Table 1 Grafting of azodicarboxylate-terminated polystyrenes on polydiene backbones

Polystyrene			Backbone polymer	Grafting efficiency (%)
$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	Content (wt %)		
5450	1.11	40	IR[b]	73
8900	1.11	40	IR	77
		20	IR	78
17 700	1.12	40	IR	67
8900	1.11	40	NR[c]	57
		20	NR	49
5450	1.11	40	BR[d]	63

[a] Not corrected for column broadening; [b] synthetic polyisoprene, Cariflex IR305; [c] natural rubber, SMR5L; [d] polybutadiene, Intene 55NF

performed on commercial grades with no prior purification. Extraction of the NR before reaction results in grafting efficiencies comparable to those obtained with Cariflex IR305.

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Crossover from the dilute to the semidilute regime as determined from n.m.r. of poly(ethylene oxide) chains

Introduction

The purpose of this Letter is to suggest that suitable nuclear magnetic relaxation (n.m.r.) properties observed on flexible polymer chain solutions can be used to determine the point where a crossover has been predicted to occur by increasing the concentration from the dilute regime to the semidilute[1].

It is known that in the dilute regime the volume $V_G \approx R_G^3$ of an isolated chain is a function of molecular weight, M (R_G is the radius of gyration: $R_G^2 \propto M^{6/5}$) but is independent of concentration[2]. A concentration crossover line $C^*(M,T)$ to the semidilute regime has been predicted from recent descriptions of polymer–solvent systems based on analogous properties of magnetic systems considered in the critical domain[1,3]. C^* is considered as the concentration $C^* \simeq NV_G^{-1}$ of overlap of polymer chains (N is the number of monomer units). At concentrations higher than C^* overlapping chains are entangled and polymer solutions must exhibit a correlation length, ξ, such that $\xi^2 \propto C^{-3/2}$; ξ is independent of molecular weight. The concentration crossover occurs at the point where $\xi(C^*) = R_G$.

The entanglement concept[4] and the above description are reconciled by identifying ξ with the average distance between two consecutive chain coupling junctions or entanglements[5]. A spatial crossover induced by concentration or temperature variations has been recently well observed from neutron scattering experiments performed on polystyrene chain solutions[6]. The Fourier transform of the pair correlation function of monomer units exhibits a crossover length q^{*-1}. More recently, a determination of C^* has been proposed using ultra-violet spectroscopy as a technique to probe monomer unit environment[7].

Transverse magnetization correlation function

Properties of the correlation function of the transverse magnetization associated with nuclear spins bound to polymer chains in solutions have been extensively studied on polyisobutylene[8–10]. By analysing experimental results two concentration ranges can clearly be distinguished. One of these (I) spreads from the pure polymer state to a concentration C_i; the other one spreads from C_i to infinite dilution.

(i) It has been well established that the n.m.r. response observed on high molecular weight ($\approx 10^6$) polyisobutylene chain solutions in the concentration range (I) exhibits solid-like and liquid-like character. The solid-like character is clearly reflected either by a high resolution spectrum narrowing effect induced by sample rotation[9] or by a pseudo-solid spin echo whose amplitude goes to zero upon chain dilution[11]. This response is related to a residual dipolar spin coupling which is supposed to result from monomer unit non-isotropic motions induced by the presence of entanglements. It is also observed on *cis*-1,4-polybutadiene[11] and poly(dimethyl siloxane)[12] chains.

On the other hand, the spectrum narrowing effect is not observed on polymer chain solutions in the concentration range (II); in highly dilute solutions chains are free to rotate and no residual dipolar spin coupling can be observed.

(ii) Also, it has been shown that the linewidth Δ observed on polyisobutylene chain solutions in the concentration range (I) exhibits a characteristic dependence upon solvent concentration and temperature; Δ^{-1} is a linear function of $\gamma = \nu_1(1-\nu_1)^{-1}$ (ν_1 is the molar fraction of solvent); Δ reflects the probability of association of two monomer units taking the free energy of

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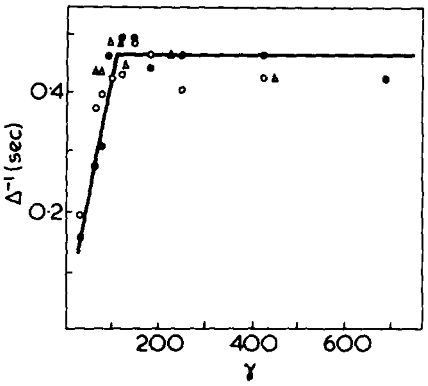

Figure 1 Variations of the reciprocal linewidth, Δ^{-1}, *versus* the number of water molecules per monomer, γ(●); cross-over concentration $\gamma_i = 110$. Effect of degradation: ○, 2 month old samples; △, 5 month old samples

polymer solvent interaction into consideration[10]. On the other hand, the linewidth variations observed in the concentration range (II) are negligible: there is a plateau. In highly dilute solutions the monomer unit concentration within a chain does not depend upon the chain concentration. Furthermore the spectrum narrowing effect and the linear variation of Δ^{-1} are closely associated with each other within the whole concentration range (I).

This Letter aims at using the two above striking features to identify the state where chains overlap with concentration range (I) and the dilute regime with concentration range (II) and to show that $C_i \equiv C^*$.

For convenience, reported experimental results were obtained from poly(ethylene oxide) chains in solution in deuterated water. This sample was chosen because it can be synthesized within a very narrow molecular weight distribution. Also, the average square radius of gyration $\langle R_G^2 \rangle$ of this polymer in dilute water solution has been already accurately determined as a molecular weight function from viscoelastic measurements[13–16]. This average value will be used to compare C_i with C^*.

Experimental

A poly(ethylene oxide) sample was prepared by adding highly purified ethylene oxide to a carbazylpotassium solution in THF, in a glass apparatus sealed under high vacuum as described elsewhere[17]. After 6 days at 35°C, the polymerization was stopped by addition of a small amount of methanol. It has been shown that anionic polymerization of ethylene oxide according to this process gives living monofunctional polymers characterized by a narrow molecular weight distribution[17]. (The molecular weight defined from viscosity measurements is $M_v = 370\,000$ at 25°C).

Solution inhomogeneities were eliminated by using wide tubes to perform good stirring; the homogeneous solutions were afterwards transferred into n.m.r. tubes. Various concentrations in deuterated water were obtained by weighing. N.m.r. spectra were run on a standard high resolution 60 MHz Jeol spectrometer.

Results

Experimental results were analysed according to the procedure described above; the inverse of the linewidth Δ^{-1} was plotted as a function of γ (*Figure 1*). Two different behaviours can be observed. At low polymer concentration the resonance lines are narrow ($\nu \approx 2.2$ Hz) and Δ^{-1} is independent of concentration. Above concentration $C_i = 20$ mg/cm^3 ($\gamma_i = 110$) the lines get broader and Δ^{-1} decreases linearly as γ is decreased.

The crossover concentration C_i observed from n.m.r. measurements may be compared with the C^* concentration. At the concentration C_i, the average size of the spherical volume occupied by a chain is defined from $R \approx (M/AC_i)^{1/3} = 315$ Å (A is the Avogadro number). On the other hand, the radius of gyration, R_G, of an isolated coil was evaluated from the mean square end to end distance $\langle r^2 \rangle$ obtained from viscosity measurements performed in the dilute regime[13–16]. We found from the literature data that the relation $\langle r^2 \rangle = KM^{6/5}$ holds as expected and for $M_v = 3.7 \times 10^5$, $R_G = \langle r^2 \rangle^{1/2}/7^{1/2}$ is found to vary from 270 to 380 Å depending on the model used to derive $\langle r^2 \rangle$ from viscosity data.

The good agreement between R and R_G shows that the C_i concentration observed from n.m.r. is very close to C^* the crossover point where isolated coils of the dilute regime start overlapping in the semidilute regime.

Also, dilute and semi-dilute regimes may be distinguished from one another by the spectrum narrowing effect. Spectra recorded during sample rotation on polymer chain solutions defined by $\gamma > \gamma_i$ exhibit a small narrowing effect quite analogous to that observed on a tetramethyl silane sample. This narrowing effect only reflects field inhomogeneities. When spectra are recorded during sample rotation on polymer chain solutions defined by $\gamma < \gamma_i$ the linewidth is found to be divided by ~2 (*Figure 2*); the rotation axis is perpendicular to the magnetic field direction. This property reflects the presence of a weak dipolar spin coupling; it is analogous to that observed on polyisobutylene[9] or on polybutadiene[18] chain solutions. This weak interaction is considered as a non-zero average of the dipolar coupling established between all protons located on chains. Such a property indicates that polymer chains are in a state where they cannot freely rotate because of constraints exerted on chain segments. This state is identified with the semidilute regime and it is considered that constraints are due to entanglements. Monomer unit motions observed on a time scale Δ^{-1} are not completely isotropic. The C_i concentration must then be considered as the point where a quenching effect of entanglements occurs.

It must also be noticed that a rapid rotation of the tubes (≈50 Hz) induces perturbations in the concentrated solutions; when the rotation is stopped the linewidth is found to vary with time. This does not occur in the dilute regime; it is supposed that in this case there are no entanglements preventing solutions

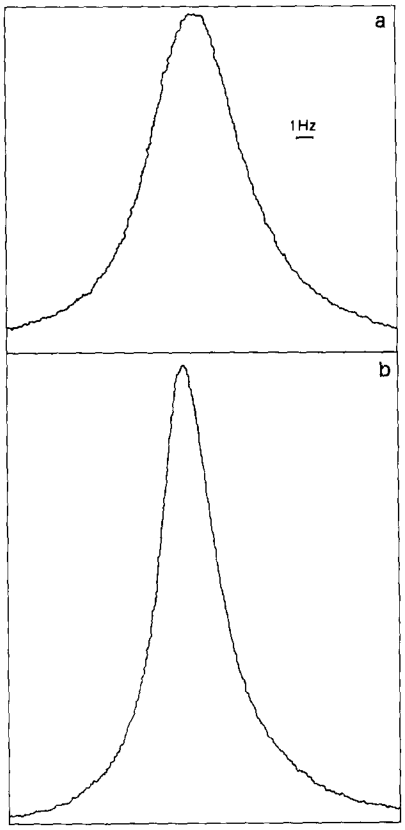

Figure 2 Spectrum narrowing effect in the semidilute regime ($\gamma = 31$, $C = 71$ mg/cm^3). Spectra recorded: A, without sample rotation; B, with slow rotation (~10 Hz)

from regaining homogeneity rapidly.

Finally, it must be emphasized that it is possible to follow sample degradation by n.m.r. The degradation of PEO chains in water is known[19]. It was observed that n.m.r. properties of samples change with time. Five months old samples all give narrow line spectra corresponding to dilute solutions. The C_i concentration was found to increase (from 20 to more than 35 mg/ml); this reflects the chain molecular weight decrease from 3.7×10^5 to less than 1.8×10^5. However spectra observed on one month old samples do not exhibit any change.

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