spheres. For a polymer liquid, a question arises as to what the appropriate molecular weight should be for these hypothetical units, but we will assume that such a unit can be defined with molecular weight M. The phonon velocity is then given by

$$V_l = \left(\frac{\gamma RT}{M}\right)^{1/2} \left[\frac{1 - \frac{2}{3}(V_0/V)^{1/3}}{(1 - (V_0/V)^{1/3})^2}\right]^{1/2} \tag{6}$$

The value of M calculated from the measured phonon velocity of n-hexadecane at 120 °C is 159 g/mol. This is approximately the molecular weight of n-undecane.

If the free volume is small relative to V_0, eq 6 can be approximated as

$$V_l = K \left(\frac{\gamma RT}{M}\right)^{1/2} \left(\frac{V_0}{V_f}\right)^{1/3} \tag{7}$$

where K is a constant. Thus, the relation found by Champion and Jackson[1] appears reasonable for a homologous series of molecules.

The fact that the Brillouin results yielded $V_l(0)$ demands that the local structural relaxation times in molten polyethylene be fast relative to 10^{-10} s. The relaxation time for trans-gauche conformational changes in butane would be near 10^{-10} s at 120 °C,[11] but for longer chains the internal bonds should relax much slower. Thus, rapid local structural relaxation must be taking place essentially without change of conformation from trans to gauche states. The above results also suggest that conformation changes contribute a negligible fraction to the total compressibility of the fluid in molten polyethylene.

It has previously been shown that the local orientational order in molten polyethylene is essentially constant for chains larger than about 20 carbons compared at constant density.[12] The present results also confirm the similarity of the local structure in polyethylene melts. It seems reasonable to conclude that the lower homologues of polyethylene are good representatives of the local melt properties of the whole series.

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Local Polymer-Segment Density as Studied from NMR Observed on Highly Concentrated Polyisobutylene Chain Solutions. Determination of Thermodynamic Interaction Parameters Characterizing High Polymer–Solvent Mixtures

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ABSTRACT: It is attempted to relate high-resolution nuclear magnetic spectroscopy measurements to thermodynamic interaction parameters of high polymer chain concentrated solutions. It is proposed to use the characteristic polymer concentration and temperature dependences of the line width observed on polyisobutylene chain solutions in $CDCL_3$, CS_2, and C_7D_8 to calculate: (i) the variation of enthalpy as a temperature function for the formation of a single unlike contact pair; (ii) the variation from a reference temperature of the change in free energy for the formation of an unlike contact pair. These parameters are shown to have an order of magnitude in satisfactory agreement with that of parameters derived from other types of experiments.

I. Introduction

When time-dependent chain fluctuations can be left aside, properties of concentrated polymer–solvent mixtures at equilibrium may be considered as characterized in two ways. The first one is the determination of the structure of high polymer chain solutions, concentrated enough to give rise to entanglement formation. An accurate description of such a structure has been recently given from elegant neutron scattering experiments performed on polystyrene.[1,2] The other way corresponds to the determination of thermodynamic properties on a macroscopic scale. Solvent vapor pressure measurements or osmometry lead to the determination of the solvent activity.

Numerous polymer–solvent systems have been experimentally studied to attempt to establish the relationship existing between macroscopic thermodynamic data and molecular interaction parameters.[3,4] Several interpretations based on combinatorial analysis have been proposed besides the simple and illustrative model leading to the Flory–Huggins equation.[5-7] More recently, a magnetic analogue of polymer chain–solvent systems has been found. The state equation of polymer solutions has been derived from the properties of second order phase transitions observed on magnetic systems.[8]

The present paper aims at defining a complementary experimental way to characterize polymer–solvent mixture properties. It will be shown that thermodynamic parameters derived from NMR data and characterizing polymer–solvent interactions are contrasted to those obtained from osmometry or vapor pressure measurements because they are defined on a molecular scale, only. Nuclear spins are local probes sensitive to magnetic interactions averaged over volumes of molecular size; NMR data will lead to the determination of properties of a single unlike contact pair polymer segment–solvent molecule. In other words, NMR data and macroscopic thermodynamic data should be compared with each other to establish the appropriate statistical law governing polymer–solvent mixture properties, at equilibrium.

II. Two Characteristic Properties of the Transverse Magnetization

It has been recently shown that the resonance line width, $\delta\omega$, observed on high molecular weight ($\simeq 10^6$) polyisobutylene chain solutions in $CDCl_3$, CS_2, and C_7D_8 exhibits characteristic solvent concentration and temperature dependences.[9] These properties have been perceived from either of two experimental procedures. At constant temperature, T, the quantity, $\delta\omega^{-1}$, obeys linear variations as a function of the variable $\gamma = \nu_1(1 - \nu_1)^{-1}$; ν_1 is the solvent molar fraction. While at constant polymer concentration, the product $T\delta\omega^{-1}$ obeys linear variations as a function of T; more precisely it has been carefully demonstrated that in no case could the line width evolution be represented as a function leading to Arrhenius or free volume laws. Also, the variation of $\delta\omega^{-1}$ as a γ function cannot be confused with the mean monomer unit concentration.

No interpretation was given in ref 9 about these characteristic properties. However, a strong sample rotation effect upon high resolution resonance lines was reported in this reference. It was interpreted as reflecting the presence of a residual dipolar nuclear spin interaction. Such a dipolar interaction has also been observed on polybutadiene high molecular weight chains in solution, from two experimental procedures, either by observing pseudo-solid spin echoes, or by considering sample rotation effect on resonance lines.[10,11] It was supposed in ref 12 that NMR lines observed on high polymer chains in concentrated solutions are not broadened by a mechanism based on dynamical processes; line broadening was assumed to result from residual dipolar interactions which are not averaged to zero by chain segment motions because of the presence of entanglements. A rough analysis of some NMR data was given in ref 12, without any quantitative discussion.

The purpose of the present paper is to give a complete analysis of all NMR data reported in ref 9. New experimental results were added to those of this reference to obtain a more accurate interpretation. Before discussing NMR data basic assumptions underlying the interpretation will be presented.

III. Basic Assumptions

(A) Entanglement Relaxation and Magnetic Relaxation. The interpretation of NMR data is first based on the clear picture of the structure of high polymer chain solutions recently obtained from neutron scattering experiments. Concentrated solutions are characterized by the presence of entanglements.[1,2] The average distance between two consecutive entanglements is ξ, the correlation length. Any chain can be divided into several coils of average size ξ. Within a given coil, chain segments undergo excluded volume effects; the monomer unit distribution function is analogous to that of a free chain in a diluted solution. On the other hand polymer chain solutions undergo fluctuations around the equilibrium. One of the main characteristic times of these fluctuations is the disentanglement relaxation time, T_r. It has been long supposed that chain entanglements can dissociate on a time scale which has been predicted to strongly vary with chain molecular weight.[13] Also, chain segments undergo fluctuations inside any coil; these are supposed to occur on a time scale much shorter than T_r.

The interpretation of NMR data to be discussed in the present paper will be based on the following assumption: entanglements can form and dissociate over time intervals much longer than relaxation times of the transverse nuclear magnetization. This assumption will account for the observation of a residual dipolar spin coupling.

(B) Residual Dipolar Spin Coupling. In most polymer systems the dipolar spin coupling can be considered as the only interaction responsible for observed relaxation processes. Two properties characterize this dipolar spin coupling. First, it is expressed as a tensorial function of space coordinates of nuclei located on polymer chains. As a consequence, the dipolar spin coupling averaged over all chain segment motions is not equal to zero if NMR measurements are performed during time ranges shorter than the disentanglement relaxation time. Although chain segment motions are fast enough compared with the dipolar coupling strength to give rise to a motional narrowing process there is a residual dipolar coupling due to nonisotropic motions. Chain segments cannot rotate completely in space because of the presence of entanglements. Isotropic motions should be observed on time scale longer than T_r only. More precisely, it can be assumed that the dipolar coupling within a given monomer unit is completely averaged to zero because high frequency collective motions of a few monomer units are probably isotropic. But low frequency motions of long chain segments cannot be isotropic with respect to each other because of the presence of entanglements. The strongest contribution to the residual dipolar spin coupling probably comes from interactions between spins located on different chain segments. Hence, the local polymer-segment density will be involved in the interpretation.

The second property is that the dipolar spin coupling is a short-range interaction; it necessitates the description of relaxation mechanisms on a local space scale. More precisely, it will be shown in the present paper that it is not the mean monomer unit concentration which must be taken into consideration to interpret NMR data but the probability function for the formation of an unlike contact pair. The decrease of the dipolar spin coupling observed upon dilution will be assumed to result mainly from an increase of the probability for the formation of polymer segment–solvent molecule pairs.

(C) Standard Resonance Line Shape. To have any physical significance, NMR studies of polymer–solvent interactions must be based on the following crucial property. All resonance lines must be described according to a standard way applying over the whole polymer concentration and temperature ranges which are investigated. The analysis of NMR results according to a standard way must define a parameter appropriate to the characterization of resonance lines. If such a crucial property is not satisfied, nothing ensures that physical properties of the polymer–solvent system will be reflected as a monotonic function of temperature and concentration. In the case of high molecular weight polyisobutylene (PIB) chain solutions in $CDCl_3$, CS_2, and C_7D_8 it has been carefully demonstrated that resonance lines exhibit a common shape over the concentration range where polymer chains are supposed to form entanglements.[9] Such a property will not be discussed again in the present paper. Also the use of a double time scale to distinguish effects on NMR due to fluctuations inside coils of size ξ, from effects of disentanglement processes, has been discussed at length in ref 12. It will not be considered again. All contributions to line broadening due to dynamical processes are excluded from the following interpretation.

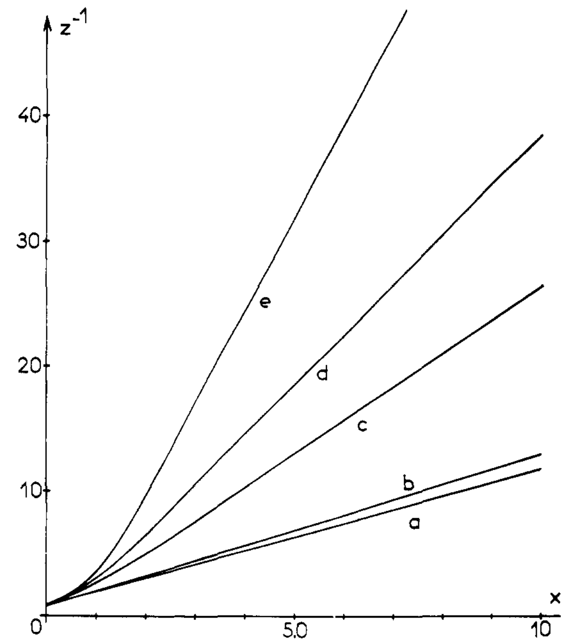

Figure 1. Representations of the variations of $\delta\omega^{-1}D(z-2) = Z^{-1}$ calculated from eq IV.2 as a function of $x = z\gamma/(z-2)$. The parameter $-w/RT$ has been given the values: $a = 0.05$, $b = 0.10$, $c = 0.5$, $d = 0.7$, and $e = 1.0$, respectively.

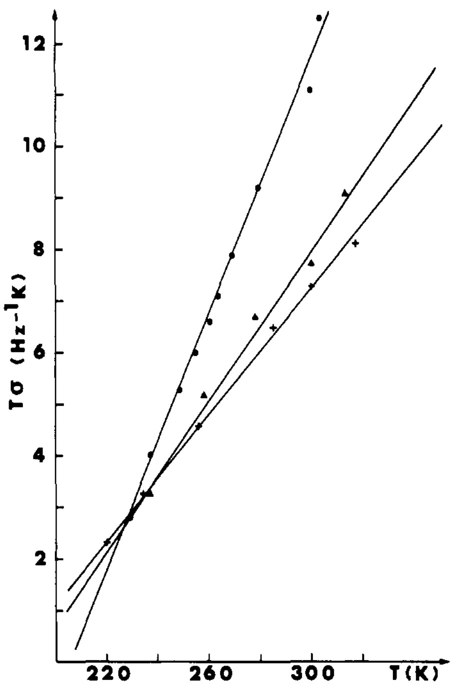

Figure 2. Experimental variations of $T\sigma(T)$ observed as a function of the temperature. Solvents of the polyisobutylene chains are: (●) C_7D_8; (▲) $CDCl_3$; and (+) CS_2.

IV. Number of Pairs of Adjacent Polymer Segments

Let N_B be the number of chain polymers. The chain polymer may be considered to consist of r_B segments. According to Flory's lattice model the probability that a particular site adjacent to a polymer segment is occupied by another polymer segment is supposed to be equal to the volume fraction v_2 of monomer units in the solution.[4] Hence, the total number of pairs of adjacent polymer segments around a given polymer segment is zv_2; z is the lattice coordination number. Accordingly, the average dipolar spin coupling, considering nearest neighbors only, is equal to zDv_2; D is the average dipolar spin coupling between two nearest neighbors only. Such a simple formula does not depend explicitly on the temperature and varies as the mean polymer concentration. It cannot account for the observed temperature and solvent concentration dependences of the NMR line width, because it is not exactly the mean monomer unit concentration which must be considered but the local monomer unit concentration. This may be different from the mean concentration because of the presence of pairs or, more generally, of clusters of monomer units, reflecting the polymer–solvent interaction on a molecular scale. In other words, the mean monomer unit concentration must be modified by taking polymer–solvent interactions into consideration. Such a modification can be illustrated by considering the lattice model proposed by Guggenheim.[14] The number of pairs of unlike neighbors zX becomes a complex temperature and concentration function obeying the condition of quasi-chemical equilibrium:

$$\frac{X^2}{(N_A - X)(q_B N_B - X)} = \exp(-2w/RT) = y^{-1} \quad \text{(IV.1)}$$

N_A is the number of solvent molecules; $q_B = (2 + (z-2)r_B)\cdot z^{-1}$; w is the change in free energy for the formation of a single unlike contact pair (it is usually the thermodynamic quantity $\chi_1 = zw/RT$ rather than w which is considered). The number of pairs of adjacent polymer segments is $z(q_B N_B - X)/2$. Neglecting the dipolar spin coupling which is not due to nearest neighbors, the average coupling strength is proposed to be expressed as:

$$\delta\omega = (z-2)D\left(1 + \frac{1+x}{2(y-1)} \times \left[1 - \left(1 + \frac{1 + x(y-1)}{(1+x)^2}\right)^{1/2}\right]\right) \quad \text{(IV.2)}$$

with $x = \gamma z(z-2)^{-1}$. To calculate the probability that an unlike contact pair is formed, it is essential to regard w as independent of the composition of the solution. But, according to numerous studies about thermodynamic properties of polymer–solvent systems, nothing requires that w should be independent of the temperature; w will be determined from experimental results. Since w is probably an unknown temperature function, eq IV.2 will be first discussed at fixed temperature values.

V. Characteristic Slopes. The Exclusion Parameter

Detailed mathematical properties of eq IV.2 are without importance here. A complete numerical analysis of eq IV.2 can be made at given fixed values of the parameter, y. Typical representations of the variations of $\delta\omega^{-1}$ are shown on Figure 1. They strikingly illustrate the linear behavior of $\delta\omega^{-1}$ over a wide range of x values. This property can be perceived from the approximate expression of eq IV.2 obtained for $x \gg 1$:

$$\delta\omega^{-1} \simeq (z-2)^{-1}D^{-1}(x - 1 + y) \quad \text{(V.1)}$$

with $x \gg 1$. It applies well in the concentration range where monomer unit pairs do not interfere with one another. The linear behavior of eq V.1 is in agreement with the observed linear variation of $\delta\omega^{-1}$ as a function of γ. Accordingly, the analysis of experimental results will be based on the general expression of the slope derived from eq V.1:

$$\sigma(T) = z(z-2)^{-2}D^{-1}y^{-1} \quad \text{(V.2)}$$

Equation V.1 can be given the following physical meaning. When x and y have large values $\delta\omega^{-1}$ is roughly proportional to $y^{-1}x$. Now, in the absence of any polymer–solvent interaction ($w = 0$) eq IV.2 shows exactly that $\delta\omega^{-1}$ is proportional to v_2 and $v_2 \simeq x$ when $x \gg 1$. Therefore polymer–solvent interactions ($w \neq 0$) are involved through a factor y^{-1} which we

Table I
Experimental Values of the Slopes $\sigma(T)$ Derived from NMR Data[a]

Solvent	T, K	$10^2 \times \sigma(T)$, Hz^{-1}	$T\sigma(T)$, Hz^{-1} K	ϵ_s, Hz^{-1} K	$10^2 \times \alpha_s$, Hz^{-1}	$10^2 \times \alpha_s^*$, Hz^{-1}
$CDCl_3$	313	2.90	9.086	−13.9	7.3	6.4
	300	2.58	7.75			
	278	2.41	6.70			
	258	2.00	5.17			
	237	1.38	3.27			
	217	0.55	1.2			
CS_2	313.7	2.6	8.16	−11.3	6.2	5.3
	300	2.44	7.32			
	285	2.28	6.5			
	256	1.79	4.58			
	234.2	1.40	3.28			
	220	1.06	2.33			
C_7D_8	303	4.13	12.52	−25.7	12.5	
	299	3.72	11.11			
	279	3.30	9.21			
	269.2	2.92	7.87			
	263.4	2.70	7.11			
	260.3	2.54	6.61			
	254.5	2.35	5.99			
	248.4	2.12	5.27			
	237	1.70	4.03			
	229	1.23	2.81			

[a] α_s values are derived from linear variations of $\delta\omega^{-1}$ observed as a solvent concentration function at constant temperature, while α_s^* values are obtained from linear variations of $T\delta\omega^{-1}$ observed as a temperature function at constant solvent concentration. Two series of measurements were performed to ensure independence of results.

shall call an exclusion parameter because it tends to increase the average volume between two monomer units in good solvents. This physical meaning is probably independent of any lattice model of polymer–solvent mixtures, and polymer–solvent interactions may be involved through a more sophisticated function than y^{-1}. The proportionality of $\delta\omega^{-1}$ to y^{-1} could also have been considered as a physical assumption proposed a priori. The Guggenheim's model is only used as a mathematical support to the present illustration of the role of polymer–solvent interactions.

(A) Good Solvents. On the other hand, it has been carefully demonstrated in ref 9 that experimental values of $\sigma(T)$ vary according to the temperature function

$$\sigma(T) = \alpha_S + \epsilon_S T^{-1} \qquad \text{(V.3)}$$

This has been observed on PIB chain solutions in CS_2 and $CDCl_3$, over a temperature range of about 100 K; $T\sigma(T)$ plots are presented on Figure 2. Experimental values of ϵ_S and α_S corresponding to $CDCl_3$ and CS_2, respectively, are reported in Table I; α_S values were derived from either of two experimental procedures. At constant temperature, T, a series of straight lines $\delta\omega^{-1}$ was observed as a function of γ. Or, at constant polymer concentration a series of straight lines $T\delta\omega^{-1}$ was observed as a function of T. The two types of measurements were made separately to ensure independence of results. New experimental points were added to results of ref 9 to obtain more accuracy. α_S values derived in the two ways can be compared with each other in Table I. Since α_S values result from a two-step determination, the discrepancy can be considered as small.

(B) Theta Temperature. Experimental results corresponding to C_7D_8 necessitate a peculiar examination because toluene is known to exhibit a theta temperature at 260 K.[4] Chains of finite length are characterized by a critical temperature of precipitation, T_c, observed below theta. Phase transitions are known to occur at a temperature which depends upon the polymer concentration according to a concentration–temperature diagram. These phase transitions are apparent in the concentration dependence of $\delta\omega^{-1}$; they break its linear variation. It must be emphasized that $T\sigma(T)$ is an average quantity only referring to concentration ranges where the inverse $\delta\omega^{-1}$ of the line width exhibits a linear behavior as a function of γ. These concentration ranges are observed to narrow when the temperature is lowered. At 300 K, the linear variation of $\delta\omega^{-1}$ spreads over the concentration range $\gamma = 0, \gamma \simeq 10$, while at 229 K the linear variation of $\delta\omega^{-1}$ only spreads over the concentration range $\gamma = 0, \gamma = 0.7$. Nevertheless, $\sigma(T)$ slopes are accurately measured over well-defined concentration ranges. It is observed on Figure 2 that the function $T\sigma(T)$ still exhibits a linear behavior with respect to T below and above 260 K.

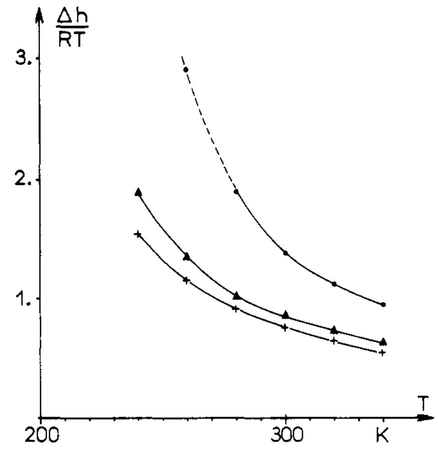

Figure 3. Representations of the variations of the molecular enthalpy interaction parameter $\Delta h/RT$ calculated from eq VI.3. ϵ_S and α_S values are derived from NMR data. Key to points same as on Figure 2.

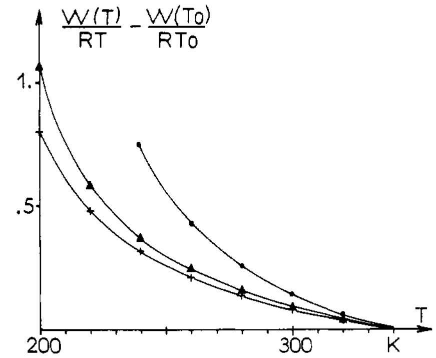

Figure 4. Variations of $w(T)/RT$ from a reference temperature T_0 = 340 K. These are calculated from experimental values of ϵ_S and α_S. Key to points same as on Figure 2.

VI. Free Energy of a Single Unlike Contact Pair

Although the free energy variation w may be involved through a more complicated function than an exponential one, it may be of interest to derive w from $\sigma(T)$ slopes. The free energy change, w, for the formation of a single unlike contact pair, may be written from eq V.2 and V.3 as:

$$w = -\frac{RT}{2}\ln\frac{(z-2)^2 D(\epsilon_S T^{-1} + \alpha_S)}{z} \qquad \text{(VI.1)}$$

Some difficulties arise in the determination of absolute values of the free energy, w, because the constant $(z-2)^2D/z$

is left undetermined. But in any case can variations of $w(T)/RT$ from a reference temperature, T_0, be determined without any ambiguities:

$$z^{-1}\Delta\chi_1 = z^{-1}(\chi_1(T) - \chi_1(T_0)) = \tfrac{1}{2} \ln \left(\frac{\epsilon_S T_0^{-1} + \alpha_S}{\epsilon_S T^{-1} + \alpha_S}\right) \tag{VI.2}$$

Such variations are illustrated on Figure 3. The free energy, w, exhibits a strong temperature dependence over the range 220 to 320 K. While the constant $(z-2)^2D/z$ must be evaluated to obtain the absolute value of w, there is another thermodynamic quantity which may be of interest and which is independent of this constant; it is the change in enthalpy, Δh, for the formation of a single unlike contact pair; from the known relation

$$\Delta h = w - T\,\mathrm{d}w/\mathrm{d}T \tag{VI.3}$$

it is found that

$$\Delta h/RT = \frac{-\epsilon_S/2}{\epsilon_S + \alpha_S T} \tag{VI.4}$$

The dipolar constant and the lattice coordination number are excluded from the above equation. Plots of $\Delta h/RT$ as a function of T are represented on Figure 4. It must be emphasized that according to the above formula $\Delta h/RT$ is defined from two parameters ϵ_S and α_S which are directly obtained from NMR data. Inconsistencies among existing values of thermodynamic interaction parameters, on the one hand, and the absence of any results about PIB solutions in CS_2 and $CDCl_3$, on the other hand, do not permit any quantitative comparison with the present results. However, the comparison of the order of magnitude of $\Delta h/RT$ with that of values reported in the literature from other types of measurements might give an interesting test of validity for the above equation. From eq VI.4 $\Delta h/RT$ is found to be equal to 0.86, 1.4, and 0.76 at 300 K, in the case of $CDCl_3$, C_7D_8, and CS_2, respectively. This must be compared with values of the reduced partial molar enthalpy κ, which is analogous to the molecular enthalpy interaction parameter, after the commonly used Flory–Huggins equation. In the case of PIB chains diluted in benzene κ has been found to be equal to 0.8 at 300 K from vapor-pressure measurements, while from recent gas–liquid chromatography it has been found to be equal to 1.8, at the same temperature; intrinsic viscosity measurements lead to 0.15 at 300 K. In the case of PIB chains diluted in other solvents κ values vary from about −1 to about +2, at 300 K.[3,15-20] It is considered that values of the molecular enthalpy interaction parameter $\Delta h/RT$ obtained from the simple expression VI.4 and from values of ϵ_S and α_S derived directly from NMR data have a satisfactory order of magnitude.

VII. Chemical Potential of Solvent

Most studies of thermodynamic properties of high polymer solvent mixtures aim at determining the change in free energy for the formation of a polymer segment–solvent molecule pair. However, it is usually the solvent activity which is first determined. Molecular interaction parameters must then be derived from an appropriate equation. It is possible to calculate the solvent partial molar free energy from molecular interaction parameters, using the quasi-chemical equilibrium model:

$$\mu_1 - \mu_1{}^0 = \Delta\mu_1 = RT\left[\ln(1 - v_2) + \left(1 - \frac{1}{r_B}\right)v_2 + \frac{z}{2}\ln\beta\right] \tag{VII.1}$$

$\mu_1{}^0$ corresponds to pure solvent.

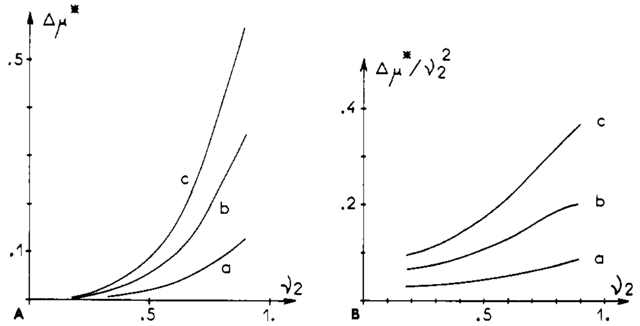

Figure 5. Variations of the chemical potential of solvent as a function of the monomer unit molar concentration. These are calculated in the case of toluene using the arbitrary value $(z-2)^2D/z = 120$ Hz. (A) $\Delta\mu^* = [(\mu_1 - \mu_1{}^0)/zRT] - [(\ln(1-\nu_2) + \nu_2)/z]$; (B) $\Delta\mu^*\nu_2^2$. Temperatures are: $a = 270$ K, $b = 290$ K, $c = 325$ K.

$$\beta = \frac{\lambda - 1 + 2x/(1+x)}{(\lambda+1)x/(1+x)} \text{ and } \lambda = (1 + 4x(y-1)/(1+x)^2)^{1/2}$$

The first two terms of eq VII.1 correspond to the pure configurational entropy contribution. Since the last term $z/2 \ln\beta$ vanishes with w, we may regard this term as the part of the chemical potential due to the thermodynamic interaction parameter, w. When the quantity $y - 1$ is considered as small enough, the last term may be written as $zwv_2{}^2/RT$; it corresponds also to the contribution derived from the Flory–Huggins free-energy equation. Since in the present paper absolute values of w are not known, variations of $\Delta\mu_1$ cannot be calculated directly. However, when w/RT may be supposed small enough to allow a series expansion of β, the variation from a reference temperature T_0 of the excess of chemical potential can be expressed as

$$\frac{\Delta\mu_1(T)}{RT} - \frac{\Delta\mu_1(T_0)}{RT_0} \simeq zv_2{}^2\left(\frac{w(T)}{RT} - \frac{w(T_0)}{RT_0}\right) \tag{VII.2}$$

Variations of $w(T)/RT$ are known; therefore the order of magnitude of the difference in (VII.2) can be compared with that of differences of chemical potentials reported in the literature. For example, the quantity which is usually considered is $\Delta\mu_1/RT - \ln(1 - v_2) - v_2$. This has been found to vary linearly with respect to $v_2{}^2$ in the case of a benzene–polyisobutylene system, over the range $0 < v_2 < 0.7$. The difference observed between 298 band 313 K is a linear function of $v_2{}^2$; its slope is 0.06.[12] From Figure 3, it is observed that over the temperature range 298 to 313 K the variation of $w(T)/RT$ is about 0.04 for $CDCl_3$. Also, the excess of chemical potential of toluene was calculated at several polymer concentrations ν_2 using an arbitrary value of the constant $(z-2)^2D/z$; it is represented in Figure 5 (left and right). All orders of magnitude are in agreement with those of data reported in the literature about polymer–solvent systems.

VIII. Conclusion

A method to interpret NMR data obtained from high resolution spectroscopy on high polymer concentrated solutions was developed in the present paper. The interpretation was given a mathematical support based on a lattice model of polymer–solvent mixtures. The interpretation applies in the only concentration range where polymer chains overlap. Values of the free energy change for the formation of a single unlike contact pair are of the same order of magnitude as those derived from other types of experiments reported in the literature. It should be emphasized that NMR measurements on highly concentrated polymer solutions are free of the difficulties experienced with activity and osmometric measurements. It might be of interest to systematically compare thermodynamic parameters derived from NMR data to those obtained from more conventional experiments, to attempt to establish the relationship existing between thermodynamics and molecular interactions.

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Proton and Carbon-13 Spin–Lattice Relaxation Studies of the Conformation and Dynamical Behavior of Poly(4-vinylpyridine) in Methanol Solution

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ABSTRACT: The segmental motions of poly(4-vinylpyridine) in CD_3OD solution have been investigated between 220 and 350 K by ^{13}C and ^{1}H spin-lattice relaxation. The experiments were performed at 25 MHz (^{13}C) and 100 and 250 MHz (^{1}H). While the relaxations of ^{1}H and ^{13}C of the main chain are interpretable in terms of an isotropic segmental motion assuming a temperature-dependent distribution of correlation times, this simple model does not hold for the pyridyl group. Theoretical expressions for ^{1}H and ^{13}C relaxation rates have been derived to interpret the anisotropic motion of this group undergoing oscillations of limited amplitude about the N–C_4 axis. The length and orientation of all internuclear vectors have been computed for the different triads included in rrmrr and rrrmr sequences. In these calculations the oscillation amplitude α of the pyridyl ring, its temperature dependence, the relevant activation energy E_G, as well as the activation energy E_R of the isotropic motion of a segment of the macromolecular chain were taken as adjustable parameters. The best consistency between the relaxation data at different frequencies was given by $E_G \simeq 3$ kcal mol^{-1}, $E_R \simeq 4$ kcal mol^{-1}, and $50° < \alpha < 80°$.

(I) Introduction

Most of the recent NMR works on the molecular dynamics of polymers in solution have been performed by T_1 and T_2 relaxation times and nuclear Overhauser effect measurements on ^{13}C.[2-12] The T_2 relaxation time cannot be determined with sufficient accuracy whenever the NMR line width is due to an unresolved fine structure as in the case of most of the atactic polymers. The nuclear Overhauser effect of ^{13}C appears as a subsidiary method of studying the molecular motion in the domain of correlation times of 10^{-10} to 10^{-8}s, characteristic of many polymers in solution, but is the less accurate of the relaxation methods and its use is not essential if T_1 measurements may be done at different spectrometer frequencies. Although difficult to interpret, the proton spin-lattice relaxation provides information on the molecular motions and local conformations of polymers since it strongly depends on interproton distances.

In the present work, the ^{13}C and ^{1}H spin–lattice relaxations of atactic poly(4-vinylpyridine) (P4VP) in methanol solution have been studied as a function of temperature at 25 MHz and 100 and 250 MHz, respectively, in order to compare the segmental motion with that of the same polymer quaternized by H^+ and alkyl bromides which will be reported hereafter. The relaxation data have been interpreted with the help of a theoretical model of restricted motion derived from a previous study on molecular motions in the solid state.[13] Although a previous work on poly(2-vinylpyridine) (P2VP) has shown that ^{13}C relaxation is virtually independent on the polymer tacticity,[11] this is not expected to be true for ^{1}H relaxation so that we have carried out some conformational energy calculations to determine the interproton distances in the most typical sequences of an atactic polymer.

(II) Experimental Procedure

The 4-vinylpyridine from Fluka was distilled twice under reduced pressure in the presence of calcium hydride. The polymerization initiated by azobis(isobutyronitrile) was performed under vacuum in methanol solution at 60 °C. The polymer was recovered and purified by successive precipitation by ethyl ether from methanol solutions. The molecular weights were determined by viscosimetry of ethanol solutions at 25 °C using the relation of Berkowitz et al.[14] The molecular weights of the polymers under study were 75 000, 132 000, 150 000, and 222 000. The NMR experiments were performed in Fourier transform with a Cameca TSN 250 spectrometer (ν_H 250 MHz) and a Varian XL100-12 WG spectrometer ($\nu_{^{13}C}$ 25.15 MHz, ν_H 100 MHz). The T_1 relaxation times were measured by inversion recovery (180°–τ–90° sequence) or in the case of ^{13}C by the Freeman and Hill[15] sequence ($90°_\infty, t \gg T_1, 180°, \tau, 90°, \ldots$). The recovery time between two sequences was taken at least five times longer than the estimated value of T_1 given by preliminary experiments. All measurements were done in CD_3OD solutions, the magnetic field being locked on the deuterium resonance. The ^{13}C NMR spectra were recorded under complete noise decoupling of protons. All T_1 mea-