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A real time neutron scattering experiment for the study of polymer dynamics

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Résumé. — On étudie la dynamique d'un polymère fondu (polystyrène amorphe) de longues chaînes ($M_w = 650\,000$) en observant à des instants successifs le facteur de forme statique de la chaîne pendant la relaxation, à longueur fixée, d'un échantillon préalablement étiré uniaxialement. Cette lettre présente des données de diffusion de neutrons aux petits angles pour une série de valeurs de la durée de la relaxation qui sont environ égales, ou supérieures au temps de Rouse de la chaîne. Les données de cette expérience couvrent tout le domaine submoléculaire du vecteur de diffusion, grâce à la combinaison de trois configurations différentes des spectromètres. Une discussion plus complète de la dépendance en temps du facteur de forme est maintenant possible. Une contribution à cette discussion est apportée dans la lettre suivante.

Abstract. — The dynamics of an amorphous polystyrene ($M_w = 650\,000$) melt is studied by successive observations of the static coil form factor during stress relaxation following a uniaxial deformation. This paper presents neutron scattering data for a duration of relaxation of the order of, or bigger than the Rouse time of the chains. The data cover the entire submolecular range for the scattering vector, as the result of the successive use of three different spectrometer configurations. A more complete discussion of the time dependence of the static form factor is now possible. A contribution to this discussion is given in the next letter.

1. Introduction. — By a real time experiment we mean successive instantaneous measurements of observables in a time dependent system.

The measured quantity is the static coil form factor obtained by small angle neutron scattering in the static approximation. Because the time required for such a measurement is long compared to the characteristic time of the system, we quench the sample for each observation. The sample is a strip of polystyrene (atactic, blend of normal polystyrene, $M_{wH} = 760\,000$, and perdeuterated polystyrene, $M_w = 680\,000$, $M_w/M_n \lesssim 1.3$) [2], suddenly stretched [3] by a factor 3 at a temperature $T_s > T_g$ (glass transition temperature) and maintained at a constant elongation. The stress relaxes while the sample returns to equilibrium, and it is observed at different states of relaxation

defined by the duration of relaxation t_R following the deformation. The strip is quenched at t_R and, subsequently, brought in front of the neutron beam of a small angle scattering spectrometer of the high flux reactor of the Institute von Laue Langevin, Grenoble (France). We assume that the configurations of the coils are not modified by quenching [4], only frozen.

The control of the experiment is difficult but results are now reproducible. This is discussed in reference [1], together with the variation of the transverse radius of gyration and the variation of the form factor in the submolecular range of the scattering vector q . The range of scattering vectors in which the static coil form factor has been measured was however limited to the interval $[7 \times 10^{-3}, 2 \times 10^{-2} \text{ \AA}^{-1}]$. Since that time, by using successively three different configurations for the spectrometers at the Institute von Laue Langevin, this form factor has been measured in the largest possible scattering vector interval covering the submolecular domain, $[7 \times 10^{-3}, 1.5 \times 10^{-1} \text{ \AA}^{-1}]$.

This interval, controlling the scattering experiment, is defined with respect to the characteristic lengths associated with the polystyrene coils. We consider here data corresponding to the orientations of q parallel (subscript $\parallel$) and perpendicular (subscript $\perp$) to the uniaxial direction.

2. Order of magnitude of polymer inverse characteristic lengths. — A typical length is the radius of gyration R_g . In the isotropic, totally relaxed, state, the radius is for our sample

$$R_{g\text{iso}} \simeq 250 \text{ \AA}.$$

The affine value for the quantity corresponding to the elongation 3, are

$$\begin{aligned} R_{g\perp} &= 250/\sqrt{3} \\ R_{g\parallel} &= 250 \times 3. \end{aligned}$$

We have checked in reference [1] the validity of the affine deformation immediately after deformation using data in perpendicular direction. Another characteristic length is often proposed in the discussion of polymer melts, although its existence is very questionable. It is the diameter D of the fixed tube in which a coil is constrained to move during a time interval equal to T_{Rouse} . It is often written :

$$D = R_{g\text{iso}} \sqrt{(N_e/N)} \quad (1)$$

where N is the number of statistical units of the chains and N_e is a number of units such as chains with $N > N_e$ show, for various physical quantities observed by various techniques, a behaviour different from that of smaller chains. Depending on the technique, one obtains [7] :

$$100 < N_e < 1\,000 \quad \text{which implies} \quad 25 \text{ \AA} < D < 90 \text{ \AA}.$$

A third characteristic length is here the size of the monomer

$$a = 2.5 \text{ \AA}.$$

Table I shows the characteristics of the three configurations of the two small angle neutron scattering spectrometers used in our experiment to cover the whole range $[7 \times 10^{-3} \text{ \AA}^{-1}, 2 \times 10^{-1} \text{ \AA}^{-1}]$.

From figure 1 it appears that the experiment is suitable to obtain data in the asymptotic range defined by

$$q_{\parallel} R_{g\parallel} \geq 4.$$

Table I.

Scattering vector range ($\text{\AA}^{-1}$)	Spectrometer	Sample detector distance	Wavelength	Wavelength resolution	Angular collimation (rad.)
$7 \times 10^{-3}, 2 \times 10^{-2}$	D11	10 m	10 $\text{\AA}$	9 %	5×10^{-3}
$10^{-2}, 6 \times 10^{-2}$	D17	3 m	13 $\text{\AA}$	10 %	7×10^{-3}
$6 \times 10^{-2}, 2 \times 10^{-1}$	D11	2 m	5.4 $\text{\AA}$	9 %	10^{-3}

Fig. 1. — Representation of the reciprocal space intervals explored in the three spectrometer configurations used in our experiment (see Table I). The inverse characteristic lengths of the coils, discussed in this letter, are also shown.

Further, we notice that, if the ratio N/N_e is sufficiently large, this asymptotic range can be divided in two subranges $qD < 1$ and $qD > 1$. Therefore, if the quantity D should have an effect on the observable, then this effect could be detected.

3. **Order of magnitude of times.** — Data are gathered at several durations of relaxation t_R . This value t_R is in fact controlled by the time interval between deformation and quenching. It will be convenient to compare t_R to characteristic times of the system. Theoretical quantities are proposed such as Rouse time, T_{Rouse} , and reptation time [5, 6], T_{rep} . The times are not presently measured experimentally ; we use an evaluation [7] of T_{Rouse} from viscosity measurements at low molecular weights to evaluate $T_{\text{Rouse}}(\propto N^2)$ for $M_w = 650\,000$. We evaluate T_{rep} from the experimental values of terminal relaxation time at this molecular weight [7]. These evaluations are displayed and discussed in reference [1] (written as T_{eq} for T_{Rouse} and T_{dis} for T_{rep}). They are strongly dependent upon temperature, T . We assume a Williams Landel Ferry temperature dependence [7] :

$$T_{\text{Rouse}(\text{rep})}(T) = \frac{a_T}{a_{T_0}} T_{\text{Rouse}(\text{rep})}(T_0) \tag{2}$$

with

$$\log_{10} a_T = \frac{1\,744 (T - 100)}{50 + T - 100} . \tag{3}$$

The temperatures used for stretching the melt in our experiment are 113 °C, 117 °C, 122 °C, 128 °C and 134 °C. But we discuss here data obtained at 128 °C and 134 °C. These temperatures are chosen because they allow exploration of a time domain in which

$$1 \leq t_R/T_{\text{Rouse}} \leq T_{\text{rep}}/T_{\text{Rouse}} . \tag{4}$$

Table II. — $S_{tr}(q)$, perpendicular direction.

value of q	T = 128°C						isotrope	$\frac{\Delta S_{tr}}{S_{tr}}$
	$t_R = 30_s$ 42	$t_R = 60_s$ 44	$t_R = 480_s$ 43	$t_R = 1800_s$ 46	$t_R = 60_s$ 49	$t_R = 960_s$ 50		
5.16e-03	1.88e 03	1.88e 03	1.87e 03	1.92e 03	2.04e 03	2.03e 03	1.81e 03	13%
5.77e-03	1.68e 03	1.68e 03	1.75e 03	1.71e 03	1.76e 03	1.75e 03	1.54e 03	
6.41e-03	1.46e 03	1.45e 03	1.54e 03	1.50e 03	1.50e 03	1.50e 03	1.26e 03	
7.04e-03	1.57e 03	1.57e 03	1.66e 03	1.61e 03	1.59e 03	1.59e 03	1.27e 03	
7.68e-03	1.54e 03	1.51e 03	1.62e 03	1.59e 03	1.54e 03	1.56e 03	1.20e 03	
8.32e-03	1.53e 03	1.53e 03	1.63e 03	1.58e 03	1.55e 03	1.56e 03	1.13e 03	
8.95e-03	1.38e 03	1.36e 03	1.46e 03	1.41e 03	1.39e 03	1.39e 03	9.59e 02	
9.58e-03	1.29e 03	1.28e 03	1.37e 03	1.34e 03	1.30e 03	1.29e 03	8.71e 02	
1.02e-02	1.27e 03	1.25e 03	1.35e 03	1.30e 03	1.27e 03	1.27e 03	8.24e 02	
1.09e-02	1.19e 03	1.18e 03	1.27e 03	1.23e 02	1.20e 03	1.17e 03	7.55e 02	
1.15e-02	1.11e 03	1.11e 03	1.18e 03	1.14e 03	1.11e 03	1.09e 03	6.84e 02	
1.22e-02	1.13e 03	1.12e 03	1.19e 03	1.16e 02	1.12e 03	1.11e 03	6.71e 02	
1.28e-02	9.75e 02	9.62e 02	1.03e 03	9.94e 02	9.66e 02	9.58e 02	5.67e 02	
1.34e-02	9.61e 02	9.52e 02	1.02e 03	9.83e 02	9.56e 02	9.35e 02	5.49e 02	
1.41e-02	8.50e 02	8.35e 02	8.98e 02	8.60e 02	8.38e 02	8.22e 02	4.69e 02	16%
1.47e-02	7.76e 02	7.66e 02	8.22e 02	7.87e 02	7.65e 02	7.47e 02	4.21e 02	
1.53e-02	7.93e 02	7.79e 02	8.40e 02	7.96e 02	7.85e 02	7.57e 02	4.23e 02	
1.60e-02	7.71e 02	7.62e 02	8.12e 02	7.69e 02	7.56e 02	7.25e 02	4.03e 02	
1.66e-02	7.14e 02	7.01e 02	7.49e 02	7.12e 02	7.03e 02	6.68e 02	3.68e 02	
1.73e-02	6.91e 02	6.83e 02	7.23e 02	6.89e 02	6.82e 02	6.49e 02	3.63e 02	
1.79e-02	6.01e 02	5.93e 02	6.30e 02	5.95e 02	5.95e 02	5.59e 02	3.09e 02	
1.85e-02	5.52e 02	5.47e 02	5.80e 02	5.48e 02	5.47e 02	5.14e 02	2.83e 02	
1.92e-02	5.47e 02	5.40e 02	5.71e 02	5.41e 02	5.38e 02	5.09e 02	2.72e 02	
5.43e-03	1.11e 02	1.11e 02	1.18e 03	1.11e 03	1.12e 03	1.13e 03	8.08e 02	65%
1.11e-02	9.92e 02	1.05e 03	9.80e 02	9.80e 02	1.00e 03	9.93e 02	6.45e 02	
1.28e-02	8.58e 02	9.08e 02	8.50e 02	8.50e 02	9.59e 02	8.50e 02	5.17e 02	
1.45e-02	7.42e 02	7.82e 02	7.30e 02	7.42e 02	7.42e 02	7.23e 02	4.21e 02	
1.62e-02	6.70e 02	7.03e 02	6.23e 02	6.66e 02	6.66e 02	6.43e 02	3.58e 02	
1.79e-02	5.66e 02	5.96e 02	5.50e 02	5.63e 02	5.63e 02	5.34e 02	2.93e 01	
1.97e-02	4.71e 02	4.88e 02	4.49e 02	4.69e 02	4.69e 02	4.42e 02	2.54e 01	
2.20e-02	4.04e 02	4.18e 02	3.83e 02	3.99e 02	3.99e 02	3.70e 02	2.09e 02	
2.40e-02	3.44e 02	3.55e 02	3.23e 02	3.40e 02	3.40e 02	3.13e 02	1.79e 02	
2.57e-02	3.00e 02	3.10e 02	2.76e 02	2.93e 02	2.93e 02	2.66e 02	1.52e 02	
2.74e 02	2.79e 02	2.85e 02	2.56e 02	2.71e 02	2.71e 02	2.46e 02	1.41e 02	
2.91e-02	2.47e 02	2.51e 02	2.25e 02	2.40e 02	2.40e 02	2.16e 02	1.26e 02	
3.07e-02	2.27e 02	2.31e 02	2.06e 02	2.20e 02	2.20e 02	1.96e 02	1.14e 02	
3.24e-02	2.06e 02	2.08e 02	1.87e 02	1.99e 02	1.99e 02	1.75e 02	1.03e 02	
3.41e-02	1.81e 02	1.82e 02	1.62e 02	1.74e 02	1.74e 02	1.53e 02	9.16e 01	
3.58e-02	1.70e 02	1.70e 02	1.51e 02	1.62e 02	1.62e 02	1.42e 02	8.53e 01	
3.78e-02	1.50e 02	1.50e 02	1.32e 02	1.43e 02	1.43e 02	1.24e 02	7.67e 01	
4.01e-02	1.35e 02	1.34e 02	1.19e 02	1.27e 02	1.27e 02	1.11e 02	6.72e 01	
4.15e-02	1.25e 02	1.24e 02	1.10e 02	1.18e 02	1.18e 02	1.03e 02	6.63e 01	
4.30e-02	1.16e 02	1.15e 02	1.01e 02	1.11e 02	1.11e 02	9.54e 01	6.20e 01	
4.46e-02	1.09e 02	1.07e 02	9.48e 01	1.04e 02	1.04e 02	8.90e 01	5.80e 01	
4.63e-02	9.96e 01	9.74e 01	8.53e 01	9.39e 01	9.39e 01	8.05e 01	5.44e 01	
4.80e-02	9.10e 01	9.19e 01	7.84e 01	8.62e 01	8.62e 01	7.33e 01	5.00e 01	
4.99e-02	8.68e 01	8.43e 01	7.39e 01	8.10e 01	8.10e 01	6.97e 01	4.73e 01	
5.15e-02	7.87e 01	7.65e 01	6.73e 01	7.39e 01	7.39e 01	6.27e 01	4.39e 01	
5.36e-02	7.46e 01	7.27e 01	6.46e 01	7.04e 01	7.04e 01	6.03e 01	4.16e 01	
3.89e-02	1.35e 02	1.33e 02	1.34e 02	1.22e 02	1.35e 02	1.16e 02	7.67e 01	65%
4.54e-02	1.01e 02	1.00e 02	9.92e 01	8.95e 01	9.87e 01	8.43e 01	5.73e 01	
5.18e-02	7.59e 01	7.48e 01	7.33e 01	6.71e 01	7.32e 01	6.18e 01	4.32e 01	
5.88e-02	5.62e 01	5.59e 01	5.45e 01	4.94e 01	5.49e 01	4.59e 01	3.38e 01	
6.48e-02	4.56e 01	4.46e 01	4.34e 01	3.89e 01	4.37e 01	3.62e 01	2.78e 01	
7.12e-02	3.69e 01	3.62e 01	3.46e 01	3.11e 01	3.47e 01	2.91e 01	2.26e 01	
7.76e-02	3.03e 01	2.98e 01	2.83e 01	2.52e 01	2.88e 01	2.39e 01	1.91e 01	
8.41e-02	2.47e 01	2.41e 01	2.30e 01	2.09e 01	2.34e 01	1.94e 01	1.61e 01	
9.09e-02	2.11e 01	2.06e 01	1.91e 01	1.75e 01	1.99e 01	1.65e 01	1.41e 01	
9.70e-02	1.72e 01	1.71e 01	1.60e 01	1.45e 01	1.62e 01	1.37e 01	1.21e 01	
1.03e-01	1.49e 01	1.47e 01	1.36e 01	1.25e 01	1.40e 01	1.19e 01	1.05e 01	
1.10e-01	1.29e 01	1.26e 01	1.19e 01	1.08e 01	1.22e 01	1.04e 01	9.27e 00	
1.16e-01	1.13e 01	1.13e 01	1.04e 01	9.45e 00	1.07e 01	9.27e 00	7.35e 00	
1.23e-01	1.00e 01	9.60e 00	8.92e 00	8.37e 00	9.36e 00	8.12e 00	6.47e 00	
1.29e-01	8.50e 00	8.50e 00	7.74e 00	7.15e 00	8.01e 00	6.94e 00	6.06e 00	
1.36e-01	7.73e 00	7.55e 00	6.93e 00	6.53e 00	7.30e 00	6.51e 00	5.35e 00	
1.43e-01	6.77e 00	6.74e 00	6.12e 00	5.79e 00	6.54e 00	5.60e 00	4.85e 00	
1.50e-01	6.21e 00	6.06e 00	5.52e 00	5.34e 00	5.71e 00	5.10e 00	4.35e 00	
1.56e-01	5.42e 00	5.28e 00	4.99e 00	4.68e 00	5.13e 00	4.41e 00	3.97e 00	
1.63e-01	4.84e 00	4.85e 00	4.40e 00	4.24e 00	4.72e 00	4.06e 00	3.66e 00	
1.69e-01	4.51e 00	4.45e 00	4.05e 00	3.84e 00	4.33e 00	3.68e 00	3.49e 00	
1.76e-01	4.13e 00	4.03e 00	3.77e 00	3.58e 00	3.92e 00	3.49e 00	3.20e 00	
1.83e-01	3.85e 00	3.78e 00	3.41e 00	3.26e 00	3.76e 00	3.17e 00	2.89e 00	
1.89e-01	3.40e 00	3.34e 00	3.06e 00	2.86e 00	3.27e 00	2.79e 00	2.63e 00	
1.95e-01	3.05e 00	3.01e 00	2.73e 00	2.62e 00	2.97e 00	2.57e 00	2.65e 00	
2.01e-01	3.06e 00	2.87e 00	2.53e 00	2.54e 00	3.00e 00	2.36e 00		

T = 129°C

T = 134°C

value of q	t _R = 30 _s 42	t _R = 60 _s 44	t _R = 480 _s 43	t _R = 1800 _s 46	t _R = 60 _s 49	t _R = 960 _s 50	Isotrope	ASTR -STR	
5.16e-03	6.05e 02	6.91e 02	7.04e 02	7.29e 02	8.36e 02	8.93e 02	2.18e 03	13%	
5.79e-03	4.81e 02	5.47e 02	5.57e 02	5.90e 02	6.59e 02	7.40e 02	1.85e 03		
6.45e-03	3.31e 02	3.70e 02	3.84e 02	4.11e 02	4.47e 02	5.25e 02	1.35e 03		
7.08e-03	3.11e 02	3.45e 02	3.60e 02	3.92e 02	4.17e 02	5.03e 02	1.35e 03		
7.71e-03	2.53e 02	2.78e 02	2.93e 02	3.22e 02	3.38e 02	4.16e 02	1.13e 03		
8.37e-03	2.28e 02	2.49e 02	2.64e 02	2.97e 02	3.09e 02	3.88e 02	1.07e 03		
9.01e-03	1.98e 02	2.17e 02	2.31e 02	2.61e 02	2.66e 02	3.47e 02	9.40e 02		
9.64e-03	1.81e 02	1.97e 02	2.12e 02	2.42e 02	2.43e 02	3.31e 02	8.71e 02		
1.03e-02	1.66e 02	1.78e 02	1.93e 02	2.23e 02	2.21e 02	3.02e 02	7.99e 02		
1.09e-02	1.41e 02	1.53e 02	1.68e 02	1.94e 02	1.91e 02	2.66e 02	6.96e 02		
1.16e-02	1.36e 02	1.44e 02	1.60e 02	1.87e 02	1.81e 02	2.59e 02	6.57e 02		
1.22e-02	1.24e 02	1.34e 02	1.49e 02	1.75e 02	1.67e 02	2.45e 02	6.13e 02		
1.28e-02	1.15e 02	1.23e 02	1.39e 02	1.62e 02	1.57e 02	2.32e 02	5.61e 02		
1.34e-02	1.06e 02	1.14e 02	1.28e 02	1.55e 02	1.45e 02	2.16e 02	5.24e 02		
1.41e-02	9.75e 01	1.07e 02	1.19e 02	1.44e 02	1.32e 02	2.03e 02	4.79e 02		
1.47e-02	9.06e 01	9.76e 01	1.11e 02	1.35e 02	1.25e 02	1.91e 02	4.45e 02		
1.54e-02	8.50e 01	9.21e 01	1.05e 02	1.29e 02	1.20e 02	1.84e 02	4.18e 02		
1.60e-02	8.13e 01	8.71e 01	1.01e 02	1.24e 02	1.13e 02	1.76e 02	3.87e 02		
1.66e-02	7.61e 01	8.17e 01	9.51e 01	1.20e 02	1.07e 02	1.66e 02	3.63e 02		
1.73e-02	6.81e 01	7.22e 01	8.48e 01	1.05e 02	9.51e 01	1.50e 02	3.20e 02		
1.79e-02	6.82e 01	7.34e 01	8.55e 01	1.05e 02	9.73e 01	1.53e 02	3.19e 02		
1.85e-02	6.21e 01	6.78e 01	8.00e 01	9.89e 01	8.86e 01	1.42e 02	2.96e 02		
1.92e-02	5.89e 01	6.28e 01	7.48e 01	9.32e 01	8.31e 01	1.33e 02	2.66e 02		
9.55e-03		1.79e 02	1.92e 02	2.12e 02	2.25e 02	2.95e 02	7.77e 02	16%	
1.14e-02		1.42e 02	1.56e 02	1.75e 02	1.75e 02	2.49e 02	6.30e 02		
1.31e-02		1.12e 02	1.23e 02	1.43e 02	1.41e 02	2.06e 02	5.30e 02		
1.48e-02		9.44e 01	1.06e 02	1.24e 02	1.20e 02	1.82e 02	5.02e 02		
1.65e-02		7.82e 01	9.92e 01	1.06e 02	1.02e 02	1.56e 02	4.21e 02		
1.83e-02		6.71e 01	7.71e 01	9.22e 01	8.75e 01	1.38e 02	3.43e 02		
2.01e-02		5.87e 01	6.80e 01	3.19e 01	7.65e 01	1.21e 02	2.87e 02		
2.22e-02		5.12e 01	5.99e 01	7.30e 01	6.78e 01	1.07e 02	2.41e 02		
2.41e-02		4.74e 01	5.60e 01	6.77e 01	6.41e 01	1.00e 02	2.03e 02		
2.58e-02		4.23e 01	5.05e 01	6.02e 01	5.65e 01	8.87e 01	1.83e 02		
2.75e-02		4.01e 01	4.74e 01	5.77e 01	5.48e 01	8.40e 01	1.58e 02		
2.92e-02		3.64e 01	4.30e 01	5.09e 01	4.85e 01	8.40e 01	1.46e 02		
3.09e-02		3.36e 01	4.01e 01	4.70e 01	4.54e 01	8.69e 01	1.27e 02		
3.26e-02		2.99e 01	3.61e 01	4.25e 01	4.11e 01	8.11e 01	1.14e 02		
3.43e-02		2.88e 01	3.39e 01	4.04e 01	3.93e 01	5.75e 01	1.01e 02		
3.60e-02		2.72e 01	3.20e 01	3.79e 01	3.64e 01	5.40e 01	9.39e 01		
3.80e-02		2.58e 01	3.08e 01	3.61e 01	3.51e 01	5.12e 01	8.46e 01		
3.99e-02		2.48e 01	2.95e 01	3.38e 01	3.31e 01	4.78e 01	7.36e 01		
4.15e-02		2.29e 01	2.70e 01	3.19e 01	3.12e 01	4.45e 01	6.75e 01		
4.32e-02		2.13e 01	2.53e 01	2.97e 01	2.90e 01	4.12e 01	6.09e 01		
4.49e-02		2.07e 01	2.39e 01	2.82e 01	2.82e 01	3.92e 01	5.85e 01		
4.66e-02		1.93e 01	2.26e 01	2.63e 01	2.59e 01	3.68e 01	5.34e 01		
4.85e-02		1.85e 01	2.16e 01	2.51e 01	2.51e 01	3.47e 01	5.05e 01		
5.03e-02		1.79e 01	2.09e 01	2.40e 01	2.39e 01	3.31e 01	4.71e 01		
5.20e-02		1.72e 01	1.96e 01	2.29e 01	2.28e 01	3.14e 01	4.48e 01		
5.35e-02		1.68e 01	1.93e 01	2.27e 01	2.26e 01	3.06e 01	4.36e 01		
5.54e-02		1.62e 01	1.90e 01	2.19e 01	2.18e 01	2.93e 01	4.21e 01		
5.65e-02		1.68e 01	1.94e 01	2.26e 01	2.23e 01	3.07e 01	4.13e 01		
3.46e-02	2.38e 01	2.58e 01	3.03e 01	3.64e 01	3.55e 01	4.98e 01	7.53e 01		65%
4.50e-02	1.93e 01	2.07e 01	2.49e 01	2.87e 01	2.84e 01	3.86e 01	5.67e 01		
5.22e-02	1.57e 01	1.69e 01	1.98e 01	2.31e 01	2.28e 01	2.99e 01	4.28e 01		
5.86e-02	1.33e 01	1.44e 01	1.66e 01	1.94e 01	1.92e 01	2.45e 01	3.38e 01		
6.50e-02	1.16e 01	1.24e 01	1.41e 01	1.63e 01	1.63e 01	2.04e 01	2.76e 01		
7.14e-02	9.99e 00	1.08e 01	1.23e 01	1.39e 01	1.44e 01	1.75e 01	2.27e 01		
7.74e-02	8.90e 00	9.16e 00	1.05e 01	1.20e 01	1.20e 01	1.49e 01	1.89e 01		
8.38e-02	7.84e 00	8.34e 00	9.32e 00	1.04e 01	1.07e 01	1.28e 01	1.62e 01		
9.07e-02	7.03e 00	7.37e 00	8.18e 00	9.08e 00	9.53e 00	1.11e 01	1.37e 01		
9.73e-02	6.39e 00	6.79e 00	7.36e 00	8.09e 00	8.37e 00	9.66e 00	1.19e 01		
1.04e-01	5.81e 00	5.96e 00	6.69e 00	7.35e 00	7.70e 00	8.85e 00	1.06e 01		
1.10e-01	5.22e 00	5.46e 00	5.95e 00	6.66e 00	6.87e 00	7.64e 00	9.25e 00		
1.16e-01	4.78e 00	5.16e 00	5.44e 00	6.01e 00	6.32e 00	7.06e 00	8.33e 00		
1.22e-01	4.44e 00	4.74e 00	4.99e 00	5.42e 00	5.70e 00	6.26e 00	7.49e 00		
1.29e-01	4.19e 00	4.32e 00	4.61e 00	4.96e 00	5.33e 00	5.65e 00	6.71e 00		
1.36e-01	3.75e 00	3.89e 00	4.14e 00	4.52e 00	4.72e 00	5.03e 00	5.95e 00		
1.42e-01	3.41e 00	3.62e 00	3.67e 00	4.02e 00	4.30e 00	4.52e 00	5.71e 00		
1.48e-01	3.20e 00	3.38e 00	3.40e 00	3.71e 00	4.03e 00	4.19e 00	4.77e 00		
1.55e-01	2.97e 00	3.10e 00	3.11e 00	3.42e 00	3.68e 00	3.77e 00	4.46e 00		
1.61e-01	2.72e 00	2.87e 00	2.97e 00	3.15e 00	3.38e 00	3.45e 00	4.11e 00		
1.68e-01	2.55e 00	2.58e 00	2.73e 00	2.96e 00	3.13e 00	3.22e 00	3.80e 00		
1.75e-01	2.36e 00	2.57e 00	2.53e 00	2.66e 00	2.94e 00	2.91e 00	3.50e 00		
1.81e-01	2.21e 00	2.40e 00	2.33e 00	2.47e 00	2.81e 00	2.74e 00	3.20e 00		
1.88e-01	2.27e 00	2.32e 00	2.21e 00	2.48e 00	2.65e 00	2.58e 00	3.03e 00		
1.94e-01	1.94e 00	2.21e 00	1.93e 00	2.16e 00	2.35e 00	2.38e 00	2.94e 00		
2.01e-01	1.88e 00	1.98e 00	1.80e 00	1.99e 00	2.18e 00	2.07e 00	2.61e 00		

To verify (4), one can use the values of T_{Rouse} and T_{rep} tabulated in reference [1] for 117 °C. Using (2), (3) we obtain :

at 128 °C : $150 \text{ s} < T_{\text{Rouse}} < 1\,500 \text{ s}$, $15\,000 \text{ s} < T_{\text{rep}} < 150\,000 \text{ s}$

at 134 °C : $60 \text{ s} < T_{\text{Rouse}} < 600 \text{ s}$, $6\,000 \text{ s} < T_{\text{rep}} < 60\,000 \text{ s}$

Fig. 2. — Representation of the measured static form factors $S_{\text{R}}(q)$ versus the scattering vector q , for samples 50 (○), 43 (×) and the isotropic sample (●), in both directions perpendicular and parallel to the stretching. For each anisotropic sample, values of S_{R} measured in the perpendicular (parallel) direction are above (below) the values corresponding to the isotropic sample.

values which can be compared to the duration of relaxation of our samples :

at 128 °C : $t_R = 30 \text{ s}, 60 \text{ s}, 480 \text{ s}, 1\,800 \text{ s}$

at 134 °C : $t_R = 60 \text{ s}, 960 \text{ s}$.

4. Neutron scattering data. — We now consider the reciprocal space dependence of the static coil form factors $S_{tr}(q_{\parallel})$ and $S_{tr}(q_{\perp})$. These quantities are tabulated in table II for all samples stretched at 128 °C and 134 °C. They are obtained in the following way :

— first, the direct neutron scattering signal for each sample is decreased by the amount of incoherent contribution, and the result is normalized to a unique sample thickness (1 mm). These two operations require a precise measurement of the thickness of the sample, which is the most important source of uncertainty. Table II gives an evaluation of the uncertainty in S_{tr} ;

— second, the data collected from three different spectrometers are normalized in such a way that continuity is obtained between adjacent scattering vector ranges.

Figure 2 shows a plot of such data, *versus* q , for the isotropic sample and two stretched samples. As t_R is increasing, the form factor is relaxing back to that of the isotropic sample. From the time dependence of these form factors, the theories for the coil dynamics in the melt can now be tested. A comparison between data and theories is discussed in the following letter of this issue.

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References

- [1] BOUÉ, F., NIERLICH, M., JANNINK, G., BALL, R., *J. Physique* **43** (1982) 137-148.
- [2] Perdeuterated PS : P. REMPP, CRM, Strasbourg (ref. SD 2440) ;
Non/deuterated PS : D. LENFANT, EAHP, Strasbourg (ref. S572).
- [3] Temperature controlled stretching machine (L. MONNERIE), ESPCI, Paris.
- [4] MONNERIE, L., Private discussion.
- [5] DE GENNES, P. G., *J. Chem. Phys.* **55** (1971) 572 and also, *Scaling Concepts in Polymer Physics*, Ch. VIII (Cornell University Press, London) 1979.
- [6] DOÏ, M., EDWARDS, S. F., *J. Chem. Soc. Faraday Trans. 2* **74** (1978) 1789, 1802, 1818.
- [7] FERRY, J. D., *Viscoelastic properties of polymers* (Wiley, New York) 1970.