–22]. Polymerization was carried out in tetrahydrofuran (THF) solution at 60°C for 2 days, using 0.3% equivalent moles AIBN as initiator. The polymer was precipitated by methanol, re-dissolved and then re-precipitated. The precipitated polymer was dried in vacuum. Gel permeation chromatography with THF as eluent gave an $M_w = 7.0 \times 10^4$ and $M_w/M_n = 2.3$ as the equivalent M_w of polystyrene standard of the same hydrodynamic volume. A heating up DSC run (TA 2910) at 10 K/min showed a melting peak T_{K-N} at 51.2°C and T_{N-I} at 78.4°C. A DSC run on cooling from isotropic state showed a T_{I-N} at 76.0°C, and no crystallization exothermic peak appeared, thus the nematic state was undercooled to a glass state. After being cooled down to 20°C, a heating up run showed a $T_g = 36^\circ\text{C}$ (from undercooled nematic glass state) and a $T_{N-I} = 78.4^\circ\text{C}$. A difference in T_{N-I} on heating and T_{I-N} on cooling by 2.4°C was observed as shown in Fig. 1, $\Delta H = 1.7 \text{ J/g}$ for the transition. Transition temperatures observed by polarizing microscopy (Olympus BH-2 with a Mettler FP-52 hot stage) on a heating up run at 10 K/min were $T_{K-N} = 50^\circ\text{C}$ and $T_{N-I} = 77^\circ\text{C}$. We believe that the DSC results are more accurate. Another sample polymerized in benzene apparently having much higher molar mass so that its solubility in THF was not good enough to perform gel permeation chromatography showed T_{K-N} at 59.5°C, T_{N-I} at 106.5°C on heating and T_{I-N} at 104.4°C on cooling. The latter value of T_{N-I} is close to the values reported in the literature: 105°C^[20] and 109°C^[23]. In the case of polyacrylate of the same pendant mesogen group it was known that polymerization in toluene gave high molar mass polymer, while polymerization in THF gave low molar mass polymer^[21]. Thus T_{N-I} is strongly molar mass dependent. This polymer as synthesized was shown by Springer and Weigelt to form polymer-monomer and inter-polymer aggregates in the polymerization solution^[22], presumably through inter-mesogen interactions. However, the possible presence of the monomer in the re-precipitated sample used in this work was not detected by IR spectroscopy. From the WAXD diagram of the sample at room temperature shown in Fig. 2, the sample could be considered as poorly crystalline with only very small crystallites in agreement with observations of Springer and Weigelt^[23].

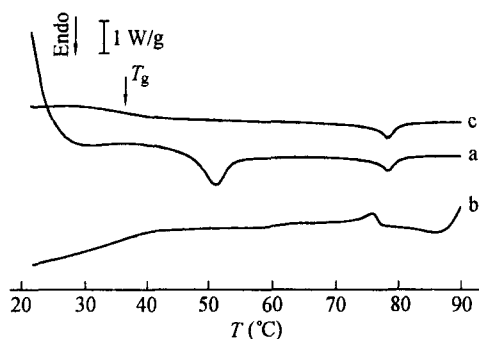


Fig. 1 DSC curves of the polymer at 10 K/min
a) Heating up of the sample; b) Cooling down from isotropic state; c) The second heating up from glass state

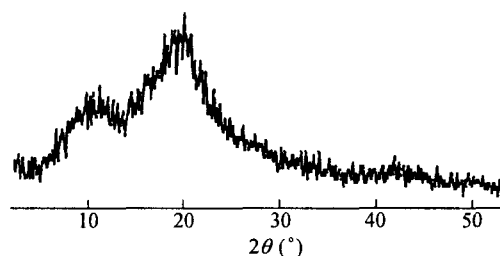


Fig. 2 WAXD diagram of the sample at room temperature, $\lambda = 0.154 \text{ nm}$

Small angle light scattering intensity measurement for I→N transition was carried out in an arrangement as shown schematically in Fig. 3. A He-Ne laser ($\lambda_0 = 632.8 \text{ nm}$ in vacuum) was used as the light source. A Sony ILX511 2048-pixel CCD Linear Image Sensor of $14 \mu\text{m}$ (pitch) $\times$ $200 \mu\text{m}$ pixel size was used as the detector.

This image sensor has very high sensitivity of 1800 V/lx-s, and a dynamic range of 270 determined at 10 ms optical integration time. Throughout the measurements in the present work an integration time of 500 ms was used. The sample stage is equipped with two separately thermostated hot plates, one of which is operated at the temperature of the isotropic state T_I of the sample, while the other is operated at the temperature of the nematic state T_N . The sample holder can be rapidly moved between these two hot plates on two guide rods. In the present work $T_I = 80.2 \pm 0.5^\circ\text{C}$, $T_N = 75.8 \pm 0.2^\circ\text{C}$ were chosen. The output current from the CCD image sensor for a single scan every 2 min was stored and plotted on a computer screen through interface software. The distance between the sample and the sensor was 145 mm. The refractive index of the polymer used is $n = 1.60$ determined at 81°C using an Abbe refractometer with circulating thermostated water. The range of $q = (4\pi/\lambda)\sin\theta/2$ values covered in the experiment is $0.03\text{--}1.5\ \mu\text{m}^{-1}$, where θ is the scattering angle in the sample and λ is the wavelength in the sample, $\lambda = \lambda_0/n$. The scattered light beam emerging from the sample has an angle θ' to the incident beam, $\sin\theta'/\sin\theta = n$. As θ is less than 0.15 radian, $n \doteq \sin\theta'/\sin\theta \doteq \theta'/\theta$, $\sin\theta/2 \doteq \theta/2 \doteq \theta'/2n$, and $q = (4\pi/\lambda)\sin\theta/2 = n(4\pi/\lambda_0)\sin\theta/2 \doteq (4\pi/\lambda_0)\theta'/2$, hence q can be calculated directly from λ_0 and θ' , even without the need to know the value of n , when θ' is very small. The CCD background noise in the dark is automatically deducted from the measured scattering intensity.

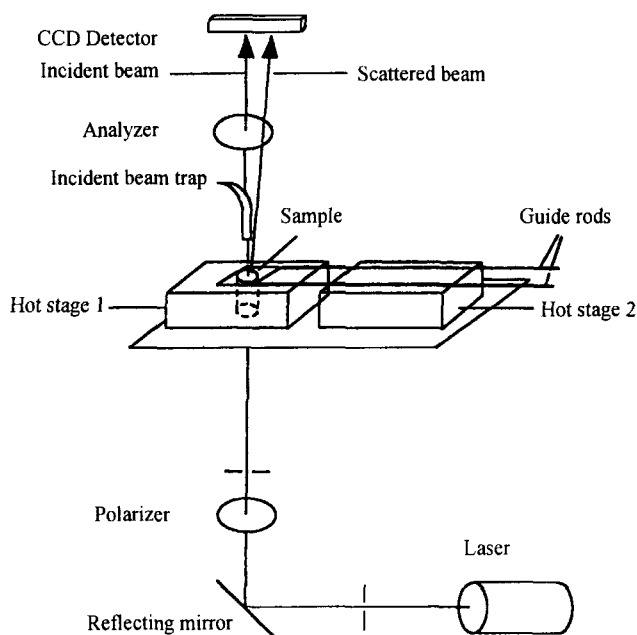


Fig. 3 Schematic showing the set up for SALS measurement

A 4 wt% solution of the polymer in CHCl_3 was dropped onto a clean glass slide and spread out. It was put in a covered petri dish to let the solvent evaporate slowly to form a film of the polymer, which was then dried in a vacuum oven at 45°C for 12 h to give a film of $35\ \mu\text{m}$ thickness. The film was covered by another glass slide and put into the sample holder. A separate experiment with a Cu-constantan thermo couple buried in the sample between two glass slides showed that when the sample holder was moved from the hot plate at 80.2°C to the other at 75.8°C , about 10 s was needed to establish thermal equilibrium.

RESULTS AND DISCUSSION

The sample film was first located on the hot plate at 80.2°C for 5 min and then it was quickly moved to the hot plate at 75.8°C and the experimental time t' was started. The recorded H_v scattering (with polarizer and analyser crossed) intensity is independent of q , i.e. scattering angle independent, and its evolution with t' is shown by the

curve of $\mathcal{I}(t')$ in Fig. 4. It is clear from the figure that the scattered intensity $\mathcal{I}(t')$ is very small and constant in the initial 10 s, indicating the time needed for the sample to reach the temperature 75.8°C for I→N transition, then the scattered intensity $\mathcal{I}(t')$ increased sharply and gradually approached a saturation value in about 2 min. So the transition is rather fast. When $\lg \mathcal{I}(t')$ is plotted versus t' as shown in the insert of Fig. 4, the initial increase in $\lg \mathcal{I}(t')$ of I→N transition follows a straight line for the initial 6 s. Hereafter, we shall take the intersection point, $t' = 10$ s, of the horizontal line and the straight line increase of $\lg \mathcal{I}(t')$ as the origin of the time t of I→N transition, i.e. $t = t' - 10$. The evolution of the scattered intensity as a function of q , $\mathcal{I}(q)$, as t increases is shown in Fig. 5. The initial fast increase of scattered intensity as shown in Fig. 4 does conform to the theory for spinodal type phase transition mediated by orientation fluctuations^[16], $\mathcal{I}(t) = e^{at}$, a being a constant. It is interesting to note that the later part of the curve $\mathcal{I}(t)$ shows a saturation so that the curvature of the curve becomes concave downward, while the initial part of the curve $\mathcal{I}(t) = e^{at}$ has its curvature concave upward. This seems to indicate that the growth of $\mathcal{I}(t)$ involves a two step process, a spinodal type phase transition to initiate the formation of a nematic phase followed by a growth of orientation order and nematic domain sizes.

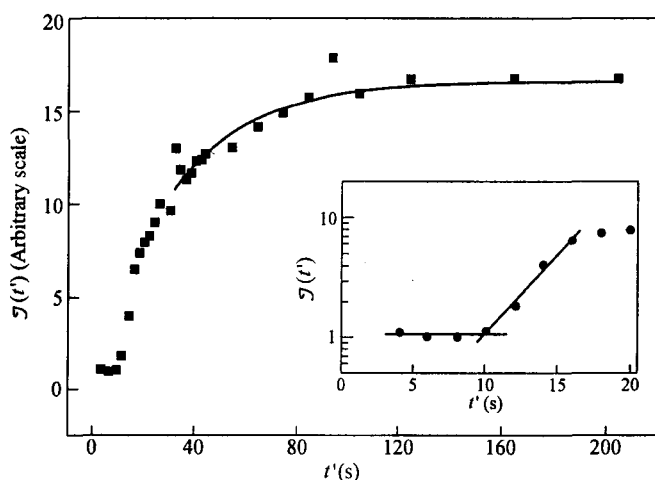


Fig. 4 Experimental data of H_v scattering intensity $\mathcal{I}(t')$; insert: $\lg \mathcal{I}(t')$ in the initial stage; solid curves as eye guides

It is also interesting to note that the evolution of the H_v scattering $\mathcal{I}(t)$ observed during I→N transition is very similar to that observed in the induction period of melt crystallization of polymers^[17, 19], although in the former case the nematic domain size is in the order of μm , while in the latter case the domain size is perhaps smaller than 50 nm, that is a difference about two orders of magnitude in the nematic domain sizes for the two cases. The characteristic features of the SALS are (i) $\mathcal{I}(q)$ is independent of q , (ii) $\mathcal{I}(t)$ shows an initial part conforming to spinodal phase transition and the later part showing a saturation, and (iii) the total change in $\mathcal{I}$ in the whole course of $\mathcal{I}(t)$ is about one order of magnitude. From the experimental result of the present work the proposition that the melt crystallization of polymers is not initiated by thermal nucleation, but by spinodal type of phase transition mediated by orientation fluctuation leading to the formation of nematic nanodomains, is now established on a firm basis.

The $\mathcal{I}(q)$ curves of V_v scattering measured with the polarizer and analyser parallel are shown in Fig. 6. It is obvious from the figure that the scattering intensity is q -dependent. H_v scattering comes from orientation fluctuation, while V_v scattering involves both orientation fluctuation and concentration (density) fluctuation. In the figure of V_v scattering the q -dependent part of the scattering intensity appears only in the region of $q < 0.6 \mu\text{m}^{-1}$. As the scattering from orientation fluctuation (H_v) is q -independent, we may deduct the q -independent part observed at $q > 0.6 \mu\text{m}^{-1}$ from the total scattered intensity to obtain the intensity of V_v scattering due to

density fluctuation. This part of scattering intensity falls very rapidly with increasing q , especially at the initial period of the transition. V_v scattering is not only scattering angle dependent, but may be azimuthal angle dependent as well. It is also noted that the $\mathcal{I}(q)$ of V_v scattering intensity shows a maximum at $q = 1.41 \mu\text{m}^{-1}$ at the later stage of the transition, which corresponds to a mean domain size of $4.5 \mu\text{m}$. Optical polarizing microscopic observation of the nematic phase formed from the sample by the same temperature program showed the morphology of birefringent domains of $3\text{--}7 \mu\text{m}$ size dispersed in an isotropic melt, in good agreement with SALS result. It should be mentioned here that the polymer studied is a side chain nematic polymer, the nematic domains are formed from molecular condensed state of side chain mesogens through the molecular motions of the flexible main chain and the flexible spacers. The main chain moiety will still be randomly interpenetrated and non-birefringent. In a study by light scattering of solutions and small angle neutron scattering of the nematic and isotropic melts with deuterated main chain H-atoms of the polymer as used in the present investigation the following results were obtained^[24] for a fractionated sample of $M_w = 4.42 \times 10^5$. The main chain is in an unperturbed state in the melts. The radius of gyration of chain does not change significantly in N $\rightarrow$ I transition. In nematic state the chain forms a coil having the symmetry of flattened rotational ellipsoid with short principal axis in the direction of mesogen directors $\mathbf{n}$, so that the radii of gyration in the directions parallel $R_g(\parallel)$ and perpendicular $R_g(\perp)$ to $\mathbf{n}$ have a ratio $R_g(\parallel)/R_g(\perp) \approx 0.8$. The value of R_g in the isotropic melt by neutron scattering is 30% smaller than that in a θ -solution by light scattering. Detailed structure of the molecular condensed state of side chain nematic polymers remains to be studied in the future.

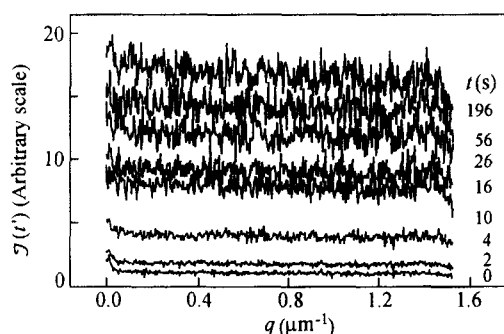


Fig. 5 H_v scattering intensity $\mathcal{I}(q)$ at different t in the course of I $\rightarrow$ N transition

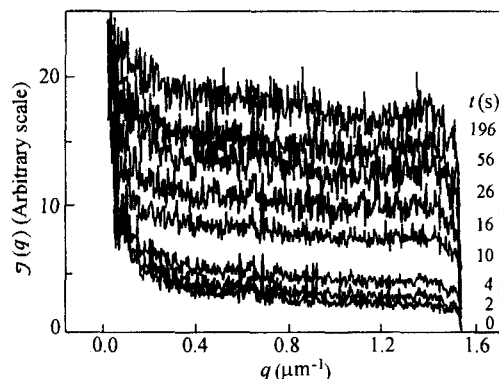


Fig. 6 V_v scattering intensity $\mathcal{I}(q)$ at different t in the course of I $\rightarrow$ N transition

The reverse process N (at 75.8°C) $\rightarrow$ I (at 80.2°C) was analogously studied, but the process was observed to be so fast that the transition finished during temperature equilibration after the jump.

CONCLUSION

The process of I $\rightarrow$ N transition of a side chain nematic polymethacrylate as followed by H_v small angle light scattering intensity measurements has been shown to be a spinodal type phase transition mediated by orientation fluctuation. In the initial stage of the transition the intensity of depolarized light scattering increased exponentially with time and is scattering angle independent. At later stage of the transition the scattering intensity approaches a saturation value.

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