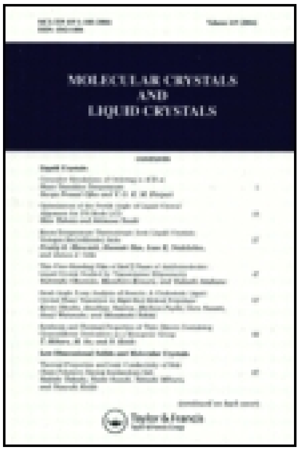

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Solubilization of a Polymer Chain in a Nematic Phase; Effect on the Twist Viscosity

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Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. Vol. 41 (Letters), pp. 239-244

SOLUBILIZATION OF A POLYMER CHAIN IN A NEMATIC PHASE ; EFFECT ON THE TWIST VISCOSITY.

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(Accepted for Publication May 12, 1978)

Abstract : We have dissolved short polymer chains ($M = 2.10^3$ and 8.10^3) of poly-ethylen-oxide in the nematic phase of para-azoxy-anisol. On these solutions we measured the twist viscosity γ_1. We find an increase of γ_1 with the polymer content, correlated to the anisotropy of the polymer chain.

Introduction : The aim of this work is to get an insight on the conformations of a long, flexible, chain in a nematic solvent. A nematic fluid has five independent coefficients of friction (1) : all of them are expected to be significantly modified by a polymeric solute, even at rather low concentrations (2). We chose to measure here the twist viscosity γ_1 which is relatively simple to reach.

The first stage of this work was to find a compatible polymer-nematic system. Indeed, when we started this study, there was no clear information in the published literature on the possibility of solubilization of a polymer phase, except some results on polymerized nematogenic molecules (3) (4). More recently, C. Noël et al (5) studied phase diagrams of similar systems. In this letter, we give results obtained for the para-azoxy-anisol (PAA) - poly ethylen oxide (PEO) system.

PAA-PEO phase diagrams The PAA (Princeton Organics) was of good purity and gave a sharp peak in differential scanning calorimetry (clearing temperature T_C = 135.5°C) ; the PEO samples were obtained by anionic synthesis (F. Candau - Strasbourg) and have a fairly good monodispersity (M_w/M_n < 1.1). We used three molecular weights : 2100 (number of monomer units = 45), 7800 (178) and 44000 (1000) Mixtures of PAA with various polymer concentrations were homogenized by nitrogen bubbling in the isotropic phase of PAA (T_C ≈ 137°C) during three hours. We then observed a droplet of each samples under polarizing microscope to determine the transition temperatures T_I and T_N (see below) as a fonction of concentration and chain length :

PAA-POE 2100 The macromolecules of such chain length are soluble in the isotropic phase for concentration by weight, c, up to about 5 %. But, when we slowly cool down a mixture droplet, we observe that if c > 1 %, one part of the sample remains isotropic, even down to the crystallization temperature. For concentrations lower than 1 %, we obtain a phase diagram as shown on fig. 1 for which we can determine two caracteristic temperatures T_I and T_N for each value of c: when the temperature

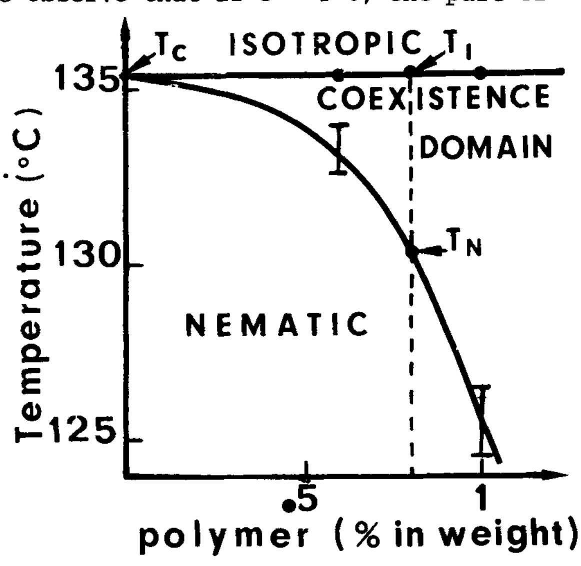

Figure 1

is decreasing, the nematic phase begins to appear at T_I and the isotropic phase completly disappears at T_N (For $c = 0$, $T_I = T_N = T_C$). We notice that variation of T_I is very slow ($T_C - T_I$ 0.2°C for c = 1 %) while T_N decreases rapidly ; this last point explains the inaccuracy of our determination of T_N.

PAA-POE 7800 In this case, we observe a liquid-liquid phase separation in the isotropic phase even for c as low as 0.5 %. Only the fraction poor in polymer gives a nematic transition with $T_C - T_I \simeq 0.2$°C, and $T_C - T_N \simeq 2.5$°C.

PAA-POE 44000 For this molecular weight, there is also a partial solubility in the isotropic phase, but a quasi-total insolubility in the nematic phase +.

We determine γ_1 by a study of a dynamics in a Freedericksz transition following the experimental method of Pieransky et al [7] which gives γ_1 with an accuracy of 5%. The samples had a thickness of 190μ. They were oriented in a planar texture between glass plates grinded with diamond paste (which ensures a strong anchoring). The sample temperature were regulated at ± 0.1°C.

On fig. 2, we report the γ_1/χ_a as a function of temperature (χ_a : diamagnetic anisotropy) for pure PAA, and PAA-PEO 2100 (c = 0.6 % and 1 %). For pure PAA, the accuracy is within 5 %, for the mixtures, the dispersion is somewhat larger (probably due to fluctuations in polymer concentrations). The points on the plot are averaged from several measurements. It appears clearly that γ_1 is increased by the solute polymer chains.

+ These results are qualitatively similar to these of Kronberg [6] for an another polymer-nematic system.

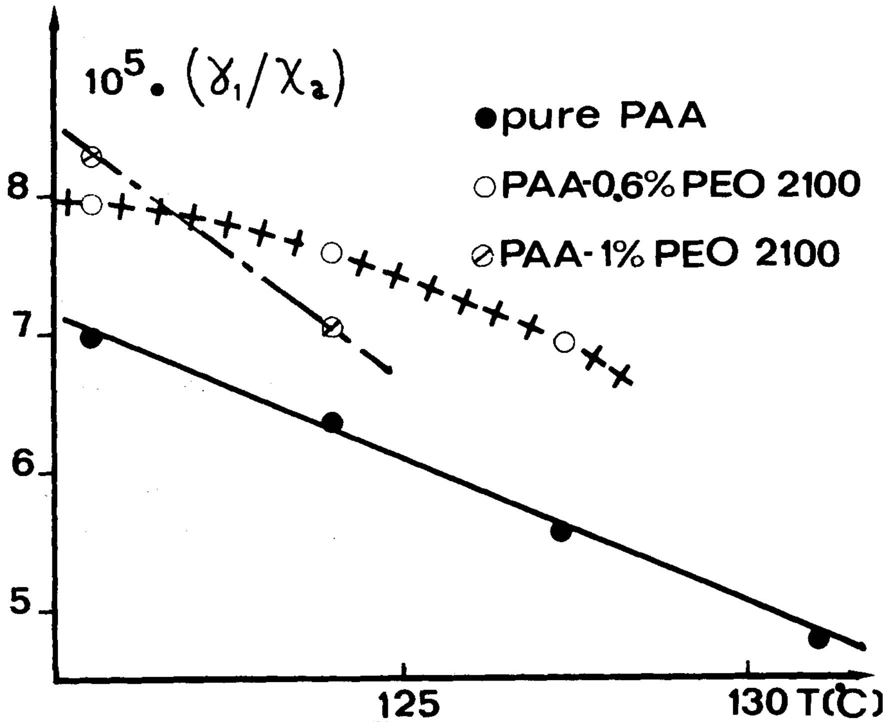

Figure 2

To get more significant results, we plotted on Fig. 3 the γ_1 values as a function of the reduced temperature T/T_N. For each concentration, the T_N value is obtained from the binary diagram ; for χ_a, we used the PAA values given by Gasparoux et al [8] (renormalized as a function of the reduced temperature T/T_N). This plot shows that the increase $\Delta\gamma_1$ of the twist viscosity, depends on the polymer concentration ; for instance, the ratio $\Delta\gamma_1$ (c = 0.6 %)/ $\Delta\gamma_1$ (c = 1 %) at $T/T_N = 0.987$ is equal to 0.52, $\Delta\gamma_1$ is essentially linear in the polymer concentration. Note that this effect is strong $\Delta\gamma_1/\gamma_1 \approx 0.7$ for c = 1 %. This is an argument for a swollen, anisotropic conformation of the polymer.

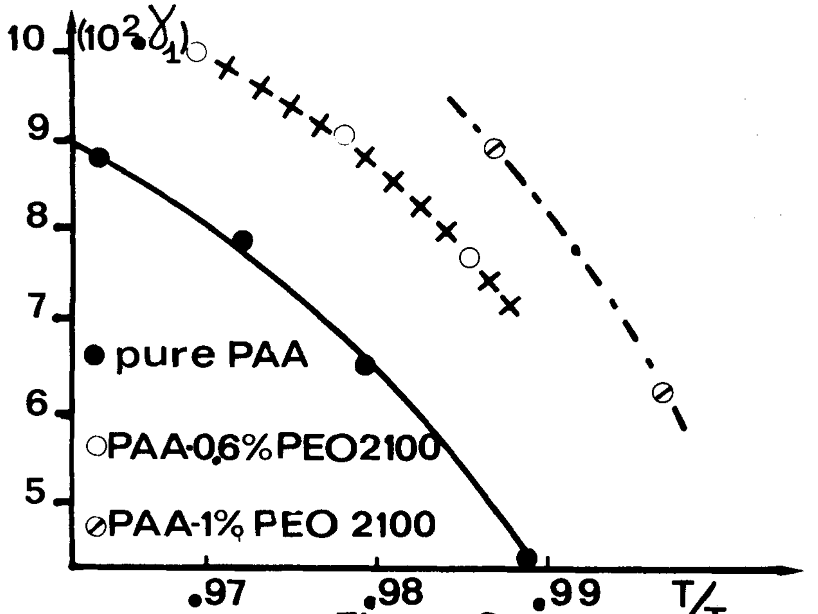

Figure 3

These experimental results have to be compared to a theoretical expression for $\Delta\gamma_1$ due to F. Brochard [1] :

$$\Delta\gamma_1 = \frac{c_m\, kT}{N} \quad \tau \, \frac{(R_{/\!/}^2 - R_{\perp}^2)^2}{R^4}$$

where

- c_m is the monomer concentration (proportional to c)
- N the number of monomer units by chain,
- τ is the rotational relaxation time of the coil,
- $R_{/\!/}$ and $R_{\perp}$ are the radius of gyration parallel and perpendicular to the director ($R^2 = R_{/\!/}^2 + 2\, R_{\perp}^2$).

Conclusion : We showed that it is possible to solubilize PEO chains (of molecular weights 10^3 - 10^4) into a nematic phase up to concentrations of the order of 1 %. The resulting increase of γ_1 implies an anisotropy of polymer conformation. Further experiments are currently underway to specify the dependance of $\Delta\gamma_1$ with M.

Acknowledgements : We are grateful to F. Candau for the polymer samples, to L. Léger and A. Martinet for their help in twist viscosity measurements, and to F. Brochard and P. G. de Gennes for fruitful discussions.

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