# Concentration effects on polymer coil overlap as perceived from n.m.r. observation on high molecular weight polyisobutylene chains

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Chain segment motions observed on a n.m.r. time scale are perceived as non-isotropic ones because of slow isotropic relaxation of chain constraints such as entanglements. This property, observed on protons bound to polyisobutylene chains, is applied to the investigation on a molecular scale of the crossover from the dilute to the semi-dilute regime. It is shown that coil overlap of polyisobutylene chains in $CS_2$ is perceived from n.m.r. at a monomer unit concentration $C_\nu$ about eight times greater than the ideal concentration $C^*$ defined from measured radii of gyration. By considering different chain lengths and different solvents, it is shown that the coil overlap concentration $C_\nu$ corresponds to a virtual partition of the chain into about 15 blobs.

## INTRODUCTION

The purpose of the present paper is twofold. First, we report n.m.r. properties, observed on protons bound to polyisobutylene chains in solution, to investigate the cross-over transition from the dilute to the semi-dilute regime. It will be shown below that coil overlap can be observed only when chain segment motions are perceived as non-isotropic ones from n.m.r. This corresponds to relatively high chain concentrations.

The present paper aims at gathering already reported and new results to elaborate a simple and general description of n.m.r. properties of polyisobutylene chains in solution. The qualitative level of discussion is sufficient to picture motions in polymer–solvent systems as they are observed from n.m.r. On the other hand, the present paper develops an attempt to apply n.m.r. properties to the study of a practical problem: the evaluation of chain dimensions in dilute solution.

### *Chain dimensions*

It is well known that a flexible polymer chain in solution form a coil which is not a rigid sphere and which can be characterized by several types of mean dimensions[1]. The radius of gyration, $\langle (R_G^0)^2\rangle^{1/2}$, obtained from elastic scattering radiation measurements (light, neutron, X-rays) and defined as the root of the mean-square distance of a chain element from the centre of mass is currently used to evaluate a coil size: $\langle (R_G^0)^2\rangle \propto N^{2\nu}$ ($N$, the number of chain elements); the critical exponent $\nu$ is equal to 0.588[2]. The mean square end-to-end distance, $\langle (R_F^0)^2\rangle$, also gives a coil dimension evaluation: $\langle (R_F^0)^2\rangle = \epsilon \langle (R_G^0)^2 \rangle$ ($\epsilon = 6$ or 7 for a theta or a good solvent, respectively). Chain dimensions determined from $\langle (R_G^0)^2\rangle$ correspond to an average over all instantaneous configurations of all chains in solutions. This static average does not involve any time dependence of fluctuations.

The hydrodynamic radius, $R_H$, obtained from the self-diffusion coefficient of the coil, determines its ability to move in a solvent. The equivalent hydrodynamic sphere fluctuates in position as if it were being driven by a stochastic force $f(t)$ such that the average $\langle f(t_1)\, f(t_2)\rangle$ is equal to $\delta(t_2 - t_1)\, 6\pi\eta_0 kT R_H$ ($\eta_0$, the solvent viscosity). The dynamic dimension, $R_H$, can be expressed from $\langle R_G^0)^2\rangle^{1/2}$; clearly, this expression strongly depends upon the model used to describe frictional properties of a chain in solution. Very recently, Des Cloizeaux demonstrated the inequality $R_H > B\, \langle (R_G^0)^2\rangle^{1/2}$ ($B = 0.265$ for a theta solvent, Large $N$)[3].

The definition of coil dimensions directly governs the determination of the overlap concentration of chains $C^*$. This is a practical problem which may be encountered in bio-polymer physics, too. The overlap concentration is also related to the cross-over line $C^*(T)$ from the dilute to the semi-dilute regime[4]. The cross-over concept results from the most recent descriptions of polymer chains in solutions. The configurational partition function of these systems and the correlation function of a magnetic system made of spins with nearest neighbour interaction have been shown to be related through a Laplace transform[5]. This analogy has been widely developed by Des Cloizeaux[6], Daoud and Jannink[4]. It gives an elegant description of scaling properties induced by concentration or chain length variations. This description is based on a virtual partition of the chain into blobs[7]. It is now well established from neutron scattering experiments that the pair correlation function of monomer units $i$ and $j$ exhibits a gaussian character when $|j - i| = n < n_c$ with $n_c = \tau^{-2}$ and $\tau = (T - \theta)\theta^{-1}$ ($\theta$, the theta temperature of the

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polymer–solvent system)[7]. A correlation length $\xi$ may be defined from $n_c$: $\xi^2 = n_c l^2$, with $l$, the length of flexibility. The pair correlation function exhibits an excluded volume character when $i$ and $j$ are such that $|j - i| > n_c$; then, the radius of gyration of the whole chain is written as:

$$\langle (R_G^0)^2 \rangle = (N/n_c)^{2\nu}\xi^2/7 = N^{2\nu} l^2 \tau^{2q}/7 \qquad (1)$$

$q = 2\nu - 1$; $\xi$ may be considered as defining a space volume ($\simeq \xi^3$) or a blob within which chain segments behave specifically.

*Concentration effects*

The blob picture is also involved in the description of semi-dilute chain solution properties. However, excluded volume effects are now observed between $i$ and $j$ monomer unit pairs when $|j - i| < n_c$; the correlation length and $n_c$ are connected with each other by the relation:

$$\xi^2 = n_c^{2\nu} l^2 \tau^{2q}$$

they both depend upon the concentration, $C$, from the definition:

$$C = 3n_c(7)^{3/2}/(4\pi\xi^3);$$

$\xi$ only depends on chain concentration; it is independent of chain length. A gaussian character is observed on the mean square end-to-end distance of the whole chain[7]:

$$\langle (R_G[C])^2 \rangle = (N/n_c)\xi^2/X$$

or

$$\langle (R_G[C])^2 \rangle = [3(7)^{3/2}/4\pi]^{-\beta} \quad N(\tau^q l)^{(1-2\nu)^{-1}\beta} C^\beta/X$$

with

$$X^{-1} = 6^{-1} + [(2\nu + 1)^{-1} - 2^{-1}]x^2 + (3^{-1} - (2\nu + 2)^{-1}]x^3$$

and

$$x = n_c/N; \beta = (1 - 2\nu)(3\nu - 1)^{-1}$$

As was emphasized in reference 7 a given chain must not be considered as a succession of blobs; these do not represent any space volume of infinite life times like beads; they only define a virtual partition of the chain. The blob concept has also been used as a convenient tool to describe collective motions of chain segments[8]. The ideal cross-over line is defined at the concentration $C^*(T)$ such that $\langle [R_G(C^*)]^2 \rangle = \langle (R_G^0)^2 \rangle$ i.e.

$$C^*(T) = (3N/4\pi)\langle (R_G^0)^2 \rangle^{-3/2} \qquad (2)$$

However, even from a theoretical point of view the cross-over cannot be described as a sharp transition induced by concentration variations. It must be rather considered as a smooth evolution of thermodynamic variables[9]. This property is well illustrated by neutron scattering experiments performed on polystyrene chains[10]. The radius of gyration was found to decrease slowly as a chain concentration function from the dilute to the semi-dilute regime. From an experimental point of view, polymer coils cannot be considered as rigid spheres of radius $\langle (R_G^0)^2 \rangle^{1/2}$. Experimental techniques used to observe coil overlap will be more or less sensitive to the contact observed for a given time interval and established between a given fraction of a polymer chain and elements of other chains. Therefore, the coil overlap concentration will depend upon the experimental procedure used to determine it. U.v. spectroscopy measurements have been recently proposed to estimate the $C^*$ ($T$) concentration of polyoxyethylene in water, polystyrene in chloroform and polyvinylacetate in acetonitrile[11].

It will be shown below that it is convenient to express the ratio $\sigma = \langle [R_G(C)]^2 \rangle / \langle (R_G^0)^2 \rangle$ as a function of the ideal cross-over concentration C* ($T$)

$$\sigma = 7(C^*/C)^{1/4}/X = 7[3(7)^{3/2}/4\pi]^\beta N^{1-2\nu}\tau^{3\beta} C^\beta/X$$

also, whatever the virtual partition of a chain it may be of interest to know the number $P_b$ of blobs necessary to account for the value of its radius of gyration:

$$P_b = (C/C^*)^{5/4} = (X\sigma/7)^{-5}$$

It will be shown that chain segment motions are perceived as non-isotropic ones on a given time scale (nuclear magnetic relaxation time) when the number of blobs per chain $P_b$ gets higher than about 15.

*Transverse magnetic relaxation*

Polyisobutylene solutions have been widely studied from n.m.r. measurements performed on protons bound to chains[12–18]. Two striking features characterize properties of the transverse magnetic correlation function observed on concentrated chain solutions, from high resolution spectroscopy.

(i) Proton spectra exhibit a strong narrowing effect induced by sample rotation about an axis perpendicular to the steady magnetic field direction. This effect observed on linewidths of about 100 Hz cannot be confused with simple reduction of field inhomogeneities. It has been interpreted as resulting from constraints exerted on chain segments because of entanglements. The relaxation time of these constraints is called $T_\rho$. Segment motions are supposed to average tensorial nuclear spin hamiltonians, $\mathscr{H}_T$, to zero, only when this average is observed on a time scale longer than $T_\rho$: $\overline{\mathscr{H}_T} = 0$ $\overline{\mathscr{H}_T^2} \neq 0$. It is well known that the motional narrowing effect occurs when $(\overline{\mathscr{H}_T^2})^{1/2} T_\rho \ll 1$. Otherwise, the relaxation time of the transverse magnetization is determined from $(\overline{\mathscr{H}_T^2})^{1/2}$ and segment motions are perceived as non isotropic ones from n.m.r. More details about this description will be given below.

(ii) The inverse of the linewidth, $\Delta^{-1}$, obeys a linear dependence upon the ratio of molar fractions, $\gamma = \nu_1(1 - \nu_1)^{-1}$ ($\nu_1$ is the solvent molar fraction).

These two properties have been well established at several temperatures using three types of solvents: carbon disulphide) toluene ($C_7D_8$) and chloroform ($CDCl_3$). They are independent of the presence of nuclear spins on solvent molecules and can be considered as reflecting specific physical properties of polymer–solvent systems. No narrowing effect can be observed on dilute chain solutions or on short chains in molten polymers.

## POLYISOBUTYLENE RADIUS OF GYRATION. DISCUSSION

Polyisobutylene is currently considered as a material free from complications arising from chain branching. The simple structure of its monomer unit ($CH_2{-}C(CH_3)_2{-}$) eliminates problems of tacticity and cis-trans isomerism. Chain dimensions have been determined in various types of solvents, including theta solvents[19]. Writing the unperturbed dimensions of a chain as:

$$\langle (R_G^0)^2 \rangle_\theta = N l_0^2/6$$

$l_0$ is defined as the statistical flexibility length; it can be calculated from light scattering measurements performed on PIB-benzene solutions at 297 K, for example: $l_0 = 5.9$ Å; this value holds over the molecular weight range $4 \times 10^4$ to $3 \times 10^6$.

More recently, statistical radii of gyration of sharp fractions ($\bar{M}_w/\bar{M}_n \simeq 1.1$) of PIB, covering a wide range of molecular weight (from $1.6 \times 10^5$ to $4.7 \times 10^6$) have been determined in isoamyl isovalerate (IAIV) by light-scattering measurement[20]; IAIV is a theta solvent at 295.1 K; $l_o$ is found to be equal to 5.6 Å. More generally, the molecular weight dependence of the radius of gyration has been found to be represented by:

$$\langle (R_G^0)^2 \rangle_\theta = 9.5 \times 10^{-2} \bar{M}_w \qquad (3)$$

$R_G^0$ in square angströms.

Carbon disulphide is a very convenient solvent to observe n.m.r. chain properties because its molecule does not bear any nuclear spins (except $C^{13}$ nuclei in natural abundance). However, to our knowledge, no light scattering measurements have been performed on polyisobutylene–carbon disulphide systems, until now. Experimental difficulties arise from the risk to explode samples by centrifuging them. Therefore, chain dimensions must be evaluated indirectly from intrinsic viscosity measurements, using the well known empirical formula:

$$[\eta] = K M^{1/2} \alpha_\eta^3$$

$\alpha_\eta$, the molecular factor expansion may be calculated knowing $K$, a constant which should be independent of the solvent, in first approximation at least. The constant $K$ may be evaluated from intrinsic viscosity measurements reported about other solvents; from reference 20 $K = 11.4 \times 10^{-4}$ in IAIV at 295.1 K ($\alpha_\eta = 1$) while in Reference 1 $K$ was found to be equal to 10.7 in Benzene at 297 K ($\alpha_\eta = 1$). The factor expansion $\alpha_\eta$ defined from viscosity measurements is theoretically different from that $\alpha_s$ derived from light scattering measurements. By definition, the molecular weight dependence of $\alpha_s$ at a given temperature must be written as:

$$\alpha_s \propto M^\nu M^{-1/2} = M^{0.088}$$

Light scattering measurements reported in reference 20 lead actually to $\alpha_s = 0.43\, \bar{M}_w^{0.085}$ for PIB solutions in n-heptane and $\alpha_s = 0.51\, \bar{M}_w^{0.085}$ in cyclo-hexane at 298 K ($1.6 \times 10^5 < \bar{M}_w < 4.7 \times 10^6$). Experimental and theoretical exponents are in reasonable agreement with each other. On the other hand, the intrinsic viscosity of dilute polymer solutions has been very recently predicted to vary as[21]:

$$[\eta] \propto M^{0.74}$$

accordingly, $\alpha_\eta = ([\eta]/[\eta]_\theta)^{1/3}$, should vary as $\alpha_\eta = M^{0.080}$. Therefore $\alpha_s/\alpha_\eta \propto M^{0.008}$ at constant temperature; this ratio becomes significantly different from one at high $M$ values, only ($\alpha_s/\alpha_\eta = 1.08$ for $N = 2 \times 10^4$). Considering intrinsic viscosity measurements reported in reference 20, it is found that:

$\alpha_\eta = 0.47\, \bar{M}_w^{0.087}$ in cyclohexane at 298 K, in agreement with results reported in reference 1 ($1.60 \times 10^5 < \bar{M}_w < 4.7 \times 10^6$). However, it must be noticed that n-heptane solutions exhibit a slightly different molecular weight dependence:

$$\alpha_\eta = 0.52\, \bar{M}_w^{0.07}$$

From the above discussion, we shall consider that $\alpha_s \simeq \alpha_\eta$ to a good approximation and that $\alpha_s$ is proportional to $N^{0.088}$ to compare factor expansions corresponding to different chain lengths, at a given temperature.

## EXPERIMENTAL SECTION

Polyisobutylene samples (Vistanex MML 80, $\bar{M}_v = 9.9 \times 10^5$) were kindly furnished by Dr T. Kantor of BASF Company (France). They were fractionated in the Laboratoire de Chimie des Polymères (I. N. P. Grenoble). Two samples of average molecular weight $\bar{M}_v = 9.9 \times 10^5$ and $2.2 \times 10^5$ were selected. The carbon disulphide, from Merck, was over 99.9% pure (reference Uvasol 2210). Spin–lattice relaxation times were obtained by plotting, the free induction decay magnitude following a $\pi,\pi/2$ pulse sequence; $T_1$ was calculated from a least square fit method. Spin–spin relaxation times were measured from the spin-echo method ($\pi/2$, $\pi$ pulse sequence). The free induction decay magnitude was measured at the output of a Boxar integrator to improve the signal to noise ratio. The relative uncertainty about relaxation times was estimated to be ±4%.

## VOLUME – CONCENTRATION DEPENDENCE OF SOLUTIONS. DISCUSSION

The convenient thermodynamic variable used to describe n.m.r. properties observed on chain solutions is the ratio of molar fractions $\gamma = \nu_1(1 - \nu_1)^{-1}$. However, to determine chain dimensions, solution volume must be known as a $\gamma$ function. Fortunately, n.m.r. experiments are performed on calibrated sample tubes. The height of solution corresponding to a standard weight (one gram) of polymer is easily measured for any $\gamma$ value. Considering the PIB–$CS_2$ system, the volume variation $V$ has been shown with great accuracy to be a linear function of $\gamma$ over a wide range of concentrations[15] ($0 < \gamma < 40$); for one gram of polymer:

$$V = a\sigma + b\sigma\gamma$$

$\sigma = \pi d^2/4$, $d$ the diameter of calibrated sample tubes; $a$ and $b$ are experimentally determined. The specific volume of solution may be written as:

$$\pi = V \nu_p$$

$\nu_p$ is the weight fraction of monomer unit: $\nu_p = (1 + \gamma M_s/M_p)^{-1}$ ($M_s$ and $M_p$ are molecular weights of the solvent

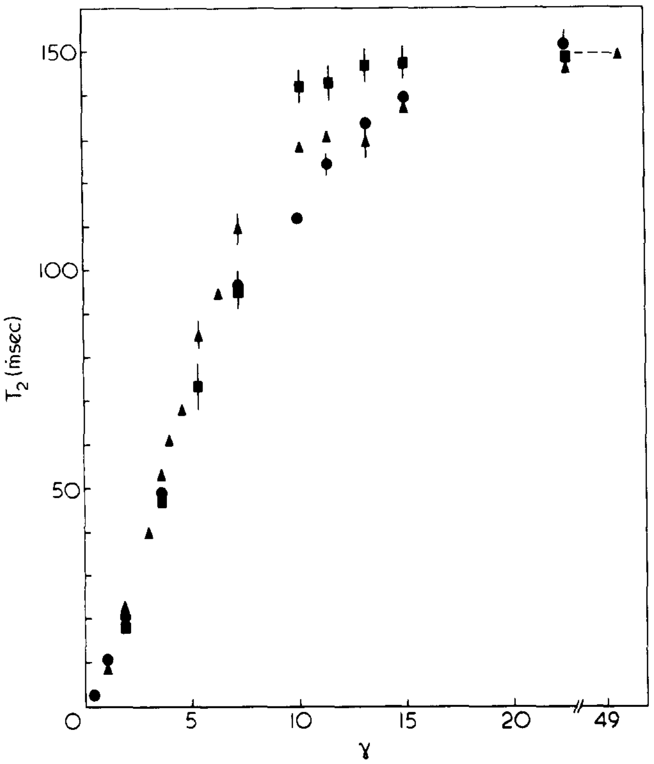

*Figure 1* Spin–spin relaxation time variations as a $\gamma$ function at room temperature (293 K). ●, 10 MHz; ▲, 32 MHz; ■, 61 MHz (Chain molecular weight $M_v = 9.9 \times 10^5$)

and the monomer unit, respectively):

$$\pi = a\sigma v_p + b\sigma v_s M_p/M_s$$

$v_s = 1 - v_p$. The partial specific volume of solvent is $\omega_s = b\sigma M_p/M_s$; that of a monomer unit is $\omega_p = a\sigma$; $\gamma = v_s M_p/v_p M_s$ and $a/b = \omega_p M_p/\omega_s M_s$. To the ratio of molar fractions $\gamma$, corresponds the concentration $C$, of monomer units by unit volume:

$$C = Av_p(M_p\pi)^{-1} = A(M_s\omega_s)^{-1}(\gamma + a/b)^{-1}$$

and

$$C' = M_pC/A \text{ (weight per unit volume).}$$

$A$ is the Avogadro number; the concentration, $C$, only depends upon the ratio $a/b \simeq 1{\cdot}01$ at room temperature; this $a/b$ value is in agreement with that calculated from specific volumes of pure polymer and solvent. Therefore, it is not necessary to know absolute values of the constants $a\sigma$ and $b\sigma$; their ratio is determined from a very simple experimental procedure. Variations of $a/b$ were found to be negligible between 220 and 300 K. At any given $\gamma$ value, the volume of solution per chain is:

$$v = M(M_pC)^{-1} = A^{-1}M(M_p/M_s)(\gamma + a/b)\omega_s$$

To the radius of gyration $\langle(R_G^0)^2\rangle^{1/2}$ corresponds an ideal cross-over concentration calculated from equation (2):

$$C^* = A\,[M_s\omega_s(\gamma^* + a/b)]^{-1}$$

or

$$\gamma^* = -a/b + 2.52M_p\langle[R_G^0]^2\rangle^{3/2}(MM_s\omega_s)^{-1} \qquad (4)$$

[$\langle(R_G^0)\rangle^{1/2}$, in angströms].

Considering only unperturbed dimensions of PIB chains and using formula (3), a cross-over value $\gamma_u^*$ can be defined in $CS_2$ as a molecular weight function as:

$$\gamma_u^* = -a/b + 6.85 \times 10^{-2}(M)^{1/2}$$

For PIB chains $\gamma_u^* = 67$ and $C_u^* = 13.6$ mg/cm$^3$. The molecular factor expansion $\alpha_s$ must be taken into account to calculate the ideal cross-over value: $\gamma^* \simeq \alpha_s^3\gamma_u^*$; $\gamma_u^*$ values obtained from the above formula only apply to very sharp polyisobutylene fractions in $CS_2$. This formula rapidly gives a useful rough estimate of ideal overlap concentrations in this solvent.

## N.M.R. PROPERTIES OF PIB-$CS_2$ SOLUTIONS

Variations of the spin–spin relaxation time, $T_2$ observed at room temperature are represented as a $\gamma$ function, in *Figure 1*; they correspond to a chain molecular weight $\bar{M}_v = 9.9 \times 10^5$. Three concentration ranges are clearly perceived. At solvent concentrations lower than $\gamma = 7$, the relaxation time, $T_2$, exhibits a linear dependence upon $\gamma$. At solvent concentrations higher than $\gamma \simeq 20$, variations of $T_2$ observed until $\gamma = 49$ are negligible within experimental uncertainty; it will be considered that there is a plateau. A transition zone occurs between $\gamma \simeq 7$ and $\gamma \simeq 15$. This typical dependence of $T_2$ upon $\gamma$ is observed at 10, 32 and 61 MHz (*Figure 1*) and at temperatures lower than 300 K (*Figure 2*). It was also observed from the inverse of the linewidth measured from high resolution n.m.r. spectroscopy, without sample rotation[15]. However, this technique was not found to be accurate enough because it is very sensitive to field inhomogeneities in the transition zone, in the absence of sample rotation ($T_2 \simeq 170$ msec, i.e. the linewidth is less

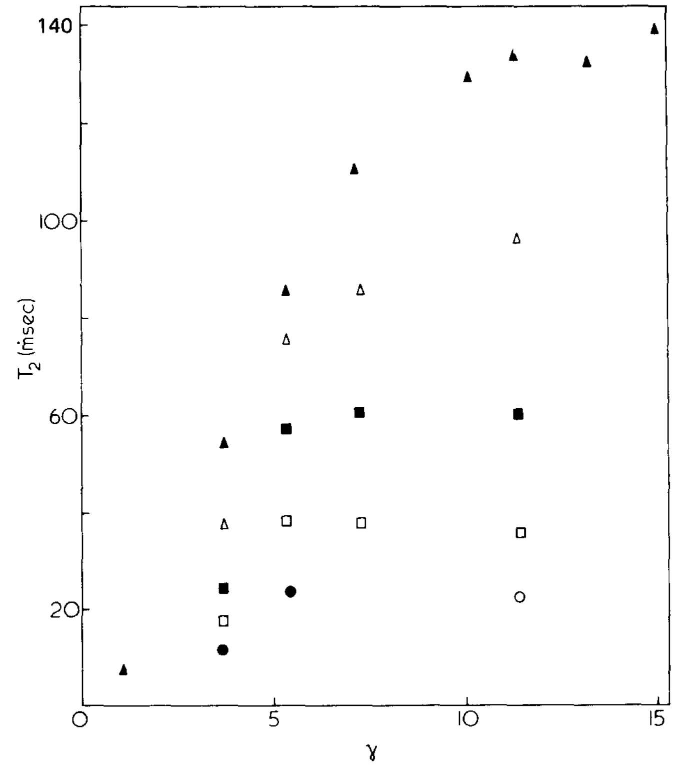

*Figure 2* Spin–spin relaxation time variations as a $\gamma$ function at several temperatures. ●, 253 K; □, 263 K; ■, 273 K; △, 283 K; ▲, 293 K

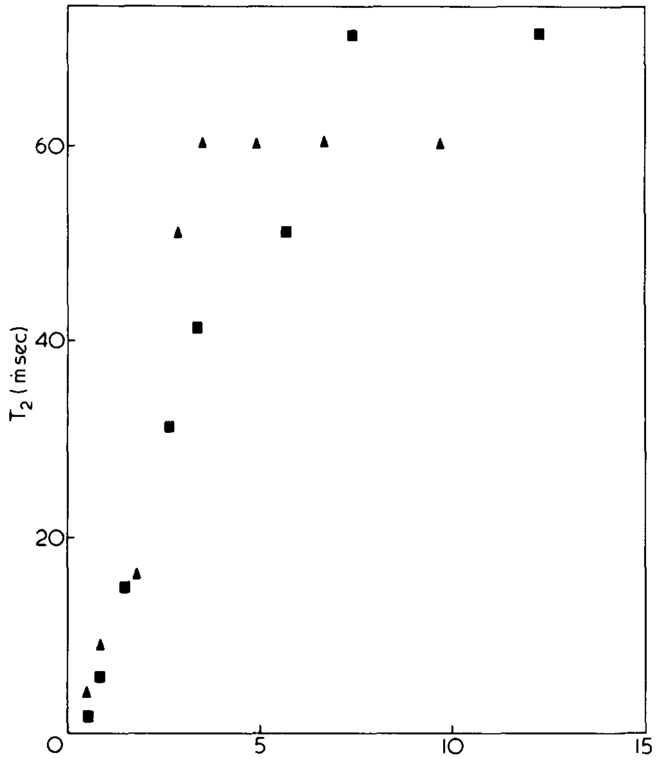

*Figure 3* Spin–spin relaxation time variations as a γ function reported from reference 13. Polyisobutylene chains are in $CCl_4$ solutions at 298 K (■) and $C_6D_6$ solution at 303 K (▲) ($M_v$ = 1.13 × $10^6$)

than one hertz); it is the reason why spin–spin relaxation times are reported in the present paper. The typical behaviour of $T_2$ can also be illustrated from measurements reported by Slichter and Davis[13]; they studied PIB chains in solution in $CCl_4$ or in $C_6D_6$ ($\bar{M}_v$ = 11.3 × $10^5$). These measurements are plotted in *Figure 3* after reference 13.

It may be noticed from *Figure 2* that the transition zone is shifted towards low γ values (more concentrated chain solutions) when the temperature is lowered or when the chain length is decreased (*Figure 4*). This feature will be shown below to be qualitatively associated with the decrease of chain dimensions

$\langle[R_G(c)]^2\rangle \propto N_\tau^{1/4}$, induced by lowering $N$ or $\tau$.

The concentration ranges defined above will now be characterized with more details.

## *The plateau zone: high frequency isotropic motions*

The plateau zone can be characterized by the general features following.

(i) The spin–lattice relaxation time, $T_1$ (170 msec) observed on high molecular weight chains ($\bar{M}_v$ = 9.9 × $10^5$) is slightly longer than the relaxation time $T_2$ (150 msec), *Figure 5a.*

(ii) $T_2^{-1}$ relaxation rates observed at 10, 32 and 61 MHz are equal to each other at room temperature, *Figure 1*; $T_1^{-1}$ rates measured at 10 and 32 MHz are also equal to each other, within the plateau zone, (*Figure 5, a, c).*

(iii) Relaxation rates observed on polymer chains of lower molecular weight (2.2 × $10^5$) are not very sensitive to chain length variations, at room temperature (*Figure 5a,c*). Slichter and Davis have also reported that $T_2$ approaches a limit upon dilution in a given solvent ($CCl_4$) and that this limit is independent of molecular weight ($\bar{M}_v > 7 \times 10^3$).

(iv) No spectrum narrowing effect can be perceived.

The above features indicate that relaxation rates $T_1^{-1}$ and $T_2^{-1}$ ($T_1^{-1} \lesssim T_2^{-1}$) must both depend upon a single dominant relaxation mechanism described within the extreme narrowing approximation (they are Larmor frequency independent). This mechanism must reflect isotropic motions at frequencies higher than the Larmor frequency ($\simeq 10^8$ rad. $sec^{-1}$). Several attempts to describe relaxation processes observed on dilute chain solutions have been proposed[22,23]. They were based on the description of local monomer unit motions (semi rotations) and strongly depend upon the considered model. It is not the purpose of the present paper to improve such descriptions; it must only be noticed that when the temperature is decreased the plateau is lowered; in the small temperature range (50 K) which was considered the spin–spin relaxation time was found to vary according to a Arrhenius law; the activation energy is $E_a \simeq (6.8 \pm 0.5)$ kcal.$mole^{-1}$ (*Figure 6*). Such an activation energy may characterize local monomer unit motions[22]

On the other hand, it must be noticed that chain molecular weights $\bar{M}_v$ = 11.3 × $10^5$, 9.9 × $10^5$ and 2.2 × $10^5$ correspond to $\gamma_\theta^*$ = 72, 67 and 36, respectively. Clearly, the plateau zone describes semi-dilute solution properties. Therefore, in this concentration range, chain overlap does not hinder monomer unit motions strongly enough to induce non-isotropic diffusion. Concentrations higher than γ = 49 (γ = 10 in reference 13) have not been yet studied for reasons of n.m.r. sensitivity.

## *The linear zone*

In the linear zone spin–spin and spin–lattice relaxation rates take values very different from each other (*Figures 3, 4 and 5 a, b, c*). Several striking features must be noticed to characterize this concentration range.

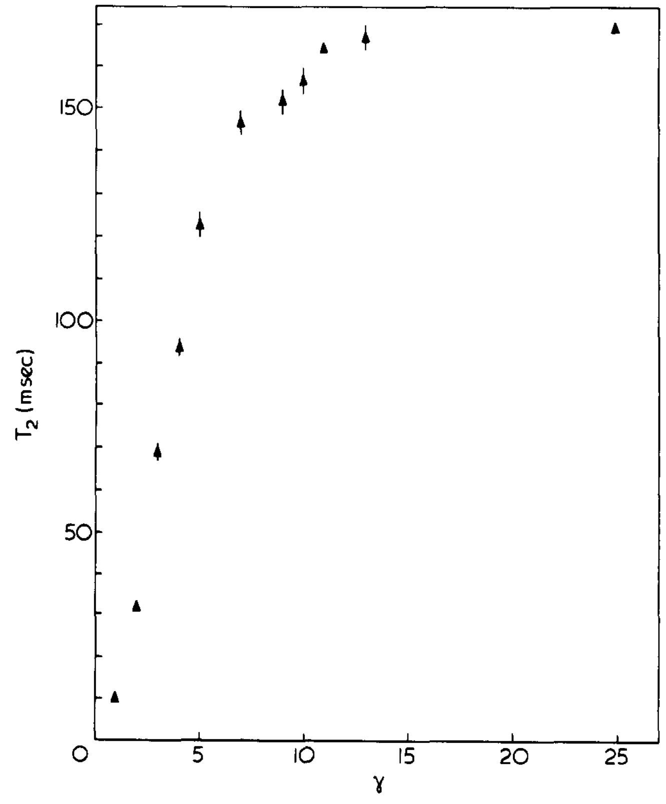

*Figure 4* Spin–spin relaxation time variations as a γ function at room temperature (297 K) at 32 MHz ($M_v$ = 2.2 × $10^5$)

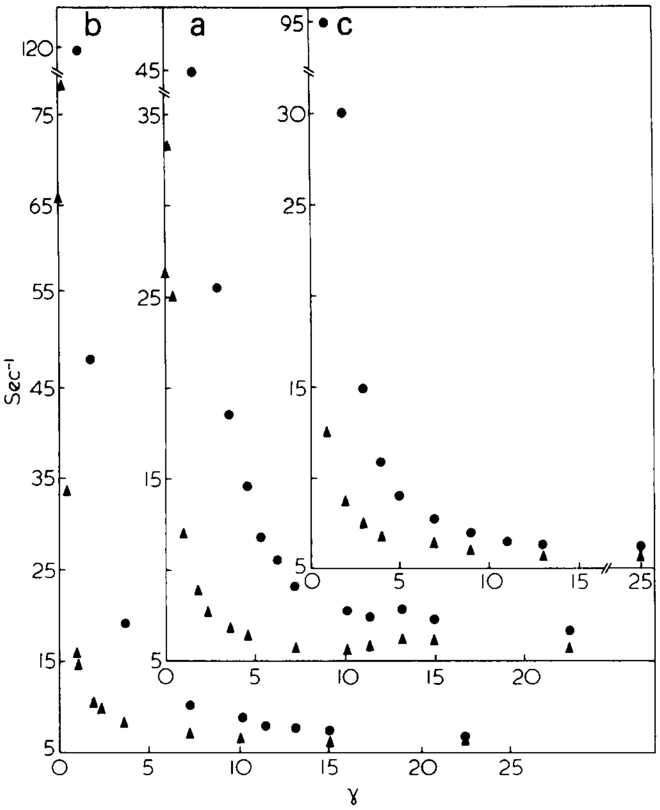

*Figure 5* (a) Spin–lattice and spin–spin relaxation rates as a $\gamma$ function observed at room temperature (293 K) at 32 MHz ($M_v$ = 9.9 X $10^5$). $T_2^{-1}$ (●) and $T_1^{-1}$ (▲) (b) Spin–lattice and spin–spin relaxation rates as a $\gamma$ function observed at room temperature at 10 MHz ($M_v$ = 9.9 X $10^5$). $T_2^{-1}$ (●) and $T_1^{-1}$ (▲) (c) Spin–lattice and spin–spin relaxation rates as a $\gamma$ function observed at room temperature at 32 MHz ($M_v$ = 2.2 X $10^5$). $T_2^{-1}$ (●) and $T_1^{-1}$ (▲)

*High frequency non-isotropic motion.*

(i) Spin–lattice relaxation rates observed on high molecular weight polyisobutylene chains ($\bar{M}_v \simeq 10^6$) in $C_6D_6$ and $CCl_4$ at 50 MHz[13] and in $CS_2$ and $CDCl_3$ at 32 MHz[17] are not very sensitive to the nature of solvent at room temperature. On the other hand they strongly depend upon the Larmor frequency.

(ii) Relaxation rates, $T_1^{-1}$, measured on chains of two different molecular weights in solution in $CDCl_3$ or $CS_2$ are not sensitive to chain length[17] (*Figure 5c*).

(iii) Spin–lattice relaxation rates are found to exhibit a maximum value at a concentration $\gamma$ depending upon the Larmor frequency, $\omega_0$: $\gamma$ = 0.33 and 0.2 at 32 and 10 MHz respectively.

These three characteristic properties lead us to assume that the spin–lattice relaxation process still reflects high frequency motions similar to those characterizing the plateau zone. Spectral densities describing these motions have been recently studied, using different concentrations, temperatures and Larmor frequencies. Within a reasonable accuracy they have been shown to be homogeneous functions of the Larmor frequency and a single correlation time of motion, characterized by a shift factor which depends upon polymer concentration.

For the purpose of the present paper we need only note that high frequency motions ($\simeq 10^7$ Hz) undoubtedly occur in concentrated solutions. This result must now be associated with the very contrasted properties of the spin–spin relaxation rates.

*Low frequency isotropic motions.*

(i) Spin–spin relaxation rates are sensitive to the nature of solvent. For example, the linewidths observed at room temperature, on PIB–$CS_2$, PIB–$CDCl_3$ and PIB–$C_7D_8$ systems are 18, 14 and 10 Hz, respectively. The same inequalities between linewidths hold at any temperature and concentration[15].

(ii) Relaxation rates are very sensitive to chain length (*Figure 1, 4*).

(iii) A strong spectrum narrowing effect is observed on resonance lines[15].

The last above property clearly indicates that although monomer units undergo motions fast enough to induce a motional narrowing effect, tensorial energies, $\mathscr{H}_T$, of the

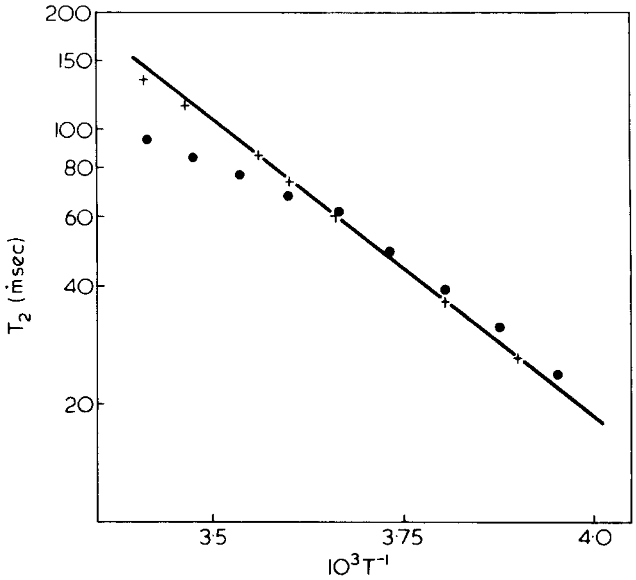

*Figure 6* Arrhenius plot of the spin–spin relaxation time as a temperature function at 32 MHz. (●) $\gamma$ = 5.35; (+) = 11.4 ($M_v$ = 9.9 X $10^5$)

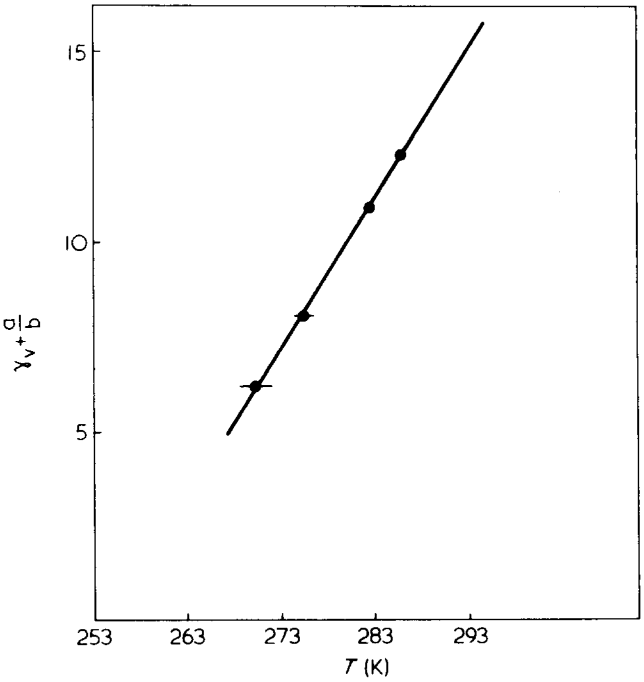

*Figure 7* $\gamma_v$ variations as a temperature function ($M_v$ = 9.9 X $10^5$)

nuclear spin system are not averaged to zero during n.m.r. observations: $|\mathscr{H}_T| \simeq 10^5$ rad. sec$^{-1}$ as in any solid. However, the order of magnitude of observed linewidths ($\simeq 50$ Hz) shows that there is at least a partial average of $\mathscr{H}_T$ :$\langle\mathscr{H}_T\rangle_1 \neq 0$. Therefore a two-step motional narrowing process is supposed to occur. In the first step high frequency motions such that rotations of $CH_3$– groups about their own axis, semi-rotations of $CH_2$–groups induce a spin–lattice relaxation rate which can be generally expressed as:

$$(T_1^{-1})_1 = \langle(\mathscr{H}_T - \langle\mathscr{H}_T\rangle_1)^2\rangle_1 g_1(\omega_0)$$

$g_1(\omega_0)$ is a function of spectral densities describing high frequency motions. $\langle\mathscr{H}_T\rangle_1$ is supposed to be different from zero because of slight constraints exerted on chain segments inducing non-isotropic rotations of $CH_3$ group axis, for example. A second average is now supposed to occur corresponding to isotropic relaxation of constraints exerted on chain segments. In other words, the partial average $\langle\mathscr{H}_T\rangle_1$ is a time function, its time average is zero:

$$\langle\langle\mathscr{H}_T\rangle_1\rangle_2 = 0$$

The relaxation time, $T_\rho$, of constraints characterize the time variation of $\langle\mathscr{H}_T\rangle_1$. The second step of the motional narrowing process occurs in the only case where $|\langle\mathscr{H}_T\rangle_1|$ and $T_\rho$ obey the inequality:

$$|\langle\mathscr{H}_T\rangle_1| T_\rho \ll 1$$

When $|\langle\mathscr{H}_T\rangle_1|_2 T_\rho \ll 1$, monomer unit motions are perceived as non-isotropic ones and $\langle(\langle\mathscr{H}_T\rangle_1)^2\rangle_2$ determines the spin–spin relaxation rate, as in solid samples. This mechanism of relaxation has been already called a pseudo-solid effect; a specific spin echo technique has been proposed to observe it directly[24]. There is actually another contribution added to this line broadening mechanism and depending upon non-isotropic high frequency motions:

$$(T_2)_1^{-1} = \langle(\mathscr{H}_T - \langle\mathscr{H}_T\rangle_1)^2\rangle_1 g_2(\omega_0)$$

$g_2(\omega_0)$ is a function of spectral densities describing high frequency motions.

The relative weight of these two contributions can be determined from a spectrum narrowing effect. This effect has been theoretically and experimentally described, recently[25,26] When the linewidth is exactly divided by two upon sample rotation, it can be considered that the non-zero average tensorial spin energy entirely governs the spin–spin relaxation process. Such a property is well observed in the linear zone. Therefore, in this concentration range the first average $\langle\mathscr{H}_T\rangle_1$ decreases upon solvent addition. The relaxation time $T_\rho$ of constraints is also probably a decreasing $\gamma$ function like the disentanglement time[8] $T_r \propto C_p^{3/2}N^3$.

### *The transition zone*

The transition zone corresponds to a smooth evolution of the spin–spin relaxation time towards the plateau regime.

In the transition zone, the linewidth is reduced upon sample rotation by a factor giving from about two ($\gamma \simeq 7$) to about one ($\gamma \approx 16$). It is concluded that both types of mechanisms are involved in the line broadening: high frequency non-isotropic motions and the pseudo-solid term $\langle(\langle\mathscr{H}_T\rangle_1)^2\rangle_2$. But the relative weight of the pseudo-solid contribution goes to zero when the plateau zone is reached; or, more precisely, this contribution decreases and becomes insensitive to sample rotation effects. This may occur either because $\langle\mathscr{H}_T\rangle_1$ goes to zero or because the relaxation time $T_\rho$ shortens enough to permit a second step motional narrowing process leading to the contribution:

$$(T_2)_2^{-1} = \langle(\langle\mathscr{H}_T\rangle_1)^2\rangle_2 G_2(\omega_0);$$

$G_2(\omega_0)$ is a function of spectral densities describing constraint relaxation i.e. low frequency isotropic motions. The above contribution might perhaps account for the slight difference between the spin–lattice and the spin–spin relaxation rates measured with the plateau zone. The slight frequency dependence observed within the transition zone is induced by the contribution of non-isotropic high frequency motions, $(T_2)_1^{-1}$.

Details about n.m.r. formalism supporting the above description are given in references 25 and 26.

## COIL OVERLAP AS PERCEIVED FROM N.M.R.

Whatever the exact contribution of $\langle|\langle\mathscr{H}_T\rangle_1|^2\rangle_2^{1/2}$ or $\langle|\langle\mathscr{H}_T\rangle_1|^2\rangle_2 G_2(\omega_0)$ to the spin–spin relaxation mechanism it is considered that coil overlap is perceived from n.m.r. as soon as the spin–spin relaxation rate measured at constant temperature as a concentration function is found to exhibit a deviation from the plateau value; the corresponding ratio of molar fractions will be called $\gamma_\nu$. Another experimental procedure may be used by determining $\gamma_\nu$ at constant concentration; $\gamma_\nu$ is located at the observed deviation from the Arrhenius plot of the spin–spin relaxation time. $\gamma_\nu$ values obtained from PIB–$CS_2$ systems at room temperature are $18 \pm 2$ ($\bar{M}_\nu = 9.9 \times 10^5$) and $10 \pm 1$ ($\bar{M}_\nu = 2.2 \times 10^5$); $\gamma_\nu$ values derived from measurements reported in reference 13 are $6.5 \pm 1$ in $CCl_4$ and $3.2 \pm 0.4$ in $C_6D_6$ at room temperature ($\bar{M}_\nu = 11.3 \times 10^5$).

It may be of interest to compare $\gamma_\nu$ values obtained from n.m.r. measurements to the ideal values $\gamma^*$ calculated from measured chain dimensions in the same solvent. More precisely, we consider the ratio:

$$\sigma = 7(\gamma_\nu + a/b)^{1/4}(\gamma^* + a/b)^{-1/4}/X,$$

which is also theoretically equal to:

$$\langle[R_G(c)]^2\rangle/\langle(R_G^0)^2\rangle$$

For PIB chains, $\gamma^* + a/b$ is expressed as:

$$\gamma^* + a/b = 4.13\bar{M}_\nu^{1/2}\alpha_s^3/(M_s\omega_s)$$

When PIB chains are observed in $CS_2$ solvent, at room temperature ($\omega_s = 0.80$ cm$^3$ g$^{-1}$, $a/b = 0.88$):

$$\gamma^* + a/b = 0.068M_\nu^{-1/2}\alpha_s^3 = 0.068[\eta]/K$$

Intrinsic viscosity measurements performed on PIB–$CS_2$ systems at 300 K gave $[\eta] = 2.10$ and 0.70 dl g$^{-1}$ for $\bar{M}_\nu = 9.9 \times 10^5$ and $2.2 \times 10^5$ respectively. Therefore, $\sigma = 0.7$ and 0.80 for $\gamma_\nu = 19$ and 10, respectively. When PIB chains are observed in $C_6D_6$ solvent, at room temperature ($\omega_s = 1.14$ cm$^3$ g$^{-1}$, $a/b = 0.6$):

$$\gamma^* + a/b = 49.50\,\alpha_s^3$$

This solvent is of particular interest because the PIB–$C_6D_6$ system is known to have a theta temperature equal to 297K (chain of infinite length); therefore at 303 K the expansion factor may be considered as equal to one; unperturbed dimensions may be used. The $\gamma_\nu$ observed value ($\simeq 3.5$) is quite different from that observed in $CS_2$ ($\simeq 19$), nevertheless the $\sigma$ ratio is still found to have a value close to 0.6: $\sigma = 0.63$.

It must be emphasized that although $\gamma_\nu$ values observed in $CS_2$ and $C_6D_6$ are quite different from each other they all give the same approximate $\sigma$ value: $0.60 \pm 0.1$.

### *Uncertainty about $\sigma$*

It is not possible to consider that a general property about coil overlap perceived from n.m.r. has been established from the above few measurements. However, the ratio $\sigma$ is defined within a reasonable accuracy because of the 0.25 exponent appearing in its definition. Starting from:

$$\sigma = 7(\gamma_\nu + a/b)^{1/4}(\gamma^* + a/b)^{-1/4}/X$$

with

$$\gamma^* + a/b = 2.52 \frac{M_p}{M_s\bar{\omega}_s\bar{M}_\nu} \langle(R_G^0)^2\rangle_\theta^{3/2}\alpha_s^3$$

and

$$\langle(R_G^0)^2\rangle_\theta = \beta\bar{M}_\nu$$

the main uncertainty comes from $\beta$, $M_\nu$, $\alpha_s$ and $\gamma_\nu$; assuming that in the worst conditions $\Delta\beta/\beta = \Delta M_\nu/M_\nu = 0.1 = \Delta\gamma_\nu/\gamma_\nu = \Delta\alpha_s/\alpha_s$, the relative uncertainty about $\sigma$ is:

$$\Delta\sigma/\sigma = 0.15$$

It is believed that $\sigma = 0.70 \pm 0.1$ may be an empirical number measuring the degree of n.m.r. sensitivity to coil overlap of polyisobutylene chains. This number may be specific to a given polymer. It is worth noting that if $\sigma$ is supposed a constant number specific to a given polymer then the number of blobs $P_b = (x\sigma/7)^{-5}$ characterizing the virtual partition of a chain is also a constant number. In other words, the above results show that monomer unit motions become hindered enough to be perceived as non-isotropic ones when the virtual partition of a chain is about 15. On the other hand, the overlap concentration $C_\nu$ is about 8 times greater than the ideal overlap concentration $C^*$.

Temperature effects were explored over a small temperature range. Variations of $\gamma_\nu$ as a temperature function are plotted in *Figure 10*. If it is assumed that is a constant number independent of temperature, then $\gamma_\nu$ should vary as:

$$\gamma_\nu + a/b \propto (A/M_s\omega_s)[(T - 0)/0]^{3/5}$$

for a given chain length. The accuracy of our low temperature measurements was not high enough to demonstrate that $\gamma_\nu$ obeys the above relation; however the $\gamma_\nu$ decrease induced by lowering the temperature is well observed.

Finally, the coil overlap process has recently been studied from n.m.r. measurements performed on PEO chains in solution in $D_2O$[27]. Chain molecular weight ($\bar{M}_\nu \simeq 3.7 \times 10^5$) and $\gamma_\nu$ (110) were defined within a good accuracy; however, the radius of gyration, $R_G$, in $H_2O$, derived from viscosity measurements was known with a large uncertainty: (330 ± 50) Å; it may be easily shown from a logarithmic plot of data of reference 28 that the average end-to-end distance $\langle r^2\rangle^{1/2}$ depends on molecular weight according to the relation:

$$\langle r^2\rangle^{1/2} = M^\alpha$$

the $\alpha$ exponent has a satisfactory value: 3/5 whatever the model used to connect $\langle r^2\rangle^{1/2}$ with $[\eta]$; unfortunately absolute values of $\langle r^2\rangle^{1/2}$ strongly depend upon the considered model. Nevertheless, the $\sigma$ ratio calculated from $[\eta] = 2.96$ dl $g^{-1}$ and $\phi = 2.5 \times 10^{21}$ is found to be equal to: $0.73 \pm 0.15$ ($\phi$ is the universal constant used to describe intrinsic viscosity variations).

## CONCLUSION

Coil overlap of polyisobutylene chains in $CS_2$ was studied by observing the spin–spin and spin–lattice relaxation processes of protons bound to polymer chains. The cross-over from the dilute to the semi-dilute regime was investigated, considering a wide range of polymer concentrations. It was shown that coil overlap is observed from n.m.r. when chain segment motions are perceived as non-isotropic ones because of slow relaxation of isotropic chain constraints. This effect gives rise to a specific contribution to the spin–spin relaxation process. Coil overlap was found to occur at concentrations $C_\nu$ much higher than the ideal concentration $C^*$ calculated from measured radii of gyration. The theoretical ratio of mean square radii of gyration $\langle [R_G(C_\nu)]^2\rangle / \langle [R_G(C^*)]^2\rangle$ was shown to be equal to $0.7 \pm 0.1$ for different chain lengths and different solvents. It corresponds to a virtual partition of the chain into about 15 blobs.

It is suggested to extend the above study to other polymers using very sharp fractions and well defined temperatures to establish whether or not the above ratio is a number specific to a given polymer chain. If it can be shown that $\sigma$ is actually a constant within a reasonable accuracy then n.m.r. could be proposed as an experimental tool to characterize chain dimensions besides light scattering or viscosity measurements.

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## REFERENCES

1 Flory, P. J., 'Principles of Polymer Chemistry' Cornell University Press, New York (1966)
2 Le Guillou, J. C. and Zinn-Justin, J. *Phys. Rev. Lett.* 1977, **39**, 95
3 Des Cloizeaux, J. *J. Phys. (Paris) Lett.* 1978, **39**, L-151
4 Daoud, M. and Jannink, G. *J. Phys. (Paris)* 1976, **37**, 973
5 De Gennes, P. G. *Phys. Lett. (A)* 1972, **38**, 339
6 Des Cloizeaux, J. *J. Phys. (Paris)* 1975, **36**, 281
7 Farnoux, B. *et al. J. Phys. (Paris)* 1978, **39**, 77; Boots, H. and Deutch, J. M. *Macromolecules* 1977, **10**, 1163
8 De Gennes, P. G. *Macromolecules* 1976, **9**, 587
9 Cotton, J. P. *et al. J. Chem. Phys.* 1976, **65**, 1101
10 Daoud, M. *et al. Macromolecules* 1975, **8**, 804
11 Destor, C., Langevin, D. and Rondelez, F. *J. Polym. Sci., Polym. Lett. Edn.* 1978, **16**, 229
12 Powles, J. G. *Proc. Phys. Soc. (London)* 1956, **69B**, 281

13 Slichter, W. P. and Davis, D. D. *Macromolecules* 1968, **1**, 47
14 Anderson, J. E., Liu, K. J. and Ullman, R. *Discussions of the Faraday Soc.* 1970, **49**, 257
15 Cohen-Addad, J. P. and Roby, C. *J. Chem. Phys.* 1975, **63**, 3095
16 Cohen-Addad, J. P. and Roby, C. *Macromolecules* 1977, **10**, 738
17 Cohen-Addad, J. P. and Messa, J. P. *J. Phys. Lett. (Paris)* 1976, **37**, L-193
18 Jones, A. A., Lubianez, R. P., Hanson, M. A. and Shostak, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1685
19 Fox, T. G. Jr. and Flory, P. J. *J. Am. Chem. Soc.* 1951, **73**, 1909
20 Matsumoto, T., Nishioka, N. and Fujita, H. *J. Polym. Sci (A-2)* 1972, **10**, 23
21 Daoud, M. and Jannink, G. *J. Phys. (Paris)* 1978, **39**, 331
22 Jones, A. A. and Lubianez, R. P. *Macromolecules* 1978, **11**, 126
23 Valeur, B., Jarry, J. P., Geny, F. and Monnerie, L. *J. Polym. Sci. Polym. Phys. Edn* 1975, **13**, 675
24 Cohen-Addad, J. P. and Vogin, R. *Phys. Rev. Lett.* 1974, **33**, 940
25 Cohen-Addad, J. P., Domard, M. and Herz, J. *J. Chem. Phys.* 1978, **63**, 1194
26 Cohen-Addad, J. P. *J. Phys. Lett. (Paris)* 1978, **10**, L-147
27 Meyer, C. T., Cohen-Addad, J. P. and Boileau, S. *Polymer* 1978, **19**, 1107
28 Boiley, F. E. and Koleske, J. V. Non-ionic surfactants (Ed. M. J. Schick), Marcel Dekker, 1967, Vol 1, p 794