

INVESTIGATION ON THE CONFORMATION OF THE MAIN-CHAIN NEMATIC POLYMER BY SMALL ANGLE X-RAY SCATTERING

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ABSTRACT

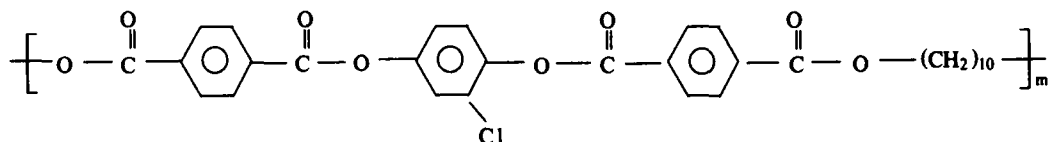
The experimental investigation on the conformation of a thermotropic main-chain nematic polymer by small-angle X-ray scattering (SAXS) has been carried out. The average radius of gyration of the polymer has been determined in nematic and isotropic state respectively. The experiment shows that the boundary between domains is not sharp but diffuse, and the diffuse-boundary thickness of the polymer as a function of temperature has been given.

INTRODUCTION

The investigation on the conformation of polymeric chains is of importance for developing the statistic theory of polymers. Small-angle X-ray scattering (SAXS) and neutron scattering (SANS) are the powerful analytical techniques to study the conformation of polymeric chains experimentally. The researches on the statistical properties of flexible chains in an isotropic environment have greatly advanced. However, conformation of chains in liquid crystal polymers has not yet been known well. In recent years, the related theories of nematic polymer phase and conformation have been presented.^{[1][2]} At the same time the anisotropic conformation and order parameters of side chain nematic polymer in nematic field have been investigated by SAXS and SANS as well as NMR.^{[3][4]} But these experimental results were obtained for dilute solution of mesomorphic polymers in a low-molecular-weight liquid crystal. Therefore, the situation for pure main-chain polymers is certainly different. In this paper we report the experiment on a main-chain thermotropic nematic polymer by SAXS. Although the experiment was carried out in an unoriented sample, we still obtain some available information about the conformation of polymeric chains.

EXPERIMENTAL

The mesomorphic polymer studied here is polymer of chlorohydroquinone and 1,10-bis (4-chloroformylbenzoyloxy) decane. The molecular formula of this compound is



Using DSC technique and optical observation under the polarizing microscope, the phase transition temperature of this polymer can be determined as follows



where C – crystal, N – nematic phase and I – isotropic liquid.

The powder sample is placed in a heater with aluminum foil windows. The SAXS is measured at temperature range from 160 °C to 215 °C with the interval of 10 °C. The temperature fluctuation is controlled within ± 0.5 °C.

In our experiment, the SAXS measurement is carried out by Krafty instrument and the incident parallel X-ray beam ($\text{CuK}\alpha$, $\lambda = 0.15418\text{ nm}$) is generated by a rotating anode (RIGAKU) operating at 40 kV and 100 mA. The vacuum path from sample to the detector is provided. The pulse height analysis of the output of a scintillation detector is employed. The intensity is recorded by step scanning, and the counting time is long enough to avoid the influence of noise upon the scattering intensity from the sample. The SAXS measurement is conducted by using slit collimation of the incident radiation. All SAXS experimental data are smoothed, the statistical erratic data are discarded, the background data are subtracted and the desmearing is carried out.

RESULTS AND DISCUSSION

The desmeared SAXS intensity in arbitrary units from the sample is shown in Fig. 1, from which we find the SAXS intensity from this polymer is nearly constant beyond the scattering angle of about 0.4 °. For the angle smaller than 0.4 °, the scattering intensity increases remarkably with decreasing angle. The logarithm of relative

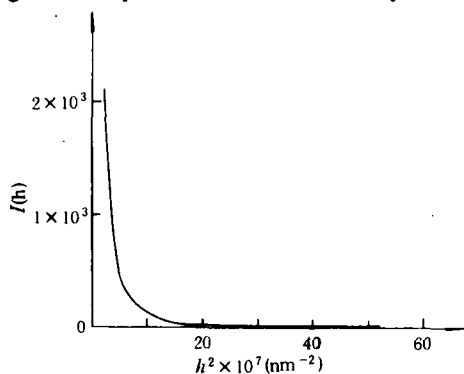


Fig.1 The desmeared SAXS intensity $I(h)$ vs. h^2 plot for the main-chain nematic polymer.

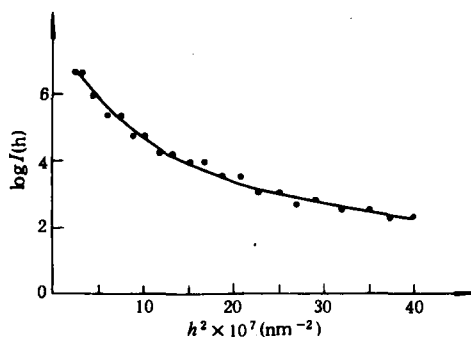


Fig.2 The dependence of the logarithm of relative intensity $I(h)$ on h^2 .

intensity $I(h)$ is plotted vs. h^2 (where $h = (4\pi/\lambda) \sin\theta$, λ is the wavelength of the radiation, 2θ is the scattering angle.) as shown in Fig.2. for the temperature of the sample $T = 190$ °C. It is known that in dilute system one can use Guinier approximation to determine the radius of gyration of the domains with uniform electron density relative

to its surroundings when the domains have the same size.^[5] However, the main – chain nematic polymer is similar to a close – packing domains system, which is not enough dilute to be consistent with Guinier approximation. On the other hand we also notice that the dependence of $\log I(h)$ on h^2 in Fig.2. is a curve rather than a straight line. Therefore, this shows that there is a distribution of the domains in size when the sample is in nematic state.

In order to derive the distribution of domains in size and average radius of gyration, we first assume that all domains have spherical shape and then employ the method developed by Schmidt and coworkers^{[6][7][8]} to evaluate the dimension distribution function. Finally, we can calculate the average radius of gyration $\overline{R}_g$ as a function of temperature (Fig. 3.). It is found that when the sample is in nematic state, $\overline{R}_g$ does not vary obviously with temperature, but in isotropic state $\overline{R}_g$ is smaller than one in nematics. In the experiment with an unoriented sample, we can not measure the characteristic size $R_{||}$ and $R_{\perp}$ (parallel and perpendicular to the nematic director)

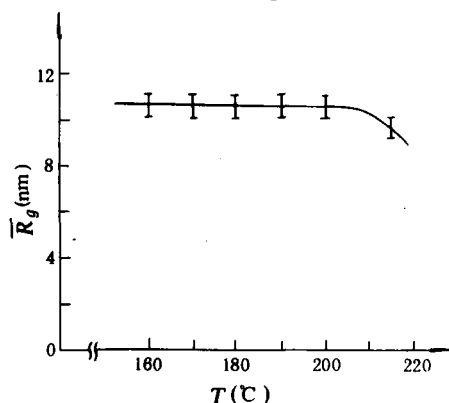


Fig.3 Variation of the average radius of gyration of main – chain polymer as a function of temperature.

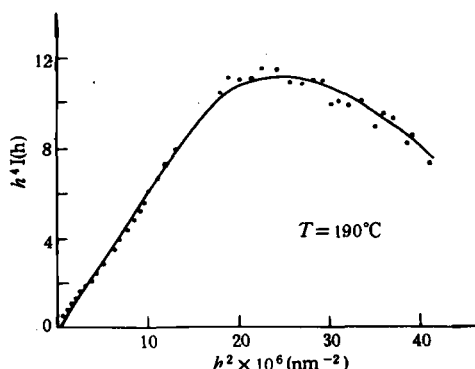


Fig.4 The negative deviation from Porod's law in main – chain nematic polymer.

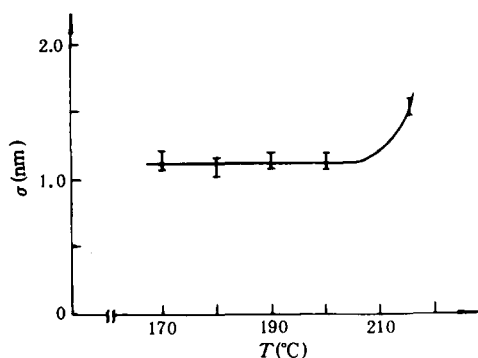


Fig.5 Boundary thickness σ between domains in main – chain polymer versus temperature.

respectively. However, we think roughly the average radius of gyration $\overline{R}_g$ is intermediary between $R_{||}$ and $R_{\perp}$ since $\overline{R}_g$ is the average over all orientations. The data in Fig.3. are comparable with some results derived by other authors. For example, in ref. [3] Mattoussi et al. showed that in the side chain mesomorphic polymer diluted in a low-molecular-weight liquid crystal the characteristic size $R_{||}$ and $R_{\perp}$ are 7.5 nm and 5.5 nm respectively and R_g (in the isotropic state) is 6 nm. We noted that the values

of $\bar{R}_g$ in our experiment are larger than that of $R_{||}$ and $R_{\perp}$ obtained in flexible chains in ref. [3][4]. This difference may be attributable to the rigidity of polymeric chains. In our case, there are three benzene rings in a building unit, and therefore the chains are relatively rigid and more extended so that $\bar{R}_g$ is larger.

Now let us examine the limiting behaviour of the scattering intensity at large values of h . According to Porod's law, the scattering intensity is proportional to the reciprocal fourth power of h at large values of h ^{[9][10]}. This relation is only valid for two ideal phase system with sharp boundary. If the phase boundary is diffuse, the product of $I_p(h)h^4$ does not reach a constant value, and there is a negative deviation from Porod's law. In our experiment, we find the scattering intensity in the tail of the SAXS curve does not decrease in proportion to h^{-4} , but has a negative deviation from Porod's law, as shown in Fig. 4. This indicates that the phase boundary is not sharp but diffuse. For this non-ideal two phase system, using Ruland's method^[11] and the sigmoidal-gradient model^[12] we can calculate the boundary thickness σ from the limiting slope of the curve in Fig. 4. The boundary thickness as a function of temperature is shown in Fig. 5. Here we notice that in nematic phase the boundary thickness does not nearly vary with temperature, but in isotropic state it becomes larger than that in nematics, i. e., the boundary is more diffuse in isotropic state.

CONCLUSION

In the main-chain nematic polymer, the domains are not uniform but have a dimension-distribution. In nematic phase the average radius of gyration does not vary obviously with temperature. On the other hand, the boundary between domains is not sharp but diffuse and the boundary thickness as a function of temperature has been given. However, the anisotropy of the polymeric chains can not be determined with the unoriented sample. Therefore, the further experiment on the oriented sample has to be done.

Keywords:

Main-chain nematic polymer; X-Ray small-angle scattering

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REFERENCES

- [1] Wang, X. J. and Warner, M., *J. Phys A: Math. Gen.*, **1986**, 19, 2215.
- [2] Wang, X. J. and Warner, M., *J. Phys A: Math. Gen.*, **1987**, 20, 713.
- [3] Mattoussi, H.; Ober, R.; Veyssie, M. and Finkelmann, H., *Europhys. Lett.*, **1986**, 2 (3), 233.
- [4] Dubault, A.; Ober, R.; Veyssie, M. and Cabane, B., *J. Physique*, **1985**, 46, 1227.
- [5] Guinier, A., "Theorie et technique de la Radiocristallographie", Dunod, Paris, **1964**.
- [6] Letcher, J. H. and Schmidt, P. W., *J. Appl. Phys.*, **1966**, 37, 649.
- [7] Brill, O. L.; Weil, C. G. and Schmidt, P. W., *J. Colloid. Interface. Sci.*, **1968**, 27, 479.
- [8] Fedorova, I. S. and Schmidt, P. W., *J. Appl. Cryst.*, **1978**, 11, 405.
- [9] Porod, G., *Kolloid-Z.*, **1951**, 124 (2), 83.
- [10] Porod, G., *Kolloid-Z.*, **1952**, 125 (1), 51; 125 (2), 108.
- [11] Ruland, W., *J. Appl. Cryst.*, **1971**, 4, 70.
- [12] Koberstein, J. T.; Morra, B. and Stein, R. S., *J. Appl. Cryst.*, **1980**, 13, 34.