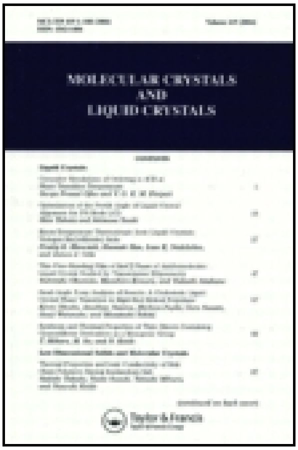

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Small Angle Neutron Scattering from Liquid Crystal-Line Main Chain Polyesters

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SMALL ANGLE NEUTRON SCATTERING FROM LIQUID CRYSTALLINE MAIN CHAIN POLYESTERS

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Abstract Small angle scattering studies were carried out on a spacer-mesogen polyester family. A strong anisotropy was observed in the nematic phase. Studies of the anisotropy in isotropic-nematic biphasic, nematic, and nematic vitrous state and the temperature variation in melts and in dilute solutions in a low molecular weight liquid crystal are presented here. The role of spacer parity is emphasized.

INTRODUCTION

Neutron scattering is a powerful tool in the study of polymer systems in both solutions and bulk. Selective deuterium labelling allows the determination of chain conformation and dynamics[1]. The chain conformation of main chain liquid crystalline polymers (LCP) in the nematic and isotropic phases has never been investigated by this technique which can directly determine the possible chain extension at the nematic/isotropic transition.

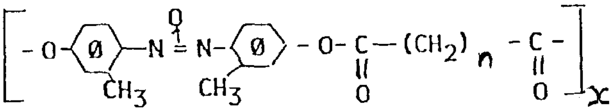
This important question has been extensively debated theoretically by several groups. Already in 1981 de Gennes[2] considered the possibility of important conformational changes at the isotropic-nematic transition. Calculations were performed in particular in the worm-like chain model[3,4] and the flexible comb-like model[5].

The experimental study of conformational changes by neutron scattering was done for the case of a flexible chain in a nematic solvent[7] or for a side chain polymer [8-10]. In the case of main chain liquid crystal polymers chain extension in the nematic phase has been mentioned already in 1981[11]. Other techniques have been used to study conformational changes in the nematic phase of this polymer[12] but the direct value of the radius of gyration and of anisotropy has to our knowledge never been determined.

EXPERIMENTAL

MATERIALS

We have used a main chain polyester based on a regularly alternating sequence of a P, P' dixoy 2,2' dimethylazoxybenzene mesogen and a flexible spacer with 10 and 7 methylene groups : n = 7 (AZA-9), n = 10 (DDA-9).



This polymer presents a large number of attractive features[13-17] which make it an ideal candidate for this study:

- well known mesomorphic characteristics : order parameter properties in magnetic and electric fields ,etc.
- Low isotropic-nematic transition temperatures allowing for extended time studies without decomposition.
- Good solubility and knowledge of phase diagrams with PAA. The good solubility of this polymer in common solvents gives the possibility of obtaining sharp fractions of degree of polymerization (DP) between 5 and 50. The fi-

gure 1 gives the dependence of the transition temperature on M_n for a series of sharp fractions [$\bar{M}_w/\bar{M}_n < 1.2$]. Figure 2 shows the phase diagramm of DDA-9 of M_n = 6,000 and PAA.

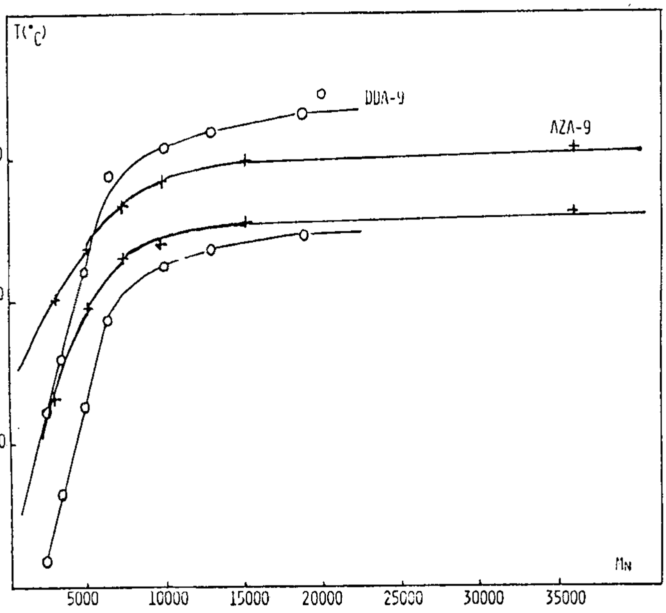


FIGURE 1. Anisotropic-biphasic and biphasic-isotropic temperature of AZA-9 (+) and DDA-9 (.). Polyesters as a function of molecular weight.

The composition of the samples used in neutron scattering was of a few weight % of protonated DDA-9 in perdeuteraded PAA. The concentration was chosen to be well below the critical concentration for chain overlaps. The additional advantages of the low concentration are a narrow biphasic interval (see fig. 2) and a weak non-coherent scattering.

EXPERIMENTAL SET-UP

The small angle neutron scattering was performed with the spectrometer Paxy of the laboratory Léon Brillouin CEA, CNRS Saclay. The wavelength chosen is λ = 15 Å and the sample-detector distance is 2m.

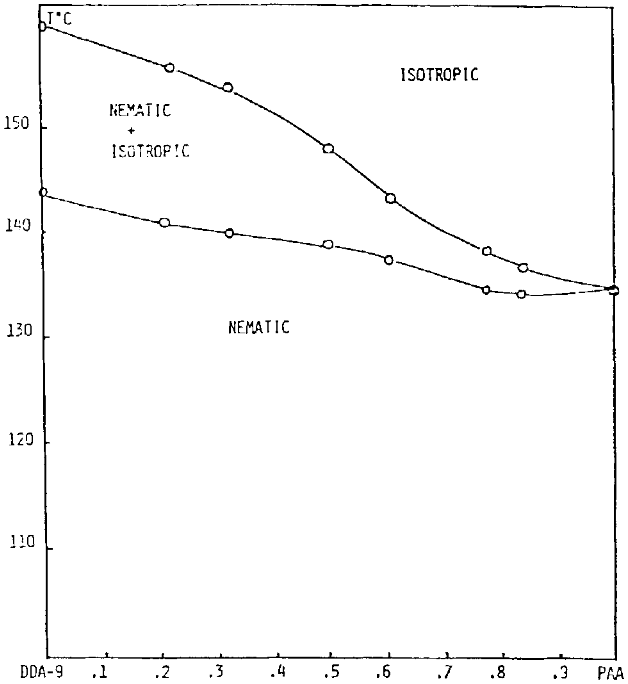


FIGURE 2. Phase diagram of DDA-9 (M_n : 6000)/PAA mixture.

A magnetic field H = 1.4 Tesla allows to orient the nematic phase of the sample. The intensity distribution of the scattered beam in space can be recorded by a system of multidetector. Thus the intensities scattered in two perpeneidcular directions can be determined.

The sample is placed in a cell of precisely controlled temperature allowing to work in the nematic, isotropic and glassy states.

A number of investigators have discussed the possibility of a determination of the radius of gyration for isotropic and anisotropic particles in the Guinier range [1].

For an isotropic sample the scattering intensity is given by

$$I^{-1}(q) = I^{-1}(0)\ (I+q^2 R_0{}^2/3) \quad \text{with } q\ R_o < 1 \text{ and}$$

$$R_0{}^2 = < R_x{}^2 > + < R_y^2 > + < R_z^2 >$$

q is the scattering vector and $R_{x,y,z}$ the dimensions of the polymer chain in the x,y,z directions.

If $q_{//}$ and $q_\perp$ are the components of q which are parallel and perpendicular to the magnetic field which aligns the polymer liquid crystal medium, then the corresponding scattered intensities are given by :

$$I^{-1}\ (q_{//}) = I^{-1}(0)\ (1 + q_{//}{}^2 R_{//}{}^2) \qquad q_{//}\ R_{//} > 1$$

$$I^{-1}\ (q_\perp) = I^{-1}\ (0)\ (1 + q_\perp{}^2\ R^2_\perp) \qquad q_\perp\ R_\perp < 1$$

$R_{//}$ and $R_\perp$ are the quadratic characteristic sizes of the polymer respectively parallel and perpendicular to the nematic director.

In this work we present the results of the study of the radius of gyration R_0 (isotropic phase) and $R_{//}$, $R_\perp$ (anisotropic phase) for a number of experimental situations :

- For melts or solutions in low molecular weight liquid crystal (PAA).
- For different $\overline{M}_n$.
- For two different spacer lengths (odd and even)
- In the isotropic, nematic, biphasic and glassy nematic systems. I (q) versus q^2 curves for typical exemples are given fig.3.

Studies of dilute solutions of the polymer in PAA

a) Molar mass variation

Studies were performed on isotropic and anisotropic phases with different molecular weights of protonated polymer in deuterated PAA. Figure 4 shows the results for two typical DDA-9 samples which have molecular weights of 6000 and 18600.

In each phase no significant temperature variation is observed. For both samples a strong anisotropy exists in the nematic phase. Due to the low polymer concentration, the anisotropic-isotropic transition is abrupt and the transition temperature is very close to pure PAA. The anisotropy seems to increase with molecular weight. The value obtained for $R_{//}$ in the M = 18,600 sample is only given as an indication: the conformation of the chain is almost linear.

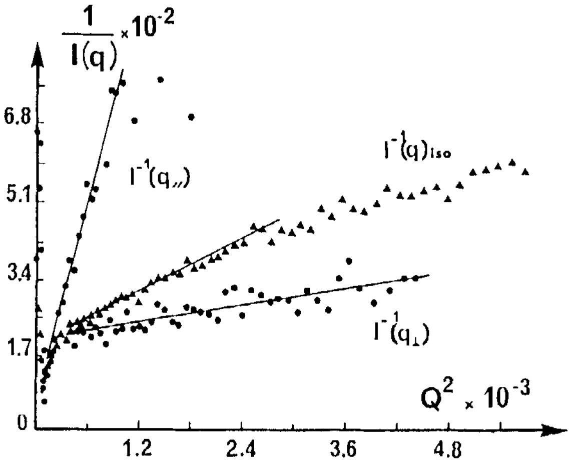


FIGURE 3. Scattering spectrum for DDA-9 18600/PAA D Mixture

I(q) = scattering intensity q = scattering vector

▲ isotropic phase 1/I versus q^2 at 148°C

● anisotropic phase 1/I versus q^2 (// and ⊥) at 125°C

b) Comparaison between the anisotropies with two polymers having different spacer length.

We did not carry out a comparison between two polymers of approximately the same degree of polymerization. However it is possible to draw a certain number of conclusions using the results of the figure 5 which illustrates the behaviour obtained with two dilute solutions in PAA : AZA-9 with a molecular weight of 36,000 in and of DDA-9 of 18,600. In the isotropic phase we obtain almost equal radii of gyration . This can be explained by the fact the molecular weight is higher and the spacer length (and consequently the monomer length) smaller in the AZA-(36,000). In the nematic phase the DDA-9 anisotropy is much higher than the one of the AZA-9. This corresponds to a greater extension of the DDA-9 chains in PAA.

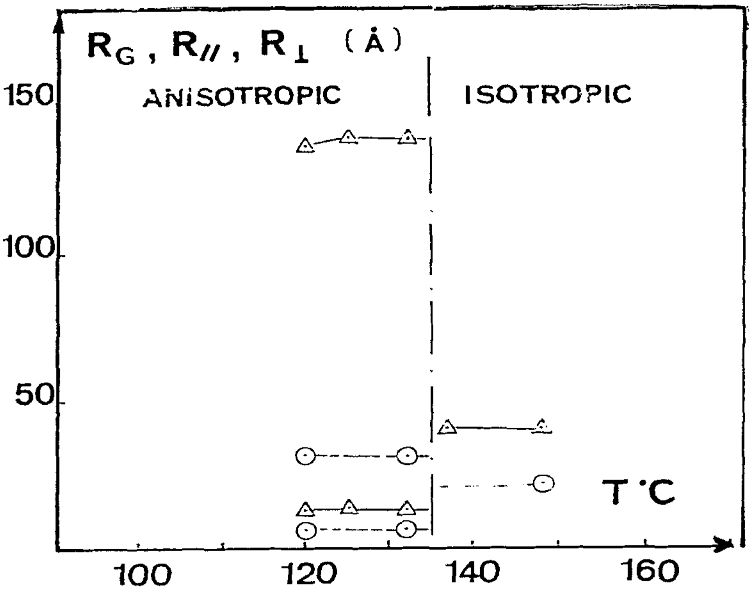


FIGURE 4. Radius of gyration as a function of temperature for :

DDA-9 (M_n = 6,000) / PAA Mixture

DDA-9 (M_n = 18,600) / PAA Mixture

Bulk melt studies

Mixtures (50/50 by weight) of protonated (P) polymer with the corresponding polymer selectively deuterated on the spacer (D) were studied. Molecular masses of P and D were the same.

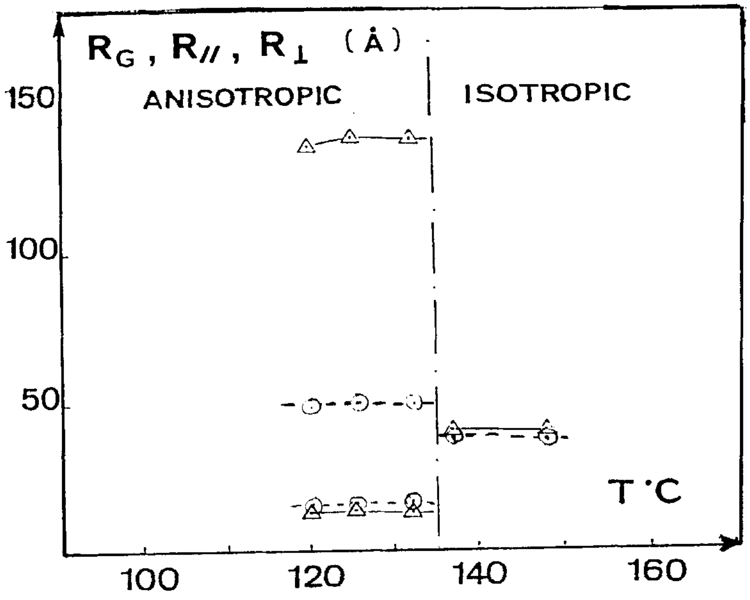


FIGURE 5. Radius of gyration as a function of temperature for
△ DDA-9 (M_n = 18,600)/PAA Mixture
○ AZA-9 (M_n = 36,000)/PAA Mixture

a) Temperature variation

Results obtained with the melt AZA and DDA with molecular weights of 6,000 are shown in figure 6. The behavior is approximately the same : a single value of radius of gyration in isotropic phase, strong anisotropy in the anisotropic phase ,time dependent (fig.7) intermediate anisotropy in the biphasic zone. A comparison between the results obtained with the two samples is difficult because the extent of the biphasic and nematic zones, are very different in the two samples. In the DDA-9 cristallisation occurs at 105°C and on the contrary, the AZA-9 can be cooled much lower without noticable cristallisation. We observe in this last case a very large increase of the anisotropy at low temperatures, and in figure 6 we only have reported the points corresponding to $R_{\perp}$ at 88 and 98°C. The corresponding values of $R_{//}$ are too high (over 250) and therefore cannot be obtained with a sufficient accuracy.

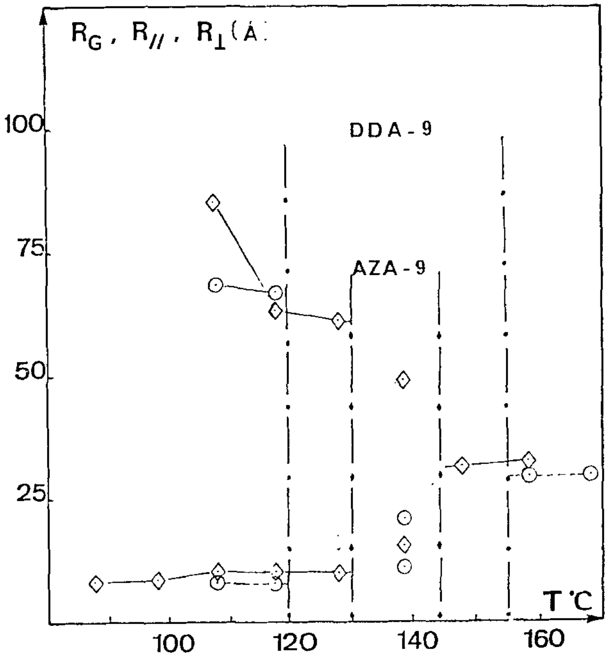


FIGURE 6. Radius of gyration as a function of temperature
⊙ DDA-9 (M_n = 6,000) in melt mixture DDA-9 D/ DDA-9 P)
◇ AZA 9 (M_n = 6,000) in melt (mixture AZA-9/AZA-9 P)

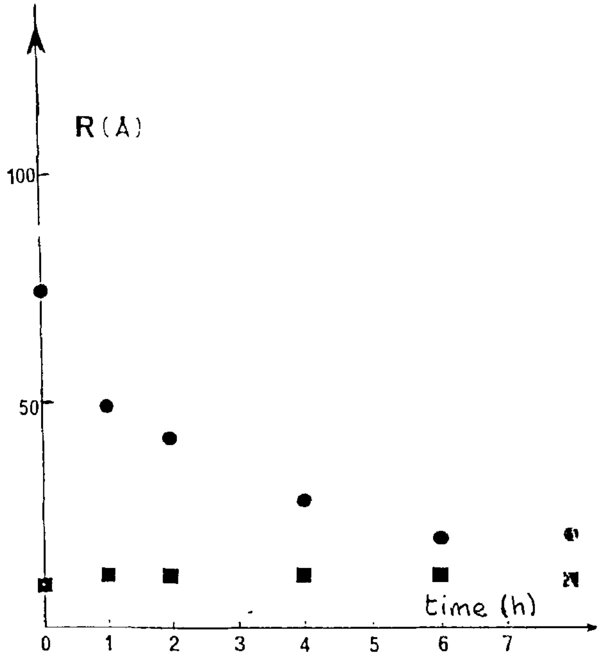


FIGURE 7. Radius of gyration in the biphasic gap as a function of time for DDA-9 . T = 132°C (M_n = 5.000) in melt (mixture DDA-9 P - DDA-9 D) At time t = 0 temperature is quickly heated from the nematic phase. (● $R_{//}$, ■ $R_{\perp}$)

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