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Neutron Diffraction from Nematic Liquid Crystalline Phase and Isotropic Liquid Phase of Para-Azoxyanisole

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Neutron diffraction patterns of the fully deuterated para-azoxyanisole (d_{14}-PAA) were obtained in the liquid crystalline phase and the isotropic liquid phase. The momentum transfer range extends from 0.5 Å^{-1} to 15 Å^{-1}. The structure factors $S_m(Q)$ of d_{14}-PAA in both phases were deduced. $S_m(Q)$ is separated into two terms of intramolecular and intermolecular contributions. The former term $S_{\text{intra}}(Q)$ is calculated on the assumption of a rigid molecule. The comparison of $S_{\text{inter}}(Q)$ in both the liquid crystalline state and the isotropic liquid state shows that the information near $Q \simeq 6.0$ $\text{Å}^{-1} \sim 8.0$ Å^{-1} plays an important part in understanding the structure of the nematic liquid crystalline state of PAA.

INTRODUCTION

The liquid-crystalline state of matter is a state intermediate between a solid crystal and a liquid. In the classical study of liquid crystals Friedel distinguished between three types of phases—nematic, cholesteric and smectic.[1] In this paper we report the results of neutron scattering experiments from deuterated para-azoxyanisole in a nematic liquid-crystalline phase and in an isotropic liquid phase.

The simplest picture of a nematic is that of a fluid of long rods which tend to be aligned in such a way that the fluid has overall uniaxial symmetry. Many attempts have been made to elucidate the molecular interaction in the liquid crystalline state. X-ray or neutron diffraction technique is a good tool to elucidate the molecular interaction in the liquid crystals. The structure of liquid crystals has been determined mainly by X-ray diffraction techniques.[2–5] In most X-ray experiments the specimen is enclosed in a glass capillary and no information is obtained about the structure in the bulk free from the glass surface effect. In a neutron diffraction experiment, however, a thick sample (e.g. 10 mm in diameter) can be used, since neutrons penetrate into matter more deeply than X-rays. Moreover, the neutron diffraction method has the following good properties for studying the structure of general liquids: i) The contribution from incoherent scattering can be calculated uniquely. ii) The scattering cross section of neutrons does not reduce even in the high Q region (where $\hbar Q$ is momentum transfer), since the scattering length does not depend on Q so strongly. iii) The effect of the scattering from a sample vessel is generally small and can be estimated easily.

As to liquid crystal structure determination, however, the neutron diffraction method is not used so frequently. The main reason is that all of the liquid crystals are substances which contain many hydrogen atoms, and the incoherent neutron scattering cross section of hydrogen is so large (about 90% of the total scattering cross section in the case of PAA) that the signal to noise ratio is very poor. This difficulty should be removed, however, if all the hydrogen atoms are substituted by deuterium. Pynn *et al.* reported neutron diffraction data obtained with a completely deuterated sample of the nematic liquid crystal para-azoxyanisole.[6] But the observed momentum transfer range was limited to about 4 $Å^{-1}$.

P. G. de Gennes has suggested that scattering experiments should be performed at large Q in order to render the analysis of results straightforward.[7] Recently we reported preliminary results of neutron scattering experiments from a completely deuterated para-azoxyanisole in the liquid crystalline phase extending a wide momentum-transfer range from 0.5 to 15 $Å^{-1}$.[8] In this paper, the results of the neutron scattering experiments for d_{14}-PAA in the isotropic liquid phase are also reported.

EXPERIMENT

Deuterated para-azoxyanisole (d_{14}-PAA, 98% deuterated) obtained from the BIO-RAD laboratories was used for the nematic liquid-crystalline sample. The set up is shown in figure 1. The sample (S) has a diameter of 10 mm and is contained in a quartz tube with 0.3 mm sides, which is set in a furnace where it can be heated electrically by the heaters H_1 and H_2. The temperature is measured by a copper-constantan thermocouple (C). In order to confirm the liquid-crystalline state, the sample can be watched through a glass window (W).

In this experiment no magnetic or electric fields are applied to the sample. Neutron diffraction experiments are performed by the time-of-flight (TOF) technique. We have used a neutron diffractometer installed at the 300 MeV Tohoku University electron linac as a pulsed neutron source.[9]

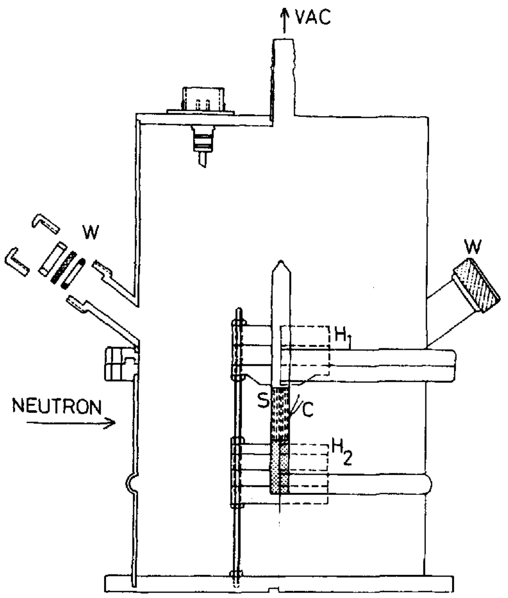

FIGURE 1 The layout of the furnace and the specimen.

RESULTS

Diffraction patterns of d_{14}-PAA were obtained at 122 ± 2°C (in the liquid crystalline phase) and at 195 ± 3°C (in the isotropic liquid phase).

The neutron scattering intensity from a specimen is given by:

$$I_S(\lambda) = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_S \cdot J_0(\lambda) \cdot A_S \tag{1}$$

where $(\mathrm{d}\sigma/\mathrm{d}\Omega)_S$ is the differential cross section of the specimen S, $J_0(\lambda)$ is the incident neutron current with wavelength λ, and A_S is the absorption coefficient of the specimen S. $(\mathrm{d}\sigma/\mathrm{d}\Omega)_S$ consists of coherent and incoherent scattering:

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_S = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{coh}} + \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{inc}} \tag{2}$$

and $(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{coh}}$ is given by

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{coh}} = \sum_{ij} \sum_{\alpha\beta} b_{i\alpha}^{\mathrm{coh}} \cdot b_{j\beta}^{\mathrm{coh}} \langle \exp(i\mathbf{Q} \cdot \mathbf{r}_{i\alpha j\beta}) \rangle, \tag{3}$$

where i and j denote all molecules in the system, α and β denote the nuclei within a single molecule, $b_{i\alpha}^{\mathrm{coh}}$ is the coherent scattering length of nucleus α in molecule i, and $\mathbf{r}_{i\alpha j\beta} = \mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}$ is the vector from nucleus α in molecule i to nucleus β in molecule j. The coherent structure factor, $S_m(Q)$ is defined as follows:

$$S_m(Q) = \frac{1}{N_m(\sum_\alpha b_\alpha)^2} \sum_{ij} \sum_{\alpha\beta} b_{i\alpha} \cdot b_{j\beta} \langle \exp(i\mathbf{Q} \cdot \mathbf{r}_{i\alpha j\beta}) \rangle, \qquad (4)$$

where N_m is the number of molecules in a unit volume. The superscript "coh" on b is omitted hereafter. The incident neutron spectrum $J_0(\lambda)$ in eq. (1) is determined experimentally by the neutron scattering from vanadium, which is an incoherent scatterer within a very good approximation. The neutron scattering intensity from vanadium is given by

$$I_v(\lambda) = N_v \sigma_v J_0(\lambda) A_v, \qquad (5)$$

where N_v is the number of vanadium atoms in a unit volume, σ_v is the total neutron scattering cross section of vanadium, and A_v is the absorption factor of the vanadium sample. From eq. (1), (2), (3), (4) and (5) the structure factors $S_m(Q)$ of d_{14}-PAA in the nematic liquid crystalline phase and isotropic liquid phase were deduced. They are shown in figures 2 and 3, respectively.

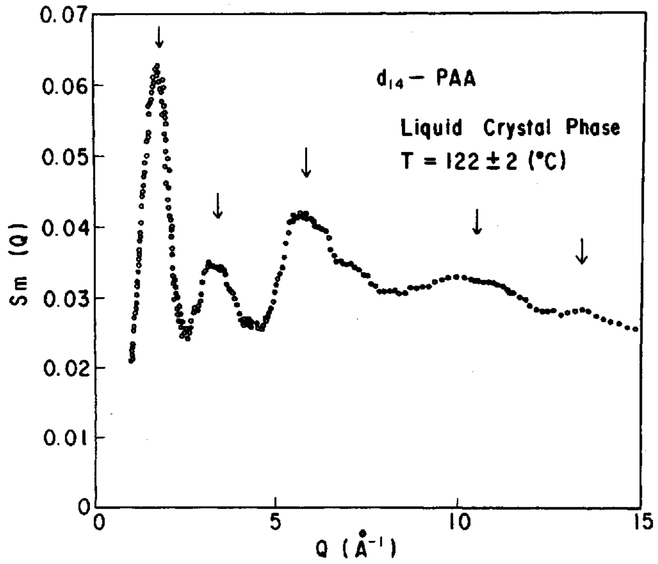

FIGURE 2 The molecular structure factor $S_m(Q)$ of d_{14}-PAA in the nematic liquid crystalline state.

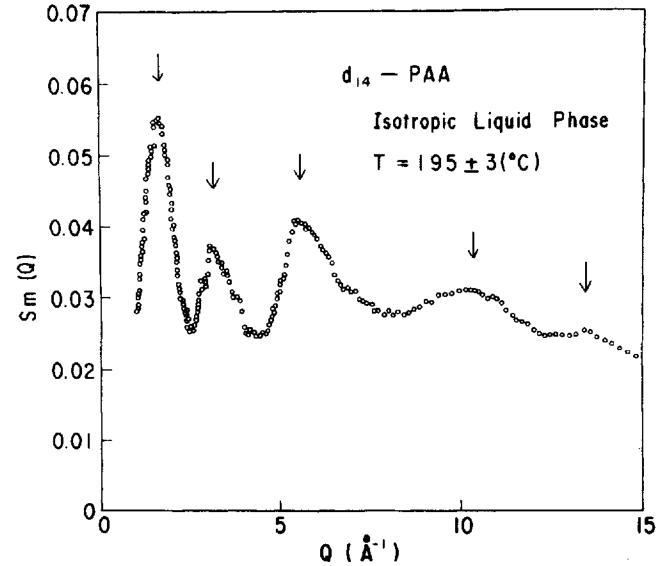

FIGURE 3 The molecular structure factor $S_m(Q)$ of d_{14}-PAA in the isotropic liquid state.

DISCUSSION

Five peaks are found in $S_m(Q)$ within the observed momentum transfer range from 0.5 to 15 Å^{-1}. The peaks at $Q \simeq 1.8\ \text{Å}^{-1}$ and $3.2\ \text{Å}^{-1}$ correspond to those observed by Pynn *et al.*[6] at $2\theta \simeq 30°$ and $54°$, respectively. The fact that there exist rather large peaks at Q larger than $5\ \text{Å}^{-1}$ demonstrates the importance of the experiments extending a wide momentum transfer range. When we write

$$\mathbf{r}_{i\alpha j\beta} = R_{ij} + (\mathbf{r}_{ci\alpha} - \mathbf{r}_{cj\beta}), \tag{6}$$

where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ is the vector between molecular centers and $\mathbf{r}_{ci\alpha}$ is the vector from the center of molecule i to the α-th nucleus of i, $S_m(Q)$ can be separated into two terms of intramolecular and intermolecular contributions,[10-12]:

$$S_m(Q) = S_{\text{intra}}(Q) + S_{\text{inter}}(Q). \tag{7}$$

$S_{\text{intra}}(Q)$ is equal to a form factor of a single molecule, and is identical with the quantities $F_1(Q)$ or $(d\sigma/d\Omega)_S$ in Ref. 10 or Ref. 14, respectively. By assuming the molecules to have a rigid structure, $S_{\text{intra}}(Q)$ of d_{14}-PAA can be calculated using molecular parameters of a crystalline state[13] as follows:

$$S_{\mathrm{intra}}(Q) = \frac{1}{(\sum_{\alpha} b_{\alpha})^2} \sum_{\alpha\beta} b_{\alpha} b_{\beta} \langle \exp(i\mathbf{Q} \cdot [\mathbf{r}_{ci\alpha} - \mathbf{r}_{cj\beta}]) \rangle. \tag{8}$$

$S_{\mathrm{intra}}(Q)$ is shown in Figure 4, and it agrees with the calculation of Pynn[14] within the Q range investigated by Pynn. A sharp peak at $Q \simeq 3.1$ Å^{-1} and a broad peak at $Q \sim 5.5$ Å^{-1} can be seen. When $S_{\mathrm{intra}}(Q)$ is transformed from Q-space to r-space, the former yields a peak at 2.03 Å and the latter at 1.14 Å, corresponding to the distances of the benzene ring diagonal and each atomic bond length, respectively. Even if there occurs intramolecular deformation in the liquid crystalline state or isotropic liquid state, the over all pattern of $F_1(Q)$ should not change so much since the form of the benzene ring and the atomic bond length could not be influenced so easily.

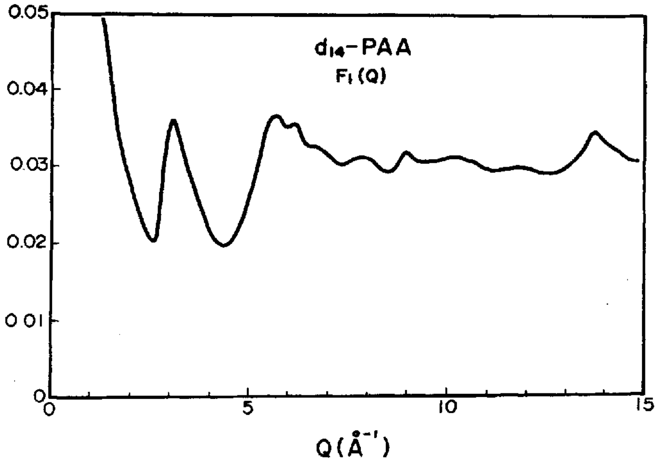

FIGURE 4 The form factor $F_1(Q)$ of a single molecule d_{14}-PAA. $F_1(Q)$ is identical with $S_{\mathrm{intra}}(Q)$.

$S_{\mathrm{inter}}(Q)$ has been obtained by subtracting $F_1(Q)$ from $S_m(Q)$ (eq. (7)). The result for the liquid crystalline state is shown in Figure 5. There exist a sharp peak at $Q \simeq 1.8$ Å^{-1} and a broad peak extending from $Q \simeq 3.0$ Å^{-1} to $Q \simeq 8.0$ Å^{-1}.

Since the value of $Q \simeq 1.8$ Å^{-1} is transformed to 3.5 Å in the r-space, the most probable arrangement of molecules in the nematic liquid crystalline state is the parallel and face-to-face arrangement.

It is interesting to compare the results of liquid crystalline state with those of isotropic liquid state to understand the structure of nematic liquid crystal clearly. As shown in figures 2 and 3, the position of the peaks is almost the

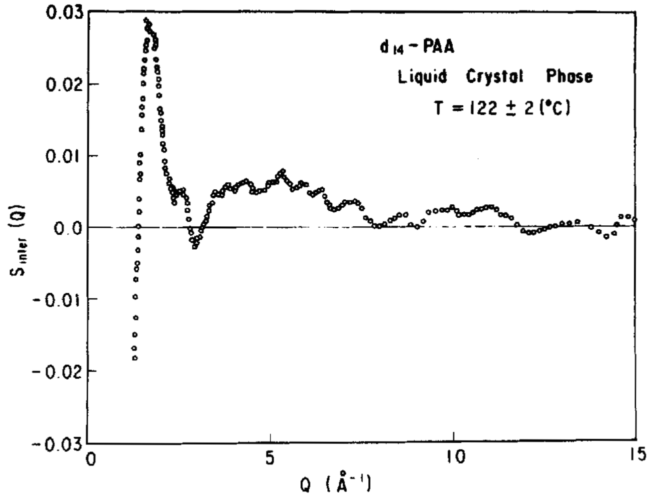

FIGURE 5 The structure factor depending on the intermolecular correlations $S_{\text{inter}}(Q)$ in the nematic liquid crystalline state.

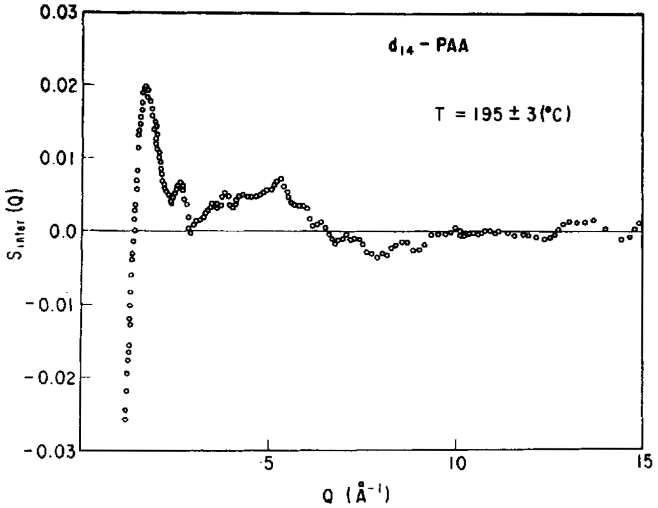

FIGURE 6 The structure factor depending on the intermolecular correlations $S_{\text{inter}}(Q)$ in the isotropic liquid state.

same, but the height changes. The ratios of the first three peaks are 0.88, 1.07 and 0.98, respectively. The third peak near $Q \simeq 6\ \text{Å}^{-1}$ has some structure in the liquid crystalline state, but in the isotropic liquid state it has not. The differences become clear when both the $S_{\text{inter}}(Q)$ of the liquid crystalline state and the isotropic liquid state are compared (Figure 5 and Figure 6). The broad peak in the liquid crystalline state extends from $Q \simeq 3.0\ \text{Å}^{-1}$ to $8\ \text{Å}^{-1}$, the one in the isotropic liquid state from $Q \simeq 3.0\ \text{Å}^{-1}$ to $6\ \text{Å}^{-1}$. The most prominent difference between both states is the fact that there is no peak near $Q \simeq 6.0\ \text{Å}^{-1} \sim 8.0\ \text{Å}^{-1}$ in $S_{\text{inter}}(Q)$ of isotropic liquid state.

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