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Dynamical Polymer Coil Overlap Observed by NMR on Polystyrene Chains

Concentration and Mass Effects

G. Feio and J.P. Cohen-Addad

Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble,
B.P. 53 X, 38041 Grenoble, France

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SUMMARY

It is shown that the transverse magnetic component of protons bound to polystyrene chains in solutions is sensitive to the slow chain diffusion through entanglements. A theoretical interpretation of the dynamical polymer coil overlap observed by NMR is proposed.

I - INTRODUCTION

One of the crucial problems associated with the analysis of viscoelastic properties is to clearly compare molecular weight and concentration dependances of chain relaxation times predicted from models with those actually observed on a single chain at a molecular scale. It has been recently shown that the relaxation process of the transverse magnetic component of protons bound to poly-dimethylsiloxane chains is partly governed by the slow diffusion of a chain through its entanglements (COHEN-ADDAD et al., 1981, COHEN-ADDAD, 1979). It is possible to observe an ensemble average of single chain motions from a quantitative characterization of several relaxation processes involved in the dynamics of the proton transverse magnetic component. Such a property must be associated with the specific behaviour of nuclear magnetic relaxation rates observed on poly-dimethylsiloxane (PDMS) solutions as well as on poly-isobutylene (PIB) systemes (COHEN-ADDAD et al., 1979, MEYER et al., 1978, CUNIBERTI, 1970). The purpose of this paper is twofold. First it aims at giving a qualitative illustration of this typical behaviour as it is observed on a third polymer species i.e. on polystyrene (PS) chains in benzene solvent. Then it gives a theorical interpretation of the dynamical polymer coil overlap onset observed from NMR measurements.

II - EXPERIMENTAL PROCEDURE

Materials : The three atatic PS fractionated samples used to prepare the solutions were Kindly furnished by Dr. Rinaudo from CERMAV (CNRS - France) and their mass characterization is given in table 1.

TABLE 1 Mass characterization of the PS samples

Ref.	$\overline{M_n}$ GPC THF	$\overline{M_w}$ GPC THF	$\overline{M_w}/\overline{M_n}$
S-504	116 500	140 000	1.20
S-505	264 600	436 200	1.64
S-507	994 800	1 318 600	1.32

0170-0839/81/0005/0277/$01.60

The solutions were prepared in deuterated benzene (from C.E.A. ref. DMM-1, 99.6 % deuterated) at several concentrations, ranging from $\gamma = 0.42$ (75 % w/w) to $\gamma = 57.3$ (2 % w/w). γ is defined as the number of solvent molecules per monomer unit in the solution. All samples were degassed and sealed under secondary vacuum in 5 mm NMR tubes.

Measurements : The ^{1}H NMR high resolution spectra were recorded at five temperatures, from 283 K to 323 K, on a continous wave spectrometer JEOL C60 HL operating at a proton resonance frequency of 60 MHz. The spin-spin relaxation rate T_2^{-1} were directly computed from the half width at half height of spectral lines, δ : $T_2^{-1} = \pi\delta$. The spectra were obtained without sample spinning and the field inhomogeneity corrections were calculated by a previous comparaison of TMS linewidths measured with and without spinning.

In order to measure the ^{1}H spin-lattice relaxation rate, T_1^{-1}, selective inversion experiments were carried out at two temperatures, 283 K and 323 K, on a BRUCKER WP 60 Fourier Transform spectrometer operating at 60 MHz.

The relaxation rates T_2^{-1} and T_1^{-1} were observed as a function of γ, a measure of the chains dilution. The plots so obtained were then compared to analyse mass and temperature effects on the general behaviour of chain spin relaxation dynamics with concentration.

Concentration Volume Dependences : When preparing the PS solutions, the variable used to describe the binary system was the molar ratio γ. As NMR sample tubes are calibrated, it was possible to establish a linear dependence between the solution height per polymer unit mass in the tube, h/m, and γ :

$$\frac{h}{m} = a + b\gamma \qquad (1)$$

The corresponding plot (Fig. 1) was used to identify aberrant characterizations of samples concentration.

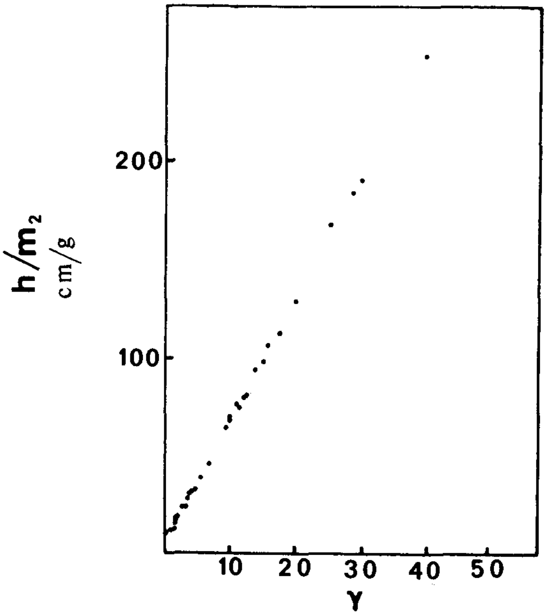

Fig. 1 : Specific height of each sample on standard NMR tubes as a γ function.

The above expression comes directly from the thermodynamic law of binary solutions volume :

$$V_{12} = m_1 v_1 + m_2 v_2 + K(m_1,m_2) \qquad (2)$$

m_1 and m_2 are the two components mass, v_1 and v_2 the volume occupied by the components unit mass in a standard solution and K a mixture factor function of the mass deviations from the standard values. Readily we have :

$$\frac{V_{12}}{m_2\sigma} = \frac{v_2}{\sigma} + \frac{M_2}{M_1}\cdot\frac{v_1}{\sigma}\gamma + \frac{K}{M_2\sigma} \qquad (3)$$

where σ is the tube section and M_1 and M_2 the molecular masses of solvent and monomer unit. Comparing (1) and (2) it is seen that the factor K must be neglected. The ratio a/b of the two experimental parameters in eq. (1) may be used to determine the polymer concentration in mass unit per solution volume unit as a function of γ :

$$c = \rho \frac{1}{\gamma + \frac{a}{b}}$$

where ρ is the solvent specific mass.

III - NMR PARAMETER

The NMR spectra of the three linear PS solutions are not resolved on all the concentration range. The line broadening prevents a rigorous quantitative evaluation of the half-width for each individual proton. The only line shape parameter present in all observed spectra is the low-field half-width at half-height of the peak on the lower field side, δ ; in resolved spectra this peak corresponds to the resonance of meta and para aromatic protons. δ was chosen as the standard spectral parameter to characterize the spectra evolution with concentration, temperature and mass. All the contributions to line broadening due to the phenyl ring dynamical processes are included in this parameter through transverse m-p proton relaxation rate.

IV - CHARACTERISTIC BEHAVIOUR OF RELAXATION RATES

Typical spin-lattice relaxation, T_1^{-1}, and line half-width at half-height, δ, of meta and para protons of the PS phenyl ring as a solvent concentration function are presented in Fig. 2.a) and 2.b).

Residual Spin Interactions : The insensitivity to mass of T_1^{-1} observed at two temperatures (283 K and 323 K),as shown in Fig. 2 a), indicates clearly that spin-lattice relaxation mechanismes of the three aromatic protons are governed by local random fluctuations only ; the experimental values obtained for each of the three fractions are disposed on the same isotherm and the disentanglement rate, partially controlled by chain length effects, is not involved in these spin relaxation properties. Another feature of T_1^{-1} behaviour is a maximum at low γ, wich is displaced towards higher polymer concentration with increasing temperatures : γ_m = 1.7 at 283 K and γ_m = 0.9 at 323 K. This observation is fully explained by admiting the presence of high frequency motions (> 10^8 Hz) in all the observed concentration range. For a γ superior to a particular value, $\gamma_{1\nu}$, the spin-lattice relaxation rate reaches a plateau zone and the dynamical neighborhood of structural units becomes independent of the solution's concentration ; however, the temperature induces a sligth increase on this limiting value : $\gamma_{1\nu} \simeq 5.0$ at 283 K and $\gamma_{1\nu} \simeq 5.5$ at 323 K. A similar behaviour has been reported on PIB solutions (COHEN-ADDAD et al.,1979).

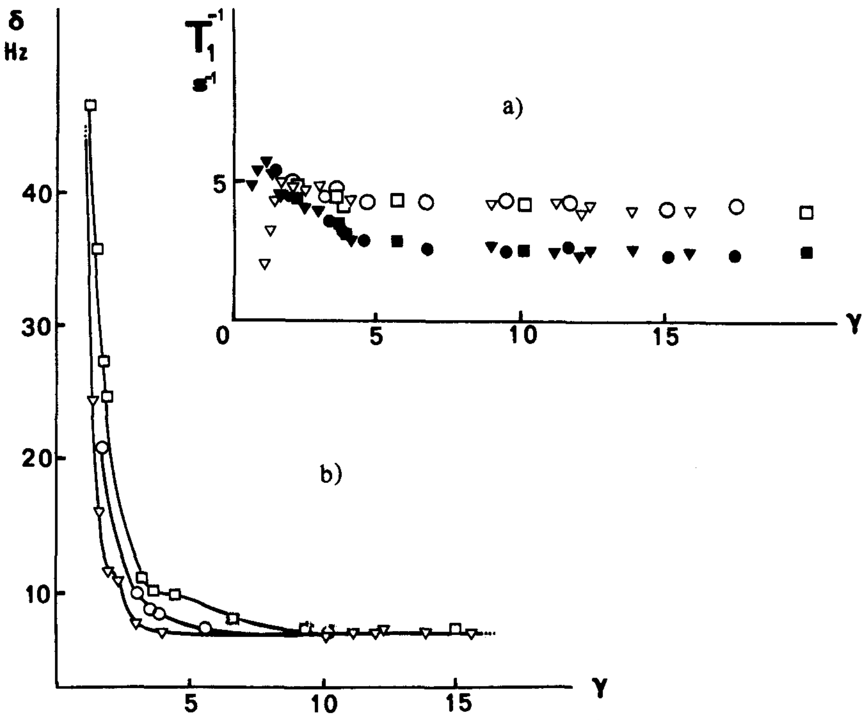

Fig. 2 : General behaviour of relaxation rate T_1^{-1} and half-width at half-height δ of m-p aromatic protons of PS solutions in benzene.
a) T_1^{-1} variation with solvent concentration γ at two temperatures : T = 283 K (open symbols) and T = 323 K (black symbols) for the three fractions : $\overline{M_w} \simeq 1.4 \times 10^5$ (△,▲), $\overline{M_w} \simeq 4.4 \times 10^5$ (□,■) and $\overline{M_w} \simeq 1.3 \times 10^6$ (○,●). b) δ variation with γ of the same three PS fractions at T = 283 K.

As a result of this T_1^{-1} general evolution relative to the PS/C_6D_6 system, it is assumed that a first motional narrowing of the NMR spectral lines has already taken place in every sample. Nevertheless, as it is seen from the width of the aromatic protons resonance lines on Fig. 2 b), the lines are still broadened at high polymer concentration ; a second motional narrowing process occurs in the presence of high frequency motions and the spin transverse magnetization rate is fastened when the solvent concentration is increased up to a limiting value $\gamma_{2\nu}$. For lower polymer concentration a plateau regime for the spin-spin relaxation rate is observed. The partial line broadening is explained in terms of a residual dipolar spin interaction. Effectively it has been already shown that the residual dipolar broadening of spectral lines is divided by two upon sample rotation (COHEN-ADDAD and ROBY, 1975) ; this effect is also observed on PS solutions (Fig. 3)

At high chain concentrations, topological constraints exerted by slowly relaxing entanglements, induce a non-zero average of the spin-spin tensorial couplings taken over the anisotropic high frequency monomer diffusion during the NMR measurement time. Increasing the system dilution, the spectrum of chain relaxation times shifts progressively to lower values. As a consequence, the fast isomeric local fluctuations recover the motional symmetry during NMR measurements ; the residual spin interactions are averaged to zero and the second motional narrowing is achieved.

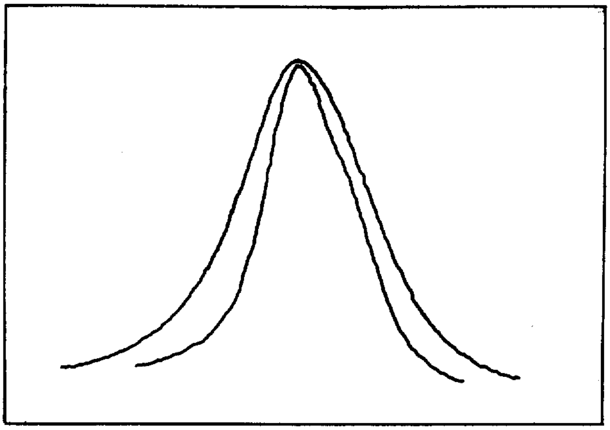

Fig. 3 : Spectrum narrowing effect upon sample rotation. The spectral line corresponds to the aromatic protons resonance of a PS solution (γ = 1.25, T = 313 K) ; the line widths are 16.9 and 29.3 Hz with and without sample rotation,respectively.

The Plateau Zone : The concentration independent zone for the spin-spin relaxation rate is related to the high frequency isotropic motions of monomer units ; there are no residual spin interactions and no spectrum narrowing effect can be perceived. Nevertheless the chains are already strongly coupled, as the PS concentration corresponding to $\gamma_{2\nu}$ obeys to $c_{2\nu}[\eta] > 10$; the cross-over concentration c^* is then far away. The concentration $c_{2\nu}$ describes the onset of a dynamical polymer coil overlap as observed by NMR. The plateau values are not very sensitive to temperature : $\delta \simeq 7.2$ Hz at T = 283 K and $\delta \simeq 6.5$ Hz between T = 293 K and T = 323 K. This behaviour is different from the one reported on PIB systems (COHEN-ADDAD et al. 1979) and with the T_1^{-1} plateau : $T_1^{-1} = 4$ s^{-1} at T = 283 K (T_1 = 250 ms) and 2.4 s^{-1} at 323 K (T_1 = 420 ms) (Fig. 2 a). However, the NMR dynamical overlap concentration, $c_{2\nu}$, is biased towards higher values with increasing temperature, as it is expected from the above picture.

V - CHAIN LENGTH EFFECTS

If the spin-spin relaxation rate, T_2^{-1}, is partially governed by the slow chain diffusion through its entanglements, the mass dependence of collective chain relaxation spectrum must be reflected on the shape of NMR spectral lines. Indeed, the evolution of the m-p protons linewidth with γ is specific for each PS fraction, as it is evident from Fig. 2 b). These plots contrast with T_1^{-1} behaviour, where no mass effects are discernable, since the high frequency domain of chain motional spectrum is not sensitive to large scale fluctuations. This clearly proves that line-shapes of NMR absorption spectra of entangled polymer solutions contains an information about the low frequency properties of macromolecular systems. A systematic study of these effects can bring up an effective method to study at a molecular level the disentanglement process wich is responsible of the viscoélastic behaviour of high polymer solutions.

In the plateau zone the linewidth doesn't varie significantly with the molecular fraction and on the Fig. 2 b) these variations are neglected.

Increasing the PS concentration above $c_{2\nu}$ the mass effect grows substantially. The overlap concentration $\gamma_{2\nu}$ is strongly displaced towards higher dilutions when the PS chain length is increased. An empirical law was found expressing a relationship between $c_{2\nu}$ and the intrinsec viscosity $[\eta]$ for each fraction :

$$c_{2\nu}\,[\eta]^{.4} = \text{constant} \qquad (4)$$

This result applies equally to PIB/CS_2 systems (COHEN-ADDAD et al., 1979).

VI - INTERPRETATION : A TWO-STEP MOTIONAL NARROWING PROCESS

One of the main difficulties arising from NMR studies of chain dynamics in polymeric liquids is to give a clear definition of molecular motions actually observed. This definition depends upon the rigorous characterization of nuclear spin interactions responsible for the transverse magnetic relaxation process. The main spin interaction involved in NMR properties observed on polymer chain systems is the well known dipole-dipole coupling ; it is a function of the vector $\vec{a}_{ij}$ joining two nuclei i and j (COHEN-ADDAD and GUILLERMO, 1981). NMR measurements reported here do not allow to discriminate dipolar interactions of protons located on different chain segments from those established between protons located within a given monomeric unit. Accordingly, it will not be possible to distinguish the internal diffusion process of a single chain from the relative translational diffusion of any two chain segments. Such a distinction has been already made by using more specific probes like CH_3 groups (COHEN-ADDAD et al., 1981). However, the aim of this section is to give a qualitative interpretation of the general behaviour of proton relaxation rates observed on concentrated polystyrene - benzene solutions.

NMR Submolecules : It is first considered that :

i) The maximum of the spin-lattice relaxation rate observed at $\gamma \simeq 1.2$ (Fig. 2 a), reflecting local motions at the Larmor frequency ($\omega_0 \sim 10^9$ rad s^{-1}).

ii) The spectrum narrowing effect observed at the same polymer concentration (Fig. 3), reflecting residual tensorial interactions, clearly demonstrates that the interpretation of NMR properties is necessarily based on the partition of a chain into submolecules. More precisely, NMR submolecules are supposed to be determined from two sets of chain relaxation times well separated from each other (FERRY, 1980). This relaxation spectrum is induced by the presence of entanglements and all topological constraints exerted on chains. The low relaxational frequency range is associated with the collective motion of submolecules. The longest relaxation time or terminal relaxation time, τ_1, characterizes the slow diffusion of a chain as a whole. While the high relaxational frequency range is associated with fast isomerisation processes within short segments.

The effect of the partition of a chain into submolecules on the spin-lattice relaxation rate and the spectrum narrowing property can be pictured as follows (COHEN-ADDAD, 1981) :

Two-step Motional Narrowing : A polymer chain is supposed to be divided into N_e^ν NMR submolecules. Any submolecule is determined from its end-to-end vector, $\vec{r}$. Accordingly, the correlation function, $\Phi(t)$, characterizing the random time function $\mathcal{D}(t)$ associated with all spin interactions is defined in two steps :

$$\Phi(t) = \overline{\mathcal{D}(0)\,\mathcal{D}(t)} = \Phi(0)g(t) \qquad (5)$$

with g(0) = 1, and :

$$\Phi(0) = \int d\vec{r}\ \mathcal{P}(\vec{r})\ \langle \mathcal{D}(t)^2 \rangle_{\vec{r}} \qquad (6)$$

The partial average $\langle\ \rangle_{\vec{r}}$ is defined over all rotational isomers compatible with the end-to-end vector $\vec{r}$. In other words the mean square value $\Phi(0)$ is calculated in two steps ; it is also written as :

$$\left\langle \left(\mathcal{D}(t) - \langle \mathcal{D}(t) \rangle_{\vec{r}} \right)^2 \right\rangle_{\vec{r}} + \left(\langle \mathcal{D}(t) \rangle_{\vec{r}} \right)^2 \qquad (7)$$

Fast random internal rotations of structural units occuring within a subchain are responsible for the spin-lattice relaxation process ; they are characterized by a correlation function $\gamma(t\ \tau_c{}^{-1})$ rapidily decreasing to zero ($\tau_c = 10^{-8}$ s) and such that :

$$\gamma(0) = \left\langle \left(\mathcal{D}(t) - \langle \mathcal{D}(t) \rangle_{\vec{r}} \right)^2 \right\rangle_{\vec{r}} = \langle \mathcal{D}(t)^2 \rangle_{\vec{r}} - \langle \mathcal{D}(t) \rangle_{\vec{r}}^2 \qquad (8)$$

The spin-lattice relaxation rate can be roughly expressed as :

$$T_1{}^{-1} \propto \int e^{i\omega_o t}\ \gamma(t\tau_c{}^{-1})dt \qquad (9)$$

The contribution to the line broadening is about :

$$\delta_1 \propto \gamma(0)\ \tau_c$$

Furthermore, the slow random variation of $\vec{r}$ is stochastically independent of random internal rotations ; it is characterized by a correlation function $\Gamma(t\tau_1{}^{-1})$ with $\tau_1 < 10^{-3}$ s and such that :

$$\Gamma(0) = \int d\vec{r}\ \mathcal{P}(\vec{r})\ \langle \mathcal{D}(t) \rangle_{\vec{r}}^2 \qquad (10)$$

$\Gamma(t\tau_1{}^{-1})$ is mostly responsible for the relaxation process of the transverse component of the magnetization observed on entangled chains.

A Low Reference Frequency : Two cases must now be considered :

i) $\tau_1\Gamma(0)^{1/2} >> 1$; this corresponds to long polymer chains ($\overline{M_W} > 10^6$): the low relaxational frequency range is such that the motional narrowing process of tensorial spin interactions is not complete ; there is a residual interaction and the observed line width is $\Delta = \Gamma(0)^{1/2}$. The residual interaction induces a pseudo-solid behaviour of NMR properties illustrated by the spectrum narrowing effect (COHEN-ADDAD, 1975).

ii) $\tau_1\Gamma(0)^{1/2} << 1$; this corresponds to short chains ($\overline{M_W} < 10^5$) ; tensorial spin interaction are completely averaged to zero ; the observed line width is $\Delta = \Gamma(0)\tau_1$. Therefore, a low reference frequency is clearly given by $\Gamma(0)^{1/2}$; the strength of spin-interaction $\Phi(0)^{1/2} \simeq 10^4$ Hz has been considerably reduced by the two step average. For a freely jointed chain $\Gamma(0)^{1/2} \simeq \Phi(0)^{1/2}\ N^{-1} \simeq 10^2$ Hz, with the number of bounds N equal to 10^2. In the case where $\tau_1\Gamma(0)^{1/2} \simeq 1$, the line width must depend upon the chain length.

Dynamical Coil Overlap : A model has been recently proposed to give a quantitative interpretation of the effects of chain dynamics on NMR properties considering specific probes (CH_3 groups) linked to the chains (COHEN-ADDAD et al., 1981). Although this model cannot be used to interpret NMR results reported here, it may illustrate the description of the dynamical polymer coil overlap onset as it is perceived from NMR. First the low reference frequency associated with each normal mode of the collective motion of all NMR submolecules is expressed as Δ_o/N ; Δ_o is the line width observed in the glassy state while N is the number of monomeric units per chain. Then, we consider the usual expression of the terminal relaxation time $\tau_1 \propto M_e^\nu \eta_o/c$ (M_e^ν is molecular weight of the submolecule, η_o is the zero shear rate viscosity and c the polymer concentration) :

$$\eta_o \propto c^{3.4} N^{3.4} \qquad \text{while}$$

$$M_e^\nu \propto c^{-1} \qquad \text{and} \qquad \tau_1 \propto c^{1.4} N^{3.4}$$

The lowest relaxation time associated with the collective motion of submolecules is called $\tau_1{}^s$. Also, according to this model, the coil overlap process is perceived from NMR when the condition :

$$\tau_1{}^s\ \Delta_o/N \simeq 1$$

is fulfilled. Two cases are to be considered :

i) if $\tau_1{}^s$ is expressed as τ_1/N^2c^2 (the number of molecules is proportional to Nc), then :

$$\tau_1{}^s\Delta_o/N \propto c_{2\nu}{}^{-0.6}\ N^{0.4} \simeq \text{constant} ;$$

this does not agree with the empirical formula (4).

ii) if $\tau_1{}^s$ is expressed as τ_1/N^2, then :

$$\tau_1{}^s\Delta_o/N \propto c_{2\nu}{}^{1.4}\ N^{0.4} \simeq \text{constant}$$

$$\text{and} \qquad c_{2\nu}[\eta]^{0.4} \simeq \text{constant},$$

in agreement with formula (4). This gives an estimate of the dependence of the shortest relaxation time associated with the long range chain diffusion process. It must not be confused with high frequency motions of structural units occuring within any submolecule.

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