

Synthesis and test of a statistical copolymer — the furtive chain

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The synthesis of a polydimethylsiloxane chain with a random distribution of deuterated and non-deuterated methyl groups is described. Cationic polymerization provides an excellent mechanism for statistical sequencing. The test for randomness is given by a neutron scattering experiment on a semidilute solution. In the reciprocal interval ($1 \times 10^{-2} \text{ \AA}^{-1}$, $1 \times 10^{-1} \text{ \AA}^{-1}$), the response is uniformly devoid of any copolymer correlation effect. A totally furtive chain can thus be inserted in a polymer solution, at zero average contrast between deuterated and non-deuterated chains.

(Keywords: small-angle neutron scattering; polydimethylsiloxane; furtive polymer; statistical copolymer; zero average contrast)

INTRODUCTION

The statistical copolymer is a linear structure that has interesting properties related to the random distribution of organic substituents along the chain. The property that is discussed here is the interaction of such a structure with incoming radiation, in a scattering experiment. However, the average physical configuration of the chain in space is assumed here to be governed by a single 'Flory' interaction parameter, identically the same for all monomers. Such a situation is found in so-called pseudo-copolymer, made of substituents that differ only by the fact that they are deuterated or not deuterated. The incoming radiation is a neutron beam. The statistical pseudo-copolymer defined in this manner can be simply considered as a polymer chain characterized by an average coherent scattering length $\langle b \rangle$ and a fluctuation Δb generating incoherent noise. This is the extreme case of a generally more complex situation, thoroughly discussed by Leibler and Benoit¹. In fact, the observed structure of such pseudo-copolymers, revealed by neutron scattering, is the result of two opposing effects: the so-called correlation hole effect, and the chemical disorder effect. The first is a consequence of the finite volume of the monomer and the uniform density of occupation. The second is the result of composition fluctuations. When the isotopic labels are randomly distributed, the chemical disorder effect is very strong and the observed structure behaves as if the correlation hole did not exist.

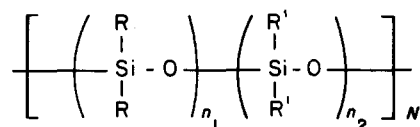
The statistical pseudo-copolymer is used in several types of scattering experiments. For instance Richter *et al.*² have been able to determine directly the 'self-contribution' to the quasi-elastic scattering due to the Brownian motion of polymer chains. Recently, Benoit³ proposed to introduce pseudo-copolymers in the experimental study of the dynamics of bidisperse polymer systems⁴. Here, the longer chains should be occulted at zero average contrast between the solvent and a mixture

of labelled and non-labelled monomers. This requirement introduces the use of statistical pseudo-copolymer.

The purpose of this note is to show that a real statistical pseudo-copolymer (hereafter called a *furtive* copolymer) can be synthesized. We first give an account of the synthesis and briefly discuss the nature of the disorder (quenched or annealed). In a second part we report the result of the characterization, proving that the copolymer is indeed furtive at a given contrast, i.e. that the correlation hole effect has disappeared.

SYNTHESIS

A good candidate for the synthesis of statistical pseudo-copolymers is polydimethylsiloxane. It belongs to the general family of polyorganosiloxanes [R_2 (or R'_2)SiO], where R and R' are organic substituents. The linear structure is:



Here the substituents are $R = \text{CH}_3$ and $R' = \text{CD}_3$. The molar fraction $[R]$ of R and $[R']$ of R' being given, the copolymer obtained by the polymerization process is characterized by a random sequence of R and R' along the chain of degree N .

The random nature of the sequence results from a complex growth mechanism⁵. Two types of reactions are involved, namely (i) an actual polymerization and (ii) a transesterification with a mechanism reminiscent of transesterification⁶, i.e. scission followed by recombination. This ensures a better randomness than in the classical synthesis process.

For the case where R and R' have different chemical nature, a test⁷ of the structure by n.m.r. has revealed that the distribution of R and R' along the chain follows a

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binomial law. Let N_{R_i} and $N_{R'_i}$ be respectively the number of R and R' substituents of the i th chain, such that $N_{R_i} + N_{R'_i} = N$ (degree of polymerization). The statistical weight of such a chain is:

$$P_i = \frac{N!}{(N_{R_i})(N_{R'_i})!} [R]^{N_{R_i}} [R']^{N_{R'_i}} \quad (1)$$

Another way to characterize the random distribution is to introduce⁸ the Markov transition probability $P_{\alpha\beta}$, where α and β are indices related to the nature of the labelling ($\alpha = H$ or D). The distribution is random if $P_{HH}P_{DD} = P_{DH}P_{HD}$ (Bernoulli law). A question of interest, related to the copolymerization process, is the quenched or annealed character of the resulting structure.

The distribution of the H and D isotopic composition along the chain follows a given law. Here we consider the hypothesis of a random distribution and we test this hypothesis. When the isotopic composition of a given monomer is invariant during the time of the scattering experiment (i.e. 1 h), the distribution is 'quenched'. On the contrary, if the isotopic labelling of a monomer varies during the time (the average composition being constant), the distribution is 'annealed'. This occurs, for instance, during transesterification, and in this case the isotopic composition can be considered as a fluctuating physical quantity in equilibrium with a bath.

Here we assume that the isotopic composition does not influence the two-body interactions. The partition function, from which the structure function is derived, is therefore not related to the nature of the composition distribution. The only effect of the annealing is to improve the randomness of the composition, as compared to a given quenched situation. (In the case of a correlation between composition and interaction, the distinction between quenched and annealed is, of course, much more important.)

Law (1) was tested on small linear molecules. We hypothesize that it holds true when the substituents are $R = CH_3$ and $R' = CD_3$ and when the degree of polymerization is a large number ($N > 10^3$). The test of this hypothesis is given by the neutron scattering experiment.

The polymer was prepared⁹ by cationic polymerization of a bulk mixture of an equal proportion ($y = 0.5$) of deuterated and non-deuterated monomers. The polymerization was done in the presence of an acid catalyst (Tonsyl, furnished by Rhone Poulenc), at a temperature $T = 70^\circ C$, in an argon atmosphere. The reaction was stopped after 6 h, by addition of potassium hydrogencarbonate and dilution with toluene. The resulting product was slightly fractionated in order to eliminate the smaller chains.

The polymer chains were characterized by size exclusion chromatography, associated with two on-line detectors: one detector for concentration (Shimadzu RID-6A) and one detector for scattered intensity (Chromatix CMX-100). The elution solvent was toluene¹⁰. It is noteworthy¹¹ that the refractive index increment for the HD sample is -0.0746 , whereas it is -0.0905 for both deuterated and non-deuterated polydimethylsiloxane at $\lambda = 632$ nm.

The average molecular weight is $M_w = 138\,000$ and the polydispersity index is 1.30. The average radius of gyration in a good solvent is estimated to be 145 Å.

THE NEUTRON SCATTERING EXPERIMENT

Three solutions were prepared with the random copolymer sample, at the same concentration (10% by weight), about $5c^*$: sample 1 in toluene, sample 2 in deuterated toluene and sample 3 in a mixture of deuterated and non-deuterated toluene. In this last sample, the fraction of deuterated toluene, $x = 0.34$, satisfies the zero average contrast condition, which will be derived below.

The general expression for the scattered intensity by these solutions is extremely complex⁴ since it reflects the competition between the correlation hole and the chemical disorder effects. A considerable simplification is introduced if we assume a random distribution of the organic substituents along the polydimethylsiloxane chain. Let then b_{PD} and b_{PH} be the coherent scattering amplitudes of deuterated and non-deuterated monomers. The average coherent amplitude is:

$$\langle b \rangle = \frac{1}{2}(b_{PD} + b_{PH}) \quad (2)$$

The random distribution introduces an incoherent contribution, the 'Laue term', with a square amplitude¹²:

$$b_L^2 = \langle b^2 \rangle - (\langle b \rangle)^2 = y(1-y)(b_{PD} - b_{PH})^2 \quad (3)$$

where y and $(1-y)$ are respectively the proportion of deuterated and non-deuterated monomers.

The total monomer incoherent scattering is b_{inc}^2 , the sum of b_L^2 and of the square of the intrinsic incoherent scattering length of atoms.

For samples 1 and 2 the scattered intensity reads:

$$I(q) = b_P^2 c^2 S_{PP}(q) + b_{inc}^2 c + b_S^2 c_S \quad (4)$$

where

$$b_P = \langle b \rangle - b_{T(H \text{ or } D)} v_P / v_T \quad (5)$$

is the contrast length; c and c_S are the monomer concentration and the solvent one, b_S is the incoherent scattering length of the solvent molecule, b_{TH} and b_{TD} are the coherent scattering lengths of non-deuterated and deuterated solvent molecules, $S_{PP}(q)$ is the polymer-polymer structure factor, and v_P and v_T are respectively the partial molar volumes of polymer and toluene.

For sample 3, the expression is slightly more complicated because of the contribution of the mixed solvent:

$$I(q) = b_P^2 c^2 S_{PP}(q) + b_{inc}^2 c + b_S^2 c_S + x(1-x)(b_{TH} - b_{TD})^2 c_S \quad (6)$$

where

$$b_P = \langle b \rangle - [x b_{TD} + (1-x) b_{TH}] v_P / v_T \quad (7)$$

The condition for zero average contrast is $b_P = 0$ and this is achieved when the deuterated fraction of solvent, x , is 0.34.

The structure factor of polymer chains in semidilute solutions, in the asymptotic range $qR_G \gg 1$, reads:

$$S_{PP}(q) = A \xi / (q^2 + \xi^{-2}) \quad (8)$$

where ξ is the correlation length,

$$A = \frac{v d - 1}{v d F_\infty} \frac{1}{\Gamma^3} \approx 30.2$$

where v , d , F_∞ and Γ are universal constants¹³: v the critical exponent associated with swelling of the polymer

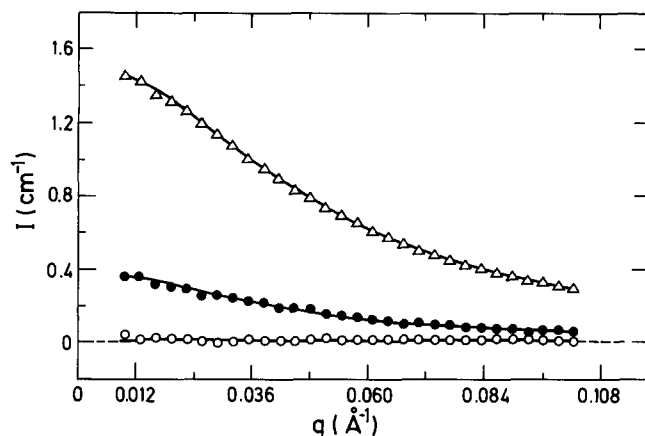


Figure 1 Absolute coherent scattered intensity (cm^{-1}) versus the scattering vector. The full curves are fits: (Δ), solution 1; (\bullet), solution 2; (\circ), solution 3. This figure shows that the observed signal is identical to that of homogeneous polymer chains. There is no evidence of the copolymer correlation hole effect. The furtive chain corresponds to the case of solution 3

($\nu \approx 0.588$), d the space dimension ($d=3$), and F_∞ and Γ constants related to semidilute solutions ($F_\infty \approx 0.486$ and $\Gamma \approx 0.165$).

Here we account only for the screening effect due to the repulsion between infinite chains (we neglect the effect of local swelling and the effect of finite chain size).

The test of the random distribution of deuterated and non-deuterated sequences is thus found in the experimental evidence of equations (4) and (6). There is no correlation hole effect, as found in block copolymers, which would be observed as a maximum in the scattered intensity plot.

The scattering experiment was performed using the PACE spectrometer at the Orphée neutron source in a q range of 10^{-2} to 10^{-1} \AA^{-1} .

Absolute calibration is made using the procedure¹² of the direct determination of the incident beam. The coherent intensity is deduced from the total intensity (equation (4) or (6)) by using the following subtraction of the backgrounds: The solvent background is deduced from the intensity of the pure solvents corrected for the mole fraction of solvent. The incoherent background of the polymer is obtained from the calculated value of b_L^2 (equation (3)) while the incoherent background of hydrogen atoms is deduced from the intensity scattered by pure toluene.

Figure 1 shows the results obtained with the three samples: curves 1 and 2 are Lorentzians, which indicate no correlation hole effects. The half-widths at half-maximum should be the same for the two samples and the predicted value¹⁴ is $\xi = 18 \text{ \AA}$. In fact $\xi = 24 \text{ \AA}$ for sample 1 and 20 \AA for sample 2. Curve 3 should be identically zero. It is indeed so, within an error of less than $2 \times 10^{-2} \text{ cm}^{-1}$. By comparison, the solvent background is 0.64 cm^{-1} in this case. We have assumed that the experiment can be interpreted with a single Flory interaction parameter, and this appears to be adequate in good solvents. Near the Θ temperature, the small energy differences between the labels may, however, have

observable consequences and will be of interest to investigate the special collapse¹⁵ effect due to the random distribution of labels.

CONCLUSION

In the introduction we were discussing the preparation of what was called a furtive polymer, i.e. a completely statistical copolymer. Practically our purpose is less ambitious. What we want to do is to prepare a polymer of variable average scattering length per monomer that gives no signal in the useful range of q values, when embedded in a solvent of the same scattering length. It is evident that this cannot be true for all q values and that for q values of the order of the distances of the atoms in a monomer one will always have a signal different from zero unless a very precise distribution of the D and H monomers is realized. In order to show qualitatively what can happen, it would be interesting to use the results of Benoit and Hadziioannou¹⁶, who showed that for a copolymer made of a regular sequence of H and D monomers one has a peak that corresponds to the correlation hole. When the sequences become polydisperse this hole disappears and one obtains a curve decreasing regularly when q increases. We did not observe such an effect; this means that our polymers are perfectly suited for the experiments we are planning to do.

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