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Notes

Dynamics of Copolymer Solutions Determined by Using Neutron Spin-Echo

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I. Introduction

In this paper we present an experiment recently made on the spin-echo spectrometer IN11 of the Institut Laue Langevin (ILL, Grenoble) which we believe shows unambiguously for the first time the internal motion of a chain in solution.

It has been shown,[1] by using the random-phase approximation (RPA), that a solution of two homopolymers always exhibits two relaxation modes. This allows us to write for the intermediate scattering function $S(q,t)$

$$S(q,t) = A_c e^{-\Gamma_c t} + A_I e^{-\Gamma_I t} \tag{1}$$

where q is the scattering vector ($q = 4\pi/\lambda \sin \theta/2$), λ is the wavelength of the incident radiation in the medium, θ is the scattering angle, and t is time. Γ_c and Γ_I are the characteristic frequencies attributed to the so-called cooperative and interdiffusion modes. They depend on the nature of the two homopolymers, their concentration, and the thermodynamic interaction parameters. The amplitudes A_c and A_I depend on the contrast factors and other physical properties of the system.

These conclusions have been verified experimentally[2-4] by quasi elastic light scattering, and without going into details there is a good agreement between the theoretical predictions and the experimental results.

This theory has been extended to one copolymer (mainly two blocks of A–B type copolymer) in solution[5] leading to a formula identical with eq 1. The theoretical expression of the quantities (A_c, A_I, Γ_c, and Γ_I) and their variations with concentration, composition, and other physical parameters have been discussed elsewhere in detail.[5,6] They are different from those obtained for a mixture of two homopolymers in solution. In this case, the relaxation frequency Γ_c corresponds to the cooperative motion of the pseudonetwork formed by the two species in solution. Its value is identical with that which could be obtained for a homopolymer of the same length and the same thermodynamical properties. The relaxation frequency Γ_I has been identified as describing the relative motion of one block with respect to the other.

Our interest was focused on this latter mode, and the purpose of this experiment was to find experimental conditions for which the amplitude A_c of the cooperative mode vanishes, thus allowing one to observe only the interdiffusion mode. The calculation shows that for a 50/50 diblock copolymer if one adjusts the total contrast factor of the solvent in order to satisfy the relation

$$(a_H - a_o)x + (a_D - a_o)(1 - x) = 0 \tag{2}$$

or

$$a_H x + a_D(1 - x) = a_o \tag{3}$$

then $A_c = 0$. In these relations, a_H, a_D, and a_o are the coherent scattering length per unit volume of the ordinary polymer, the deuterated polymer, and the solvent, respectively, and x is the volume fraction of the nondeuterated block within the copolymer. This condition has been called the "optical θ point" by Tanaka and Inagaki[7] in the case of a light-scattering experiment. It corresponds to a "zero average contrast" of the copolymer. For a monodisperse system, this leads to a zero scattering intensity at zero angle ($q = 0$). Therefore, it is of particular interest to work under these experimental conditions for a precise determination of the interdiffusion mode.

II. Experimental Section

A. Sample Preparation. In order to avoid incompatibility effects and ensure good solubility, a diblock copolymer of deuterated styrene–ordinary styrene was prepared. Its characterization was carefully made by light scattering, GPC, NMR, and small-angle neutron scattering (SANS).[8] The details are given in a recent paper,[8] and the results are collected in Table I. The neutron-scattering experiments were made on a mixture of ordinary and deuterated benzene. In order to obtain zero average contrast, we used, as in ref 8, a mixture made of 51.3% ordinary and 48.7% deuterated benzene. Since the level of intensity depends on the polymer concentration, it is advantageous to work at high concentration. In fact, we used only one concentration, $c = 0.34$ g/cm^3, since the theory,[5] which has been verified experimentally,[8] predicts that the shape of the intensity of the signal is concentration independent. Since the polymer is of a relatively low molecular weight, the solution is not too viscous at this concentration and can be handled easily. Moreover, this concentration corresponds to the so-called semidilute regime (c is of the order of $3c^*$, where c^* is the overlap concentration) where the theory is more appropriate.

B. Neutron-Scattering Experiments. Neutron-scattering experiments were performed at the ILL, Grenoble, using the NSE

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Table I
Polymer Characterization

sample	M_n,[a] g·mol^{-1}	M_w,[a] g·mol^{-1}	M_z,[a] g·mol^{-1}	polydispersity[d]	radius of gyration,[b] Å	% PSD[c]
PSD561	4900	5600	6900	1.08	22	100
PSD425	17700	18000		1.01		100
PSH155	11530	12740		1.10		0
PSD-PSH561	9100	10800	13500	1.12	28	46

[a] Measured by GPC. [b] Measured by SANS. [c] Measured by NMR. [d] Calculated from GPC by taking account of the axial dispersion.

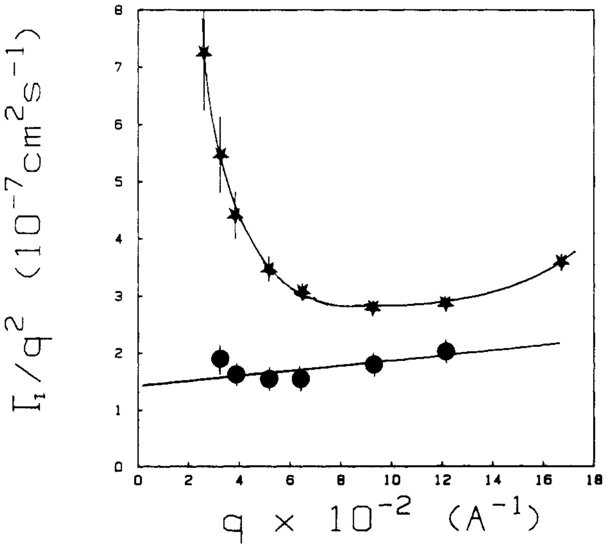

Figure 1. Experimental variations of the interdiffusion coefficient Γ_I/q^2 as a function of q at the total polymer concentration c = 0.34 g/cm^3 for the two investigated systems: (★) diblock copolymer PSD-PSH561/benzene(H) + benzene(D); (●) mixture of homopolymers PSH155/PSD425/benzene(D). The solid lines are guides to the eyes.

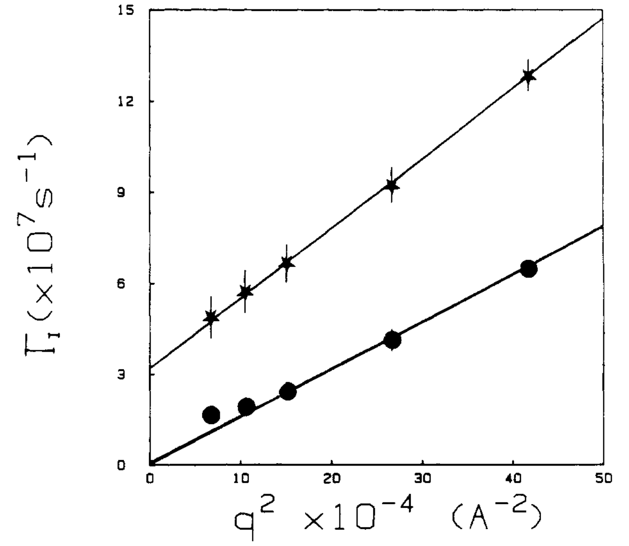

Figure 2. Experimental variations of the interdiffusion frequency Γ_I as a function of q^2 for the same system as in Figure 1.

spectrometer IN11. The principles, the mode of operation of this instrument, and the treatment of the data are described elsewhere in detail.[9] The wavelength of the incident neutrons was λ = 8.5 Å and the range of scattering angles such that $0.026 < q(\text{Å}^{-1}) < 0.17$; the uncertainty in q is of the order of ±10%. After subtraction of the background scattering and normalization by the resolution function of the instrument, we have analyzed the intermediate scattering function as a single-exponential decay in the observed time range ($0.3 < t$(ns) < 17). The quantity Γ_I/q^2 as a function of q is plotted (★) in Figure 1. These experimental data exhibit an abnormal behavior. A linear extrapolation to a finite value for $q = 0$ is not possible; the curve seems to diverge at low values of q. One can also plot Γ_I as a function of q^2 (see Figure 2). The extrapolation is linear and leads to a finite value Γ_{I_0} in the small q range considered where the last point on Figure 2 corresponds to $qR_{GT} \simeq 1.7$. In this limited range of qR_{GT}, the crossover from q^2 to q^3 cannot be detected.[10]

III. Discussion

This result is completely different from that which can be expected for a homopolymer solution or even a mixture of homopolymers in a solvent. In order to be sure that this is not an artifact, we performed the same neutron experiment on a mixture of homopolymers in a solvent where only the interdiffusion mode Γ_I can be observed.[6] This was achieved on a mixture of deuterated and ordinary PS of approximately the same molecular weight as the copolymer. Unfortunately, we did not have sufficient time to work in the zero average contrast conditions, which require long counting time. We used a mixture of 6% PSH-155 and 94% PSD-425 in deuterated benzene at the same total polymer concentration c = 0.34 g/cm^3. From the theory,[2] it can be shown that in these conditions (i.e., small composition of the "visible" polymer) one "sees" only the interdiffusion mode. The data obtained for this system are represented (●) on Figures 1 and 2 (with the same scale). The experimental results are completely different, confirming the fact that a copolymer has a different behavior, in the small q range, as compared to a homopolymer.

It is now interesting to verity semiquantitatively that the data of Figures 1 and 2 can be interpreted in the framework of the RPA theory,[1,5] which predicts for Γ_I the following relations: for two homopolymers with the same molecular weight in solution

$$\Gamma_{I,H} = q^2 \frac{kT}{N\zeta} \frac{1}{P(q)} \tag{4}$$

for diblock copolymer (50/50) in solution

$$\Gamma_{I,C} = q^2 \frac{kT}{2N_{1/2}\zeta} \frac{1}{[P_{1/2}(q) - P(q)]} \tag{5}$$

where $N_{1/2}$ and $N = 2N_{1/2}$ are the number of monomers of each block of the copolymer and of the homopolymer, respectively. $P_{1/2}(q)$ and $P(q)$ are the static form factors of each block and the total chain, respectively; ζ is the friction coefficient of each monomer. T is the absolute temperature and k the Boltzmann constant. These expressions are only valid in the framework of the Rouse model. It is also assumed that the interaction parameter between PSD and PSH is zero ($\chi = 0$).

The main difference between these expressions resides in the behavior of $P(q)$ and $P_{1/2}(q) - P(q)$ at low q values. Assuming that the chain is Gaussian, the first quantity tends to unity when $q \rightarrow 0$ and can be expanded as

$$P(q) \simeq 1 - \frac{q^2 R_{GT}^2}{3} \tag{6}$$

and the second as

$$P_{1/2}(q) - P(q) \simeq q^2 \frac{R_{GT}^2}{6}\left[1 - \frac{3}{8}q^2 R_{GT}^2\right] . \tag{7}$$

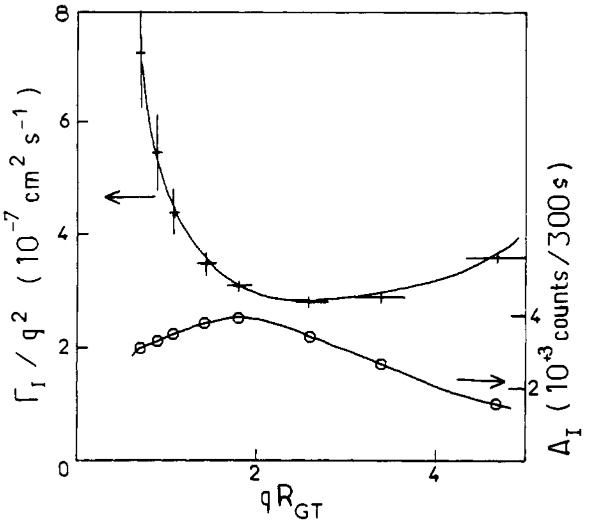

Figure 3. Experimental variation of the interdiffusion coefficient Γ_I/q^2 and of the observed scattering amplitude $A_I(q)$ as a function of qR_{GT} for the copolymer system.

where R_{GT} is the radius of gyration for a chain made of N monomers. If one writes the expansion of $\Gamma_{I,H}$ and $\Gamma_{I,C}$ introducing the translation diffusion coefficient $D_o = kT/N\zeta$, one obtains

$$\Gamma_{I,H} \simeq q^2 D_o \left[1 + q^2 \frac{R_{GT}^2}{3} \right] \qquad (8)$$

$$\Gamma_{I,C} \simeq 6 \frac{D_o}{R_{GT}^2} \left[1 + q^2 \frac{3R_{GT}^2}{8} \right] \qquad (9)$$

From the intercept of the curves $\Gamma_{I,C}$ versus q^2 and $\Gamma_{I,H}$ versus q^2, one obtains for D_o 3.4 and 1.5 × 10^{-7} cm^2·s^{-1}, respectively. These values are in reasonable agreement since the exact molecular weight of the homopolymer and its polydispersity were not accurately determined. These equations predict also that the ratio of the slopes of the curves $\Gamma_{I,C}$ and $\Gamma_{I,H}$ as a function of q^2 should be equal to 9/4; experimentally, we found 1.5. This is qualitatively acceptable, and we think that a more precise analysis could explain these results.

Another problem which has to be solved is the position of the minimum of the curve $\Gamma_{I,C}/q^2$, which is obtained for qR_{GT} = 2.5 (see Figure 3). This minimum should coincide with the maximum of the scattering amplitude $A_I(q)$ at qR_{GT} = 2 (see Figure 3 and ref 8). At first sight, this difference cannot be explained by polydispersity and could be interpreted by taking into account the hydrodynamical interactions. This problem will be discussed in a forthcoming paper.

From these results, it seems that these experiments, made using the possibility offered by labeling a part of chain, show clearly the internal motion of a linear chain in a semidilute solution.

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Registry No. (Deuteriostyrene)(styrene) (block copolymer), 108592-10-5; neutron, 12586-31-1.

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Bound Water in Collagen. Evidence from Fourier Transform Infrared and Fourier Transform Infrared Photoacoustic Spectroscopic Study

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Introduction

The triple-helical conformation of collagen requires the presence of glycine in every third position in the amino acid sequence and consequently introduces steric constraints that restrict glycines to the inner core of the triple helix with side chains of the nonglycyl residues projecting from the surface of the triple helix.[1] The presence of intrachain hydrogen bonds stabilizes the triple helix and imposes additional constraints on the normal vibrations of the peptide moieties. Collagen participates in numerous highly specific biologically important interactions and therefore an understanding of the vibrational modes of collagen will pave the way for elucidating the nature of such interactions. Infrared spectroscopy has been extensively used to investigate the structure of collagen.[2–4] Synthetic polytripeptide models of collagen have been found to be useful systems for physicochemical investigations of collagen.[5] Infrared spectroscopy has been utilized to study polytripeptide models as films cast from aqueous solutions and from solutions in organic solvents.[6–9] In a recent study, FTIR spectroscopy was utilized to monitor intermolecular interactions in collagen self-assembly.[10] Despite numerous IR studies of collagen and collagen-like polypeptides,[6–10] the characteristic vibrations of the triple-helical structures remain poorly understood.

In the present study, FTIR photoacoustic spectroscopy is utilized to investigate collagen in the solid state. A resolution enhancement of the amide I band in collagen

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