A convenient neutron scattering method for studying monomer correlations in homopolymer melts

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Small angle neutron scattering data are compared with given expressions of scattering cross section for isotropic and uniaxially stretched melts containing a large fraction ϕ_D of deuterated chains. An expression of the cross section as $\phi_D(1-\phi_D)f(q)$, where $f(q)$ is the correlation function of one chain, fits the data for *equal* molecular weights of hydrogenated and deuterated species. For *different* molecular weights in the case of isotropic melts an expression is given, which agrees well with the data. The data lie in a scattering vector range of 7.10^{-2}, 10^{-1} Å; seven values of ϕ_D were used for each mixture; the following deuterated and hydrogenated weights[19] were mixed: 138 000 and 155 000, 105 000 and 155 000, 620 000 and 675 000. Both the Guinier range and the intermediate range are explored. Possible technical artefacts of high deuteration are discussed, especially multiple scattering which is not observed under normal conditions, and void scattering which is more difficult to avoid.

Keywords Characterization; small angle neutron scattering; melts; deuteration; homopolymer

INTRODUCTION

The deuteration technique allows an efficient selective labelling of polymer chains and offers a unique possibility for studying monomer correlations in homopolymer melts[1–6]. The method hitherto applied comprised diluting deuterated chains in a hydrogenated matrix in order to measure the scattering function of the single chain. Small concentrations (1% or 2%) of deuterated chains were used. Detailed studies of melts of flexible polymers (e.g. of polystyrene) led to the conclusion that the chains in the bulk are essentially ideal and that their scattering function is of the Debye type up to scattering wave vectors $q \simeq 0.1$ Å^{-1} (e.g.[2,4]). These results confirmed the theoretical predictions[7,8].

However it has been already pointed out[2,9] that this measurement of the single chain scattering function does not require a regime of small concentration of labelled chains. The use of a high concentration of deuterated chains would be a very convenient method since the stronger scattered intensity allows either the use of neutron sources of medium flux or much more precise studies. More precise studies will be particularly important when one is interested in small changes of the scattering function and essential when the neutron scattering is weak. These two conditions occur when the conformation of the chain in a deformed material is studied[4,10]: the scattering is anisotropic and falls off along the elongation axis with greater rapidity when the elongation ratio increases.

When the deuterated and hydrogenated chains have the same degree of polymerization and when the segregation effects are weak, it has been predicted[2,8] that the coherent scattering cross-section is directly proportional to the single chain scattering function. The aim of this paper is to examine the possibility of some experimental application of the high concentration technique to the study of the chain conformation in homopolymer melts, and in melts under uniaxial deformation.

A general expression is given for homopolymer melts which takes into account the difference of molecular weights of the deuterated and hydrogenated chains, and the polydispersity of the polymers. Possible segregation effects between deuterated and hydrogenated monomers of the melt are discussed. The more general case of mixtures other than melts of ideal chains (e.g. stretched bulk) is examined.

Before comparing this expression to experimental results, the problems of the treatment of raw data, specifically related to high concentration of deuterated chains, are examined, in order to extract the coherent scattering cross-section.

Experimental results are described for isotropic polystyrene melts and for uniaxially stretched polystyrene samples. Comparisons with predictions are discussed.

Formula used for monomer density correlation function in amorphous polymer melt

Introduction. We considered a sample composed of a melt of blended deuterated and hydrogenated chains. The theoretical coherent scattering cross section, calculated for a volume v which is infinitely small, is equal to[2]

$$S(q)=(a_D-a_H)^2\frac{v}{a^3}\hat{S}(q) \tag{1}$$

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because the melt is uncompressible; a_D and a_H are the coherent scattering lengths of the deuterated and hydrogenated monomer respectively; $\frac{v}{a^3}$ is the number of monomers, of volume a^3, and

$$\hat{S}(q)=\frac{1}{a^3}\iiint_v[\langle\psi_S(0)\psi_S(r)\rangle-\langle\psi_S\rangle^2]e^{iqr}\mathrm{d}^3r \qquad (2)$$

where $\psi_S(r)$ denotes the local volume fraction of monomer of one species, indifferently the deuterated or the hydrogenated one, as they are equal because of uncompressibility. The brackets $\langle\ \rangle$ mean a statistical average on all the chains S of the volume v.

We will now give the expression of $\hat{S}(q)$, suitable to any concentration of deuterated species, and its conditions of validity; these results are derived in references 8, 14, 13.

Expression used for the scattering power per monomer Ŝ(q) *for melt of ideal chains.* The derivated[8,14,13] use of the *RPA* method, i.e. a mean field theory, is closely related to three conditions:

(i) chains must be nearly ideal. This is known to be the case for homopolymer melts[1-3], with the restriction that the smallest chains do not act as a good solvent for the biggest chains[3]. We must have[8]

$$N_H \gg N_D^{1/2} \quad \text{if}\ \varphi_H > \varphi_D \quad \text{and} \quad N_H < N_D$$

$$\text{or} \qquad N_D \gg N_H^{1/2} \quad \text{if}\ \varphi_D > \varphi_H \quad \text{and} \quad N_D < N_H$$

where N_D (or respectively N_H) is the polymerization index and φ_D (or respectively φ_H) the volume fraction of the deuterated (or respectively hydrogenated) chains.

(ii) macroscopic phase separation does not occur, i.e.[8,14]

$$\chi_F < \frac{(N_H^{1/2}+N_D^{1/2})}{2N_HN_D}$$

where χ_F is the Flory parameter[16] characterizing the interaction between hydrogenated and deuterated monomers.

(iii) segregation interactions are weak. The obtained expression is then[8,14]

$$1/\hat{S}(q)=1/\hat{S}_D(q)+1/\hat{S}_H(q)-2\chi_F \qquad (3)$$

$$\text{with} \quad \hat{S}_D(q)=\frac{1}{a^3}\iiint_v[\langle\psi_D^1(0)\psi_D^1(r)\rangle-\psi_D^1\rangle]e^{iqr}\mathrm{d}^3r$$

where $\psi_D^1(r)$ denotes the local volume fraction of deuterated monomer belonging to *one given chain only*; this chain is *independent*, like a single chain alone in a theta solvent. If we know the molecular weight distribution, we can express the average corresponding to the brackets $\langle\ \rangle$ and

$$\hat{S}_D(q)=\varphi_D\int_{N_D=0}^{N_D=\infty}\varphi_D(N_D)N_Dg\left(N_D\frac{q^2a^2}{6}\right)\mathrm{d}N_D \qquad (4)$$

$$\text{with} \qquad g(x)\equiv 2\frac{e^{-x}-1+x}{x^2}$$

φ_D has already been defined as the volume fraction of deuterated chains and $\varphi_D(N_D)$ is the fraction of the volume occupied by deuterated chains of chemical length N_D to volume of all deuterated chains, or, in other words, the usual normalized weight distribution of the deuterated polymer. $\hat{S}_H(q)$ has the same form.

In the limit of small q vectors, we can use the averages N_n,N_w,N_z[14]

$$\hat{S}(q)^{-1}=\frac{1}{N_{wD}\varphi_D}+\frac{1}{N_{wH}\varphi_H}+\frac{q^2a^2}{18}\left[\frac{N_{zD}}{N_{wD}\varphi_D}+\frac{N_{zH}}{N_{wH}\varphi_H}\right]-2\chi_F \qquad (5)$$

and another expression using N_n and N_w holds when the values of q lie in the intermediate regime for all chains:

$$\hat{S}(q)^{-1}=\frac{1}{2N_{nD}\varphi_D}+\frac{1}{2N_{nH}\varphi_H}-2\chi_F+\frac{q^2a^2}{12} \qquad (6)$$

Remarks. We will in practice use equations (3), (5), (6) where we will take χ_F equal to zero. In this case, we can remark that if the deuterated polymer has the same weight distribution then the hydrogenated polymer ($\varphi_D(N)=\varphi_H(N)$) we find the preliminary expression used[2]

$$V\varphi_D.\hat{S}(q)=\varphi_D(1-\varphi_D)f(q)$$

where $f(q)$ is independent of φ_D.

Expression used for the stretched melt. It is not obvious in this case that the chains should remain 'ideal enough' to use the *RPA* mean field theory. It can just be assumed[8] that, only in the case of the same deuterated and hydrogenated polymer ($\varphi_D(N)=\varphi_H(N)$, $\hat{S}(q)$ must be a polynomial of φ_D of order 2.

$$\hat{S}(q)\equiv\varphi_Dj(q)+\varphi_D^2h(q)$$

and that $S(q,\varphi_D=1)=0$ because the compressibility is zero. Thus,

$$\hat{S}(q,\varphi_D)=\varphi_D(1-\varphi_D)j(q) \qquad (10)$$

In particular, equation (10) may be applied to the case of identical polymer melts uniaxially stretched above the glass transition temperature. In this case the function $j(q)$ is anisotropic and depends on the orientation $f(q)$ with respect to the elongation axis. We will not use the calculated formula of $j(q)$ for stretched chains (for details see refs. 12 and 10) since the problem is still unsolved. But it does not look as if this formula would give any simple dependence on N_n, N_w and N_z.

Experimental process and high deuteration features

Sample making. Anionic polystyrene was made at CRM* and EAHP**. Mixing the hydrogenated and deuterated polymers was done by dissolution of the powders in benzene ($c=5\%$) and then methanol precipitation. After vacuum drying for 3 days at 80°C, the PSH PSD mixture was moulded under vacuum (10^{-1} Torr) at a temperature T_m of 180°C and a pressure p_m of

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Table 1 Composition of the hydrogenated and deuterated polymers

Sample		Polystyrene M_W $\frac{M_W}{M_N} < 1{,}2$	Weight fraction of PSD c	Number fraction of PSD (equal to volume fraction) ϕ_D	$\phi_D(1-\phi_D)$
$620_D/675_H$	PSH	675 000	0	0	0
			0.03	0.028	0.027
			0.06	0.056	0.053
			0.10	0.093	0.085
	PSD	620 000	0.20	0.188	0.152
			0.50	0.481	0.249
	$\left(\frac{M_{WH}-M_{WD}}{M_{WH}} = 10\%\right)$		0.70	0.684	0.216
$138_D/155_H$			0		
	PSH	155 000	0.06	0.056	0.053
			0.10	0.093	0.085
			0.20	0.188	0.153
	PSD	138 000	0.50	0.481	0.249
			0.70	0.684	0.216
	$\left(\frac{M_{WH}-M_{WD}}{M_{WH}} = 11\%\right)$		1		
$105_D/155_H$	PSH	155 000	0.20	0.188	0.153
	PSD	105 000	0.50	0.481	0.249
	$\left(\frac{M_{WH}-M_{WD}}{M_{WH}} = 48\%\right)$				
$620_D/675_H$	Stretched		0.03	0.028	0.027
	Elongation ratio $L/L_0 = 3$		0.10	0.093	0.085
	Stretching temp. $T = 126°\mathrm{C}$		0.50	0.481	0.249
	Velocity gradient $s = 0.2\ \mathrm{s}^{-1}$		0.70	0.684	0.216

Table 2 Scattering vector range for two small angle spectrometers D11 and D17

Spectrometer	Distance sample-detector (m)	λ (Å)	Δλ/λ (%)	q (Å^{-1})	$620_D/675_H$ $R_g \sim 220$Å	$138_D/155_H$ $R_g \sim 125$Å $105_D/155_H$ $R_g \sim 100$Å
D17	2.83	13	10	$2\ 10^{-2} - 10^{-1}$	$4{,}4 < qR_g < 22$ Intermediate range	$2 < qR_g < 10$ Intermediate range
D11	10	8	10	$7\ 10^{-3} - 5\ 10^{-2}$		$0.7 < qR_g < 5$ Radius of gyration

80.10^5 Pa. The thickness was 0.5 mm for standard wafers, and varied from 0.1 mm to 1.3 mm in measurements to detect a thickness effect; the diameter was 12 mm. The compositions of the samples are given in *Table 1*.

Neutron spectrometers. All experiments were performed at the Institute Lane Langevin, Grenoble. The use of the two small angle spectrometers, D11 and D17 provided us with a scattering vector range which, in comparison with the radii of gyration, overlaps both the Guinier range and the intermediate range, as can be seen in *Table 2*.

In this section we will examine the expression of the neutron intensity detected at an angle Ω, in order to discuss the effect of high deuteration on it.

Different scattering cross-sections. We have calculated the coherent scattering cross-section due to chaining of monomers which is, per unit volume, $(a_D - a_H)^2 \frac{1}{a^3} S(q)$. But we must add the cross-sections due to an imaginary randomly deuterated homopolymer melt. Finally we can write the total cross-section per unit of volume:

$$\frac{\mathrm{d}\mu}{\mathrm{d}\Omega} = (a_H - a_D)^2 \frac{\hat{S}(q)}{a^3} + \rho_H \frac{\mathrm{d}\sigma i_H}{\mathrm{d}\Omega} + \rho_D \frac{\mathrm{d}\sigma i_D}{\mathrm{d}\Omega} + \frac{\mathrm{d}\mu}{\mathrm{d}\Omega}\mathrm{voids} \quad (11)$$

where: $-1/a^3$ is the number of monomers per unit of volume; $-\rho_H \frac{\mathrm{d}\sigma i_H}{\mathrm{d}\Omega}$ is the incoherent cross-section per unit of volume of hydrogenated monomers of number per volume ρ_H; $-\frac{\mathrm{d}\mu}{\mathrm{d}\Omega}$ voids is the coherent cross-section per unit of volume due to voids. In fact, we can observe at the lowest q values, a fast decrease in scattering from a purely deuterated sample, although the scattered intensity from a one species only sample should be purely incoherent, thus flat. We observed a similar zero-peaked signal from a completely hydrogenated matrix, but it was much weaker. We think that the best explanation for this is void scattering, which would be proportional for the deuterated matrix to $(a_D - 0)^2$, which was much larger than $(a_H - 0)^2$ for hydrogenated matrix. In our case of labelled samples, the voids signal will increase as $(\rho_D a_D + \rho_H a_H)^2$, but it is also related to sample making (see *Data reduction*).

Effect of finite thickness. Defining $\frac{dF_s}{d\Omega}(x,\Omega)\,d\Omega$ the scattered neutron flux in the solid angle $d\Omega$ around direction Ω, at a path x from the entry face of sample ($x\varepsilon[0,t]$; t is the sample thickness) and the transmitted flux $F_T(x)$, we have:

$$\frac{d(dF_s}{dx\,d\Omega} = F_T(x)\frac{d\mu}{d\Omega} - F_S(x)\left(\iint_{\Omega'}\frac{d\mu}{d\Omega'}d\Omega'\right) +$$

$$\iint_{\Omega'}\frac{dF}{d\Omega}(\Omega'')\frac{d\mu}{d\Omega}(\Omega - \Omega'')d\Omega'' \tag{12}$$

This equation allows us to discuss how the variation with thickness, of scattered intensity of highly deuterated samples ($\varphi_D > 10\%$) is different from that of weakly deuterated samples ($\varphi_D \sim 2\%$).

The first and the second terms of equation (12) are always taken into account. The only peculiarity is that $\iint_{\Omega'}\frac{d\mu}{d\Omega'}d\Omega'$ is nearly equal to $\iint^{\Omega'}\rho_H\frac{d\sigma}{d\Omega'}i_H d\Omega'$ for a weakly deuterated sample, and is increased by a coherent part when φ_D increases (see Appendix A).

The third term corresponds to an increasing of the flux at angle Ω owing to a second scattering from any other direction; in the case of weakly deuterated samples we usually neglect it and obtain:

$$\frac{dF_S}{d\Omega}(\Omega,t) = F_0\frac{d\mu}{d\Omega}(\Omega)t\,e^{-t\iint_{\Omega'}\frac{d\mu}{d\Omega'}d\Omega'} \tag{13}$$

where $T \equiv e^{-t\iint_{\Omega'}\frac{d\mu}{d\Omega'}d\Omega'}$ is also the attenuation factor of the transmitted flux (transmission). In order to check whether we could still neglect this third term for $\varphi_D > 10\%$, we superimposed several samples: the overall thickness varied from 0.18 mm to 1.4 mm. We always found that, if two samples 1 and 2 of thickness t_1, t_2 and transmission T_1, T_2 scatter a flux F_1, F_2, the scattered flux of the two superimposed samples is:

$$F_{1+2} = (t_1 + t_2)T_1T_2\left(\frac{F_1}{t_1T_1} + \frac{F_2}{t_2T_2}\right) \tag{14}$$

This means that equation (13) is correct for our experiments; the scattered flux is proportional to the scattering cross-section. It is however also proportional to the transmission which depends not only on the incoherent scattering but also on the coherent scattering. The experimental variation of the transmission with φ_D is displayed in *Figure 1* and compared with a computed approximation (see Appendix A).

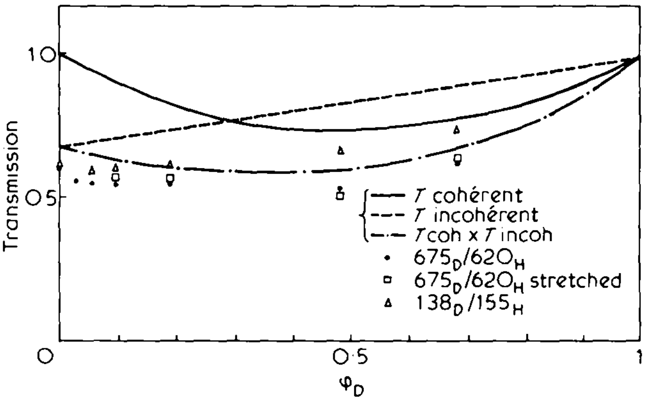

Figure 1 Transmissions of sample of thickness = 1 mm, as a function of the fraction of the labelled chains φ_D. Calculated transmissions (—, — — —, — · — · —) are compared with experimental transmissions: (●) of the $620_D/675_H$ mixture, (□) the uniaxial stretched $620_D/675_H$ mixture and (△) the $138_D/155_H$ mixture

Data reduction. After dividing the intensity $\frac{dF}{d\Omega}$, following equation (13), by monitor counting (F_0), thickness and transmission, we have to subtract the incoherent scattering and the coherent scattering of the voids. This is difficult because the first one varies linearly with φ_D and the second one varies as $(\varphi_H a_H + \varphi_D a_D)^2$. At present we do not have the perfect background which would be obtained from a randomly deuterated sample, which we plan to use.

We tried to suppress the voids by varying the moulding conditions: a pressure larger than 80.10^5 Pa, a temperature of 200°C and a longer annealing time divided this signal by five, which merely allowed us to progress $0.5.10^{-2}$ Å^{-1} further in the low q direction.

However this void signal is weak (1%) in comparison with the coherent chain scattering. So, considering our experimental neutron uncertainty, we verified that a simple subtraction of a hydrogenated matrix background, reduced to a thickness $\varphi_H t$ (t is the labelled sample thickness), was sufficient. More precise measurements would require more sophisticated methods.

EXPERIMENTAL RESULTS

We will present the reduced intensity $I(q)$, obtained as explained earlier.

Isotropic melts and polydispersity

We will set out the results for the Guinier range ($q < 1/R_g$, where R_g is the radius of gyration) and for the intermediate range ($1/R_g < q < 1/b$ where b is the length of one statistical unit of the chain); for both we will compare these results with equation (9) and also with an equation taking into account differences in molecular weight distribution.

(a) The Guinier range has been explored with the mixture $138_D/155_H$, which has a small molecular weight difference between hydrogenated and deuterated polymers, and with the $105_D/155_H$ mixture where the difference is larger (50%). For the $138_D/155_H$ mixture the plot of $\varphi_D(1 - \varphi_D)I^{-1}(q)$ *versus* q^2 (*Figure 3*) shows that the curves for different φ_D are intermingled for $q > 3.10^{-2}$ (the discrepancy for $\varphi_D = 0.093$ does not appear to have a physical meaning, and the radius of gyration is satisfactory).

For $q < 3.10^{-2}$ Å^{-1} it appears (see *Figure 4*) that values of $I(q)/\varphi_D(1 - \varphi_D)$ increase with φ_D. Since we verified that there is no multiple scattering effect (see earlier), void

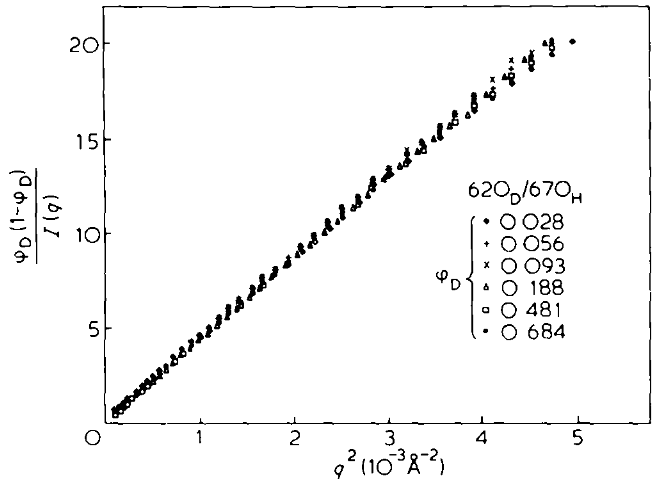

Figure 2 Inverse scattered intensities $\phi_D(1-\phi_D)/I(q)$ as a function of the square momentum transfer for six values of ϕ_D for the $620_D/670_H$ mixture in the intermediate range

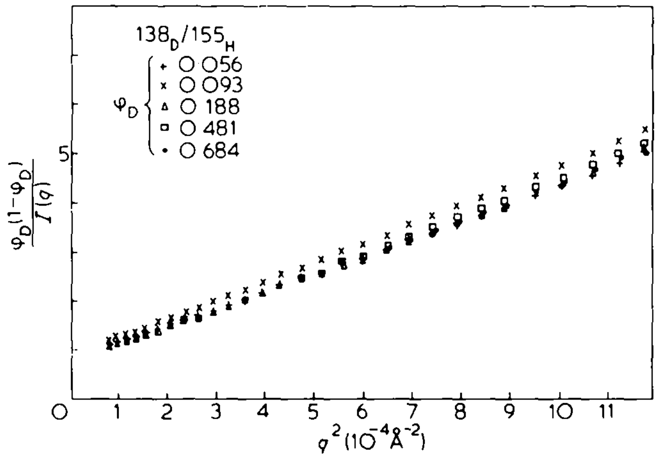

Figure 3 Inverse scattered intensities by deuterated chains for five values of ϕ_D. It is the Guinier range for the $138_D/155_H$ mixture

scattering (which increases with φ_D) explains this additional forward scattering well. We think that the curves would be, without these voids, completely intermingled as they are for $q > 1.2.10^{-2}$ (*Figure 4*); thus equation (9) may be applied with a Guinier range behaviour of $f(q)$

$$f(q) = \frac{1}{N_w}\left(1 - \frac{N_z a^2}{18}\right) \quad \text{with} \quad R_g^2 = \frac{N_z a^2}{6}$$

We then ignore the six first points of the curve $\varphi_D(1-\varphi_D)/I$ *versus* q^2 (*Figure 3*) and extract the radii of gyration from the others (see *Table 3*).

However these values of R_g increase slightly with φ_D. A difference in molecular weight explains this effect. If we introduce:

$$N_{nH} = N_{nD}(1+\Delta n)$$
$$N_{wH} = N_{wD}(1+\Delta w) \qquad (17)$$
$$N_{zH} = N_{zD}(1+\Delta z)$$

we obtain from equation (7)

$$\hat{S}(q)^{-1} = 1/N_{wD}\left(1/\varphi_D + \frac{1}{(1-\varphi_D)(1+\Delta w)}\right) +$$
$$\frac{q^2a^2}{18}\frac{N_{zD}}{N_{wD}}\left(1/\varphi_D + \frac{1+\Delta z}{(1-\varphi_D)(1+\Delta w)}\right) \qquad (18)$$

The curve $1/I$ *versus* q^2 is still a straight line and we have an apparent radius of gyration:

$$R_{g\,\mathrm{app}}^2 = \frac{N_{zD}a^2}{6}\left(1 + \frac{\varphi_D\Delta z}{1+(1-\varphi_D)\Delta w}\right)$$

The values of the correction coefficient are tabulated in *Table 4*. The correction is less than 10% and the

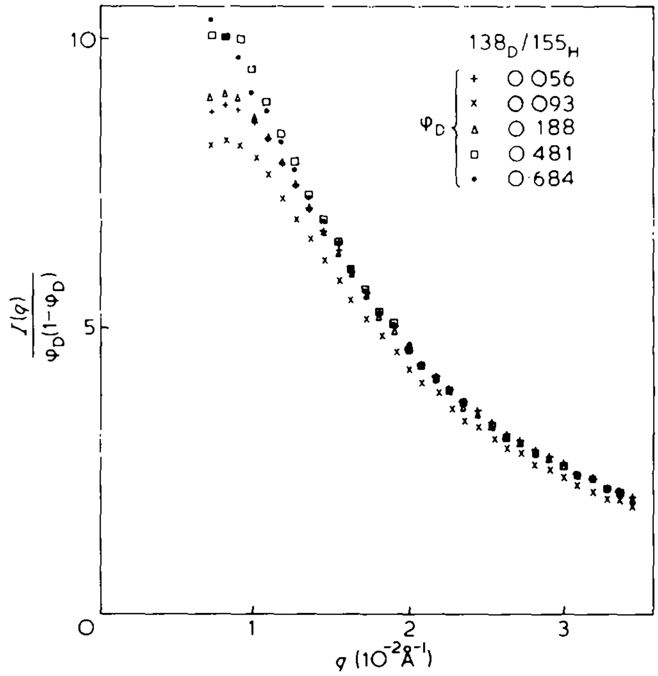

Figure 4 Scattered intensities $I(q)/\phi_D(1-\phi_D)$ as a function of the momentum transfer for the $138_D/155_H$

Table 3 Radius of gyration values for points on curve in *Figure 3* ($\phi_D(1-\phi_D)/T$ *versus* q^2 (First 6 points neglected)

M_{WD} = 138 000 $\quad R_g^2$ apparent $= R_g^2\left[1 + \frac{\phi_D\Delta Z}{1+(1-\phi_D)\Delta W}\right]$

M_{WH} = 155 000 $\quad \Delta Z \sim \Delta W = \frac{M_{WH}}{M_{WD}} - 1 = 0.123$

C_D Weight fraction %	ϕ_D number (volume) fraction	$1 + \frac{\phi_D\Delta Z}{1+(1-\phi_D)\Delta W}$	R_g Measured (Å)	R_g Corrected (Å)
6	0.056	1.006	128 ± 10	127.6
10	0.093	1.010	128	127.3
20	0.188	1.021	131	129.6
50	0.481	1.055	134	130.4
70	0.684	1.081	135	129.8
M_{WD} = 105 000 M_{WH} = 155 000	$\Delta Z \sim \Delta W = 0.476$			
20	0.188	1.065	103 ± 10	99.8
50	0.481	1.247	111	99.4

Table 4 Relative correction for the constant term in $620_D/675_H$ mixture

Weight fraction c_D	Number (volume) fraction ϕ_D	$\lim_{q\to 0} S^{-1}(q) = \frac{1}{2N_{nD}}\left(1-\frac{\phi_D\Delta_n}{1+\Delta_n}\right)$	$\frac{1}{2N_{nD}} = 9.27\ 10^{-5}$ Correction factor $= \frac{1/2\,N_{nD}}{\frac{1}{2N_{nD}}\left(1-\frac{\phi_D\Delta_n}{1+\Delta_n}\right)}$
0.03	0.028	9.26×10^{-5}	1.002
0.06	0.056	9.23×10^{-5}	1.004
0.10	0.093	9.20×10^{-5}	1.007
0.20	0.188	9.14×10^{-5}	1.015
0.50	0.481	8.93×10^{-5}	1.038
0.70	0.684	8.79×10^{-5}	1.054

experimental uncertainty in R_g is 10%: thus these data do not allow a quantitative verification of the correction, but the corrected radii are nevertheless in better agreement.

For the $105_D/155_D$ the variation of the apparent radii with φ_D is greater than the experimental uncertainty. A correction must be applied and ours works well.

(b) The intermediate range has been explored with the $620_D/675_H$ mixture. In a $\varphi_D(1-\varphi_D)/I(q)$ *versus* q^2 plot (*Figure 2*), curves for different values of φ_D are laying over one another, so that equation (9) is again verified. These curves correspond to a straight line in this $1/I$ *versus* q^2 representation, as does the Debye function for high q.

In actual fact the two molecular weights are not equal; we take this into account by using equation (8) (neglecting χ_F) and expressions (17), so that:

$$\varphi_D(1-\varphi_D)\hat{S}(q)^{-1} = \frac{1}{2N_{nD}}\left(1-\frac{\varphi_D\Delta n}{1+\Delta w}\right)+\frac{q^2a^2}{12}$$

It is clear from the above equation that the molecular weight and polydispersity affect only the constant term; the slope of the curve $1/I$ *versus* q^2 remains unchanged. The relative correction for the constant term, in $620_D/675_H$ mixture is displayed in *Table 4*; for a difference $\Delta_w = 10\%$, the maximum value is 5% for $\varphi_D = 0.684$: it remains inside our experimental uncertainty: this correction is not relevant here.

Summary of the results for isotropic melts. The formula $I(q)\propto\varphi_D(1-\varphi_D)f(q)$ applies well for large scattering vector; for the Guinier range, a correction coming from the mean-field equation (3) (neglecting χ_F) fits the data well. The void signal vanishes for q larger than a value lying between 1.10^{-2} and 3.10^{-2} A^{-1}, depending on the sample.

Stretched samples results. In section 1.2, equation (10) predicts a similar behaviour of $I(q)\propto\varphi_D(1-\varphi_D)g(q)$ for mixture of polymers of equal molecular weight, in a non ideal chains melt. With the mixture $620_D/627_H$ ($\Delta w = 10\%$) we check this assumption here.

Each sample of different φ_D is stretched separately, under the same conditions. The experimental uncertainty coming from the neutron measurements is increased by stretching uncertainties, as the scattered intensity strongly depends on the heating process, oven temperature ($\pm 2°C$) and the duration between the end of stretching and cooling ($\Delta t_R \sim 5$s). *Figure 5a* shows data in the parallel direction and *Figure 5b* in the perpendicular direction; no special artefact appears, equation (10) fits the data within our experimental uncertainty.

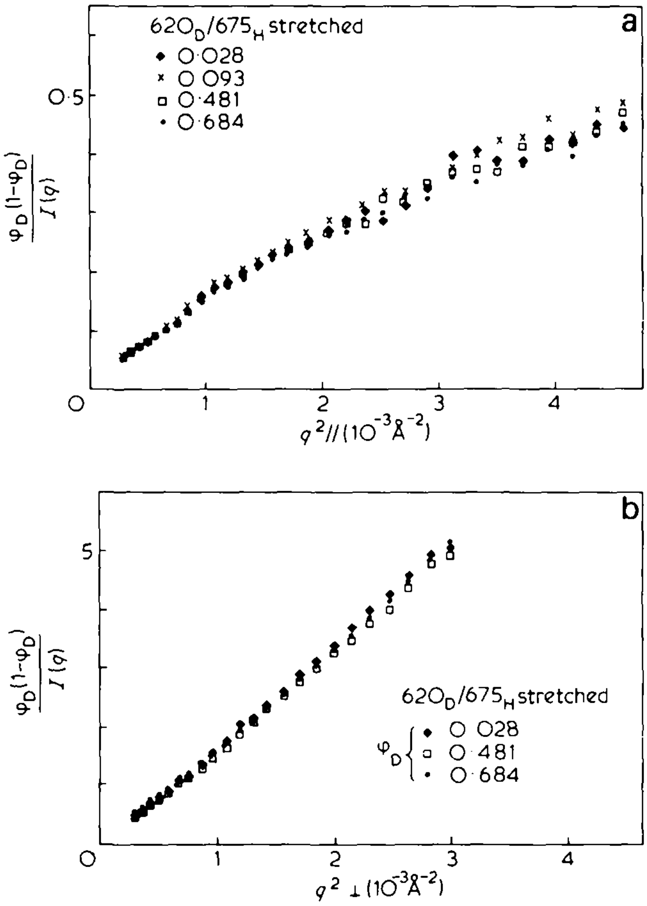

Figure 5 Inverse scattered intensities $\phi_D(1-\phi_D)/I(q)$ for the uniaxial stretched samples of the mixture $620_D/675_H$. (Elongation ratio = 3, stretching temperature T = 126°C, velocity gradient $s = 0,2\ s^{-1}$). (a) In the direction parallel to the direction of elongation (b) in the direction perpendicular

This is a new and original result, showing that the high deuteration technique allows us to study the conformation of a non-ideal chain in a melt, by measuring the correlation function $j(q)$, as yet unknown.

CONCLUSIONS

The aim of this paper was to discuss the use of strong labelling to study the conformation of the chain in isotropic and stretched polymer in bulk.

The expression of the scattering cross-section is simple in the case of isotropic melt: a formula taking into account the polydispersity and the difference in molecular weight of hydrogenated and deuterated species is given and compared with results. The good agreement is encouraging for the technique and shows also that one can use here the RPA derivation to compute the monomer density correlation function.

The scattering cross-section is also given for stretched melts, but only with equal deuterated and hydrogenated molecular weights. Experimental data agree with the prediction. We think that other cases of application of high deuteration will be numerous: a recent one has been in dried gels[18].

The extraction of scattering cross-section from raw intensity data is simple. The only remaining problem is the existence of a voids scattering for $q<2.10^{-2}$ A^{-1}; it still has to be resolved for low angle studies ($q\in[10^{-3}, 10^{-2}$ A$^{-1}]$) or very precise studies $\left(\frac{\Delta I}{I}\sim 1\%\right)$. Making materials without voids has to be investigated.

For melts of species not too different in molecular weight ($\Delta w<100\%$) and for stretched melts ($\Delta w<10\%$) only one value of φ_D is necessary to have the correlation function.

To summarize, in the range of uncertainty $\left(\frac{\Delta I}{I}\sim 5\%\right)$ and of scattering vector modulus (7.10^{-3}, 10^{-1} Å^{-1}) where our experiments lay, the high deuteration technique may be used for any value of φ_D between 0 and 1. Moreover, as one value of φ_D is enough, this method is very convenient.

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REFERENCES

1 Ballard, D. G., Schelten, J. and Wignall, G. D. *Eur. Polym. J.* 1973, **9**, 965

2 Cotton, J. P., Decker, D., Benoît, H., Farnoux, B., Higgins, J., Jannink, G., Ober, R., Picot, C. and des Cloizeaux, J. *Macromolecules* 1974, **16**, 120

3 Kirste, R. G., Krouse, V. A. and Ibel, K. *Polymer* 1975, **16**, 120

4 Boué, F., Daoud, M., Nierlich, M., Williams, C., Cotton, J. P., Farnoux, B., Jannink, G., Benoît, H., Dupplessix, R. and Picot, C. in 'Neutron inelastic scattering' (I.A.E.A., Vienna, 1978), 1977, vol. **1**, p. 563

5 Guenet, J. M., Picot, C. and Benoît, H. *Macromolecules* 1979, **12**, 86

6 Guenet, J. M. and Picot, C. *Polymer* 1979, **20**, 1483

7 Flory, J. P. *J. Chem. Phys.* 1949, **17**, 303

8 de Gennes, P. G. 'Scaling concepts in polymer physics' (Cornell Univ. Press, Ithaca, N.Y., 1979) ch. II

9 Akcasu, A. Z., Summerfield, G. C., Jahsan, S. N., Han, Charles C., Kim, Chung Yup, and Yu, Hyuk *J. Polym. Sci.* 1980, **18**, 863

10 Boué, F. and Jannink, G. *J. Phys. (Paris)* 1978, **39**, C2 183

11 de Gennes, P. G. *J. Phys. (Paris)* 1970, **31**, 235

12 Boué, F. Univ. 3rd cycle Thesis (Strasbourg, 1977); Pearson, D. S. *Macromolecules* 1977, **10**, 696, Daoudi, S. *J. Phys. (Paris)* 1977, **38**, 731; Doï, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans.* 1978, **74**, 1789

13 A more general R.P.A. derivation of $S(q)$ will be found in Leibler, L. and Benoit, H. *Polymer*, to be published

14 Joanny, J. F. *C.R. Acad. Sci. Paris* 1978, **286B**, 89

15 Turchin, V. F. 'Slow Neutrons', Israel Progress in Scientific Transactions Ltd., 1965

16 Flory, P. J. 'Principles of polymer chemistry', Cornell University Press

17 Benoit, H. *J. Polym. Sci.* 1953, Vol. XI, no. 5, 507

18 Beltzung, M., Bastide, J. and Picot, C. C.R.M. Strasbourg, private communication

19 *Note*: In this paper we use, for the deuterated polymers, the molecular weight of the hydrogenated chain of same number of monomer ($M_H=N_Hm_H$, but $M_D=N_Dm_H$ instead of $M_D=N_Dm_D$)

APPENDIX A

The transmission is calculated as $T=T_{in}\times T_{coh}$, where the incoherent attenuation is $e^{-(\rho_H\sigma_{iH}+\rho_D\sigma_{iD})t}$ with $\sigma_{iH}=80$ barn and $\sigma_{iD}=2$ barn and the coherent attenuation is written $e^{-\mu_c t}$ with, forgetting the void scattering

$$\mu_c=\int_0^{\pi}(a_H-a_D)^2\frac{1}{v_m}N_{wD}\varphi_D(1-\varphi_D)$$

$$g\left(N_{wD}\left(\frac{4\pi}{\lambda}\sin\theta/2\right)^2\frac{a^2}{6}\right)2\pi\sin\theta\,d\theta$$

To calculate the integral, the function $g(x)=\frac{2(e^{-x}-1+x)}{x^2}$ is taken as $\left(1-\frac{x}{3}\right)$ for $x<x_a$ and $\frac{2}{x}-\frac{2}{x^2}$ for $x>x_a$ with $x_a=4$. We find $\mu_c=12{,}3\varphi_D(1-\varphi_D)$ cm^{-1}; maximum value is $\mu_c=3.06$ cm^{-1} for $\varphi_D=0.481$ while $\rho_H\sigma_{iH}+\rho_D\sigma_{iD}=2.064$ cm^{-1}.