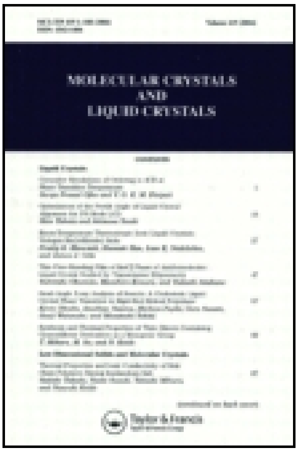

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Observation of Polymer Concentration Profile by Neutron Reflection

B. Farnoux [a] & X. Sun [a]
[a] Laboratoire Leon Brillouin, CEN Saclay, 91191, Gif Sur Yvette, France

To cite this article: B. Farnoux & X. Sun (1990): Observation of Polymer Concentration Profile by Neutron Reflection, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 180:1, 1-5

To link to this article: http://dx.doi.org/10.1080/00268949008025781

Mol. Cryst. Liq. Cryst., 1990, Vol. 180A, pp. 1–5
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Observation of Polymer Concentration Profile by Neutron Reflection

B. FARNOUX and X. SUN

Laboratoire Leon Brillouin, CEN Saclay, 91191 Gif Sur Yvette, France

Polymer solutions show remarkable effects near the free surface, reflecting the tendency for preferential adsorption of the component having the lower surface tension γ. For example, in the case of polydimethyl siloxane (γ_p = 20.6 mN/m) in solution in toluene (γ_s = 28.5 mNm), the difference between solvent and solute surface tension is positive.[1] The Polymer is adsorbed at the liquid-air interface. This strong adsorption leads to a concentration profile extending over several hundred Angströms. We present here the results of preliminary determinations of such a profile by neutron reflection.

OBSERVATION OF POLYMER CONCENTRATION PROFILE BY NEUTRON REFLECTION

The spatial resolution required for the measurement is obtained by varying the incoming inverse wavelength $k = 2\pi/\lambda$ at fixed angle on incidence ($\theta = 0.72°$) on the horizontal polymer solution surface. This time-of-flight method has the advantage of allowing the exploration of a large reciprocal space, while the geometry of the experimental device remains unchanged.[2] The inclined incident beam is characterized by a finite collimation ($\Delta\theta = 0.04$) degrees allowing reasonable reflected intensity.

The polymer solution is set in a cadmium can, the free surface being 9×4 cm^2 and the thickness 0.3 cm. This can is sealed in a quartz cell, leaving the free surface in equilibrium with the solvent vapour. Great care was taken to prevent oscillations of the surface, and the absence of large amplitude oscillations is confirmed by the fact that the size of the incoming beam and the reflected beam are the same on the detector. Measurements were preformed with the small-angle scattering spectrometer PAXY, which was set at the end of a cold neutron guide of the ORPHEE reactor. This spectrometer is equipped with an XY detector of 128 × 128 cells (size cell 0.5×0.5 cm^2) so that the direct beam and the reflected beam are recorded without any detector motion. This allows a direct comparison of the two beams by just moving the sample in a vertical direction. The mechanical selector was removed and replaced by a small chopper running at 30 Hz. The distance between the chopper and detector is 7 meters. Three samples have been used: two are solutions of protonated polydimethyl siloxane (PDMSH) ($M_w = 4.2 \times 10^6$ and $M_w = 8.98 \times 10^5$) in deuterated toluene; one is a solution of deuterated PDMSD ($M_w = 7.83 \times 10^5$) in protonated toluene. The bulk concentration for each sample is

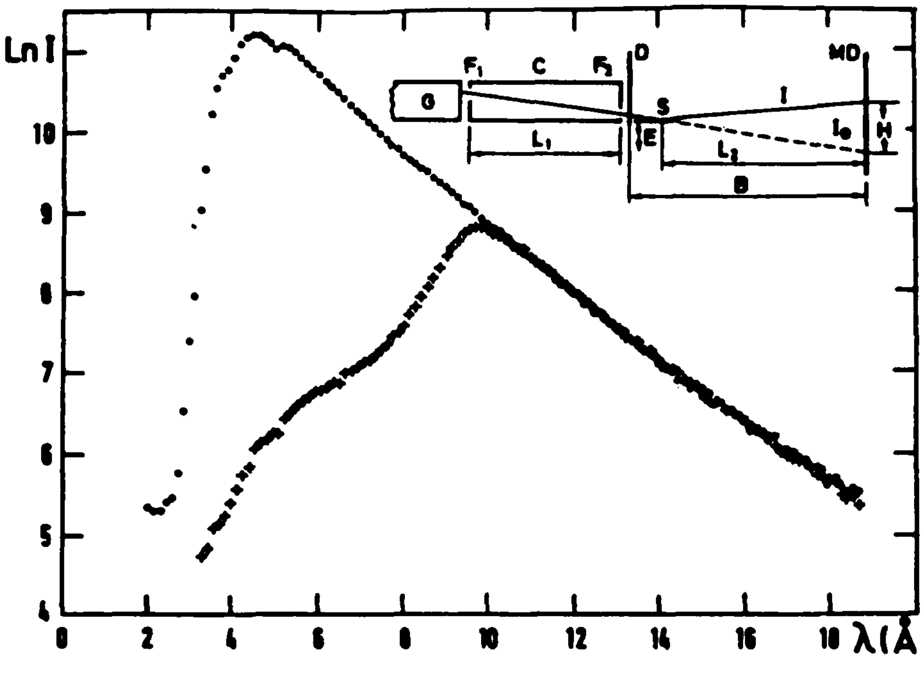

FIGURE 1 Intensity (logarithm scale) versus wavelength, recorded for the direct beam (●) and deuterated toluene (+). In the insert, schematic description of the experimental set up (vertical plane): G, neutron guide; C, collimator; F_1 and F_2, horizontal slits; L_1, collimator length; D, chopper; S, sample; E elevator; L_2, distance between sample and detector; B, time-of-flight basis; MD, multidetector; I_0, incoming beam; I, reflected beam; H, distance between the direct and reflected beam.

in the dilute range near the overlap concentration.[3] The bulk reflectivity is measured by using a mixture of deuterated and protonated toluene with the same scattering length per unit volume as that of the bulk polymer solution. The mean acquisition time is ten hours; an example of the recorded data is given on Figure 1.

The "surface pumping" of the polymer chains induces, at equilibrium, a polymer concentration profile $\phi(z)$, where z is the distance from the interface in the solution. $\phi(z)$ is the polymer volume fraction and, by definition lim $\phi(z) = \phi$, where $z \to \infty$, the bulk solution volume fraction. The theoretical prediction for this profile is expressed as[4]

$$\phi(z) = \begin{cases} 1 & z < a \\ (a/z)^{\mu} & a \leq z \leq \xi \\ \phi & \xi < z \end{cases} \tag{1}$$

The parameters are the width of the polymer layer at the interfce, the exponent μ characterizing the profile, and the screening length ξ.[3] In this equation, $\mu = (3\,\nu - 1)\,\nu = 1.21$ is related to the swelling exponent $\nu = 0.558$. For the studied solutions ξ_s is nearly equal to the radius of gyration in good solvent. A useful parameter for the interpretation of the data is the component of the wavevector perpendicular to the surface inside the solution:

$$q = \frac{2\pi}{\lambda}(n^2 - \cos^2\theta)^{1/2}$$

where

$$n = 1 - \frac{\lambda^2}{2\pi}B$$

is the refractive index of the bulk solution having a scattering length density B. This quantity is real (positive) for all wavelengths smaller than the critical wavelength λ_c and is zero for $\lambda = \lambda_c$. Neutrons with wavelength greater than the critical wavelength λ_c (in the present case 10 Å) are totally reflected. The reflectivity profile is given by the ratio of the two wavelength distributions.

The "optical" properties of the solutions are derived from the scattering length density $B(z)$ at a distance z from the interface

$$B(z) = \left[\left(\frac{b_p}{\upsilon_p}\right) - \left(\frac{b_s}{\upsilon_s}\right)\right]\phi(z) + \left(\frac{b_s}{\upsilon_s}\right) \tag{2}$$

where b_i and υ_i are the scattering length and the partial volume of the monomer (p) and the solvent molecule (s) respectively.

The reflectivity profiles recorded for i) the solution of PDMS-H (Mw = 8.98×10^5) in toluene-D, and ii) the solution of PDMS-D in toluene-H, are presented on Figure 2. The large difference between the two profiles is unexpected and can be explained by the following assumption: in the case ii) the incoming neutron radiation sees successively an optically dense and less dense medium as a thick layer of polymer is adsorbed at the surface. This is enough to shift the reflectivity curve toward higher q values (the value $q = 0$ referring to the bulk solution). On the contrary, in the case i) the incoming radiation sees at first an optically less dense medium, and next the optically dense bulk solution. This produces only a small perturbation to the reflectivity of the bulk solution.

The derivation of the concentration profile directly from the reflectivity can be achieved assuming the validity of some approximations. For this we use the result recorded for the solution of PDMS-H with high molecular weight (4.2×10^6). In that case the concentration profile extends theoretically over a large range ($z \leq 600$ Å). Therefore, it may therefore be appropriate to examine the results in the frame of the first Born approximation theory.[5] Theoretical calculations of the reflectivity profile establish a direct relation between the reflectivity and the Fourier transform of the concentration profile[6]

$$\Gamma(q) = \int_o^\infty (\exp(i\,q\,z))\,(\phi(z) - \phi)\,dz.$$

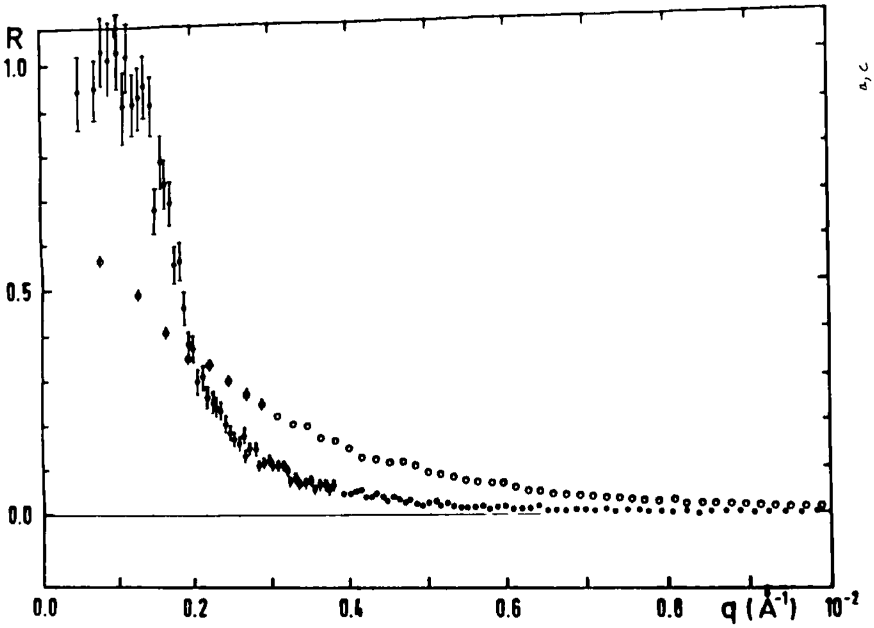

FIGURE 2 Reflectivity curves versus the internal scattering vector q(Å^{-1}) for PDMSD (•) and PDMSH (°) solution.

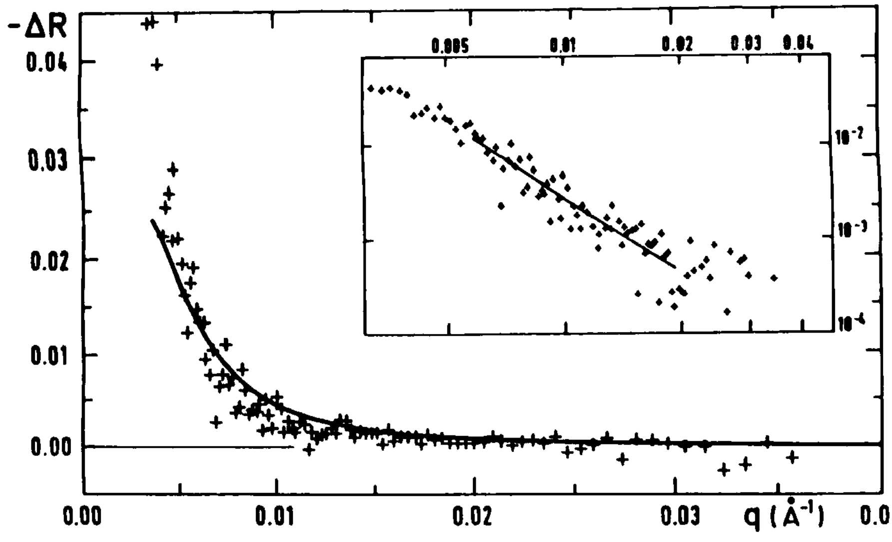

FIGURE 3 Excess reflectivity $-\Delta R$ versus the internal scattering vector q(Å^{-1}) for PDMS-H solution. The solid line is calculated from the theoretical reflectivity (Equation 3). In the insert log-log representation of the same data, the straight line is a best fit with a slope -2.61.

This relation is expressed as the "excess" reflectivity of the solution R_S in comparison to the bulk reflectivity R_F:

$$\Delta R = R_S - R_F = \frac{4\pi}{q}\left[\left(\frac{b_p}{\upsilon_p}\right) - \left(\frac{b_s}{\upsilon_s}\right)\right] \sqrt{R_F}\,(1 - R_F) I_m\, \Gamma(2q). \qquad (3)$$

The reflectivity R_F is measured by using a mixture of deuterated and protonated toluene with the same scattering length density of the bulk polymer solution.

In Figure 3 we compare experimental data with the theoretical curve calculated with the profile given by equation (1), where $\xi = 600$ Å and $a = 5$ Å. In the insert, the data are plotted on a log-log scale, and a least square fit gives a slope of -2.61. In this scattering vector range the effective exponent of the theoretical curve is -2.49. This discrepancy is caused either by the failure of the first Born approximation in the multiple collision domain $q \rightarrow 0$ or by some inadequacy in equation (2).

As a conclusion this preliminary result suggests that the concentration profile is described by a power law at some distance of the interface. It can be noted that the experiment on the deuterated and protonated polymers give complementary information. A model representing the polymer concentration profile has to fit *both* types of reflectivities.

References

1. R. Ober, L. Paz, C. Taupin, P. Pincus and S. Boileau, *Macromolecules*, **16**, 631 (1983).
2. B. Farnoux, proceedings of the AIEA, Jülich Meeting January 1985.
3. J. des Cloizeaux and G. Jannink, "Les polymères en solution: Leur modèlisation et leur structure," p. 555 Editions de Physique (France) 1987.
4. P. G. de Gennes, *Macromolecules*, **13**, 1069 (1980).
5. J. C. Charmet and P. G. de Gennes, *J. Opt. Soc. Am.*, **73**, 1977 (1983).
6. E. Bouchaud, B. Farnoux, X. Sun, M. Daoud and G. Jannink, *Europhys. Lett.*, 2(4), 315 (1986).