

¹³C n.m.r. investigation of the microdynamics of poly(vinyl butyral)

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To investigate the microdynamics of poly(vinyl butyral) in solution ¹³C nuclear magnetic resonance measurements were performed at 22 and 63 MHz. Relaxation parameters (T_1 , NOE) of CH, CH₂ and CH₃ groups were analysed using a symmetrical correlation time distribution and a defect diffusion model to describe the molecular motion. The set of fitting microdynamical parameters—the most probable correlation time and the parameter of correlation time distribution width and the isotropic motion correlation time and the mean time of local reorientation—was determined and discussed.

(Keywords: polymer physics; nuclear magnetic resonance; dielectric spectroscopy; poly(vinyl butyral); local molecular motion)

INTRODUCTION

High resolution nuclear magnetic resonance (n.m.r.) of solutions can be used to study the composition and configurative sequence microstructure, and the constitution and the microdynamics in relation to the conditions of synthesis and to the physicochemical properties and applications of the polymer. Therefore it can make an important contribution to polymer research and to the development of new macromolecular materials.

The dynamics of a polymer chain is a complicated phenomenon caused by global motions and localized modes of some segments. Information on both types of motion can be obtained using n.m.r. This paper reports investigations of the microdynamics of a poly(vinyl butyral) (PVB). The aims of this study were to support the assignment of the signals in the ¹³C n.m.r. spectra and to obtain preliminary information on the microdynamical behaviour of PVB in solution.

EXPERIMENTAL

¹³C n.m.r. spectra were obtained with a Bruker HX-90R spectrometer, equipped with a BNC 12 computer, at 22.635 MHz and with a Bruker WM 250 spectrometer, equipped with an ASPECT 2000 computer, at 62.896 MHz.

Selective relaxation times, T_1 , were determined by the inversion recovery technique at both frequencies and selective nuclear Overhauser enhancement (NOE) factors were determined by comparing the peak areas in the broad band decoupled spectrum and the spectrum measured with the inverse gated technique. Peak areas were determined by planimetry which is believed to be more accurate than instrumental integration. The error of T_1 is ~10% and that of NOE is ~20%.

The sample used was a commercial poly(vinyl butyral) with a degree of acetalation of 35 mol%¹. Acetone-d₆

was used as the solvent. The concentration of the PVB solution was 10% (w/v). The chemical structure of PVB is shown in *Figure 1* together with a 63 MHz ¹³C n.m.r. spectrum. Spectra were obtained at room temperature. The chemical shifts were referenced to the methyl carbon signal of hexamethyldisiloxane at 1.912 ppm.

Dielectric measurements of the polymer solution were performed by time domain spectroscopy^{2,3}. The dipole correlation function was obtained and divided into exponential components.

THEORY

The parameters of ¹³C relaxation in polymers can be described by well-known expressions⁴:

$$T_1^{-1} = \frac{1}{10} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r_{CH}^6} \times N[6J(\omega_H + \omega_C) + 3J(\omega_C) + J(\omega_H - \omega_C)] \quad (1)$$

$$\text{NOE} = 1 + \frac{\gamma_H}{\gamma_C} \frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{6J(\omega_H + \omega_C) + 3J(\omega_C) + J(\omega_H - \omega_C)} \quad (2)$$

where $\gamma_{H,C}$ are the gyromagnetic ratios, μ_0 the permeability of free space, \hbar is Planck's constant divided by 2π and r_{CH} is the bond length.

To express the spectral density, $J(\omega)$, it was suggested that the polymer ¹³C-¹H vector reorientation can be described by a non-exponential correlation function. The non-exponential behaviour can be explained by two different approaches. The first is purely phenomenological and uses the concept of correlation time distribution. If the distribution is of homogeneous nature, i.e. each individual relaxator performs the same but complicated motion, then the averaged orientational correlation function can be expressed using the correlation time

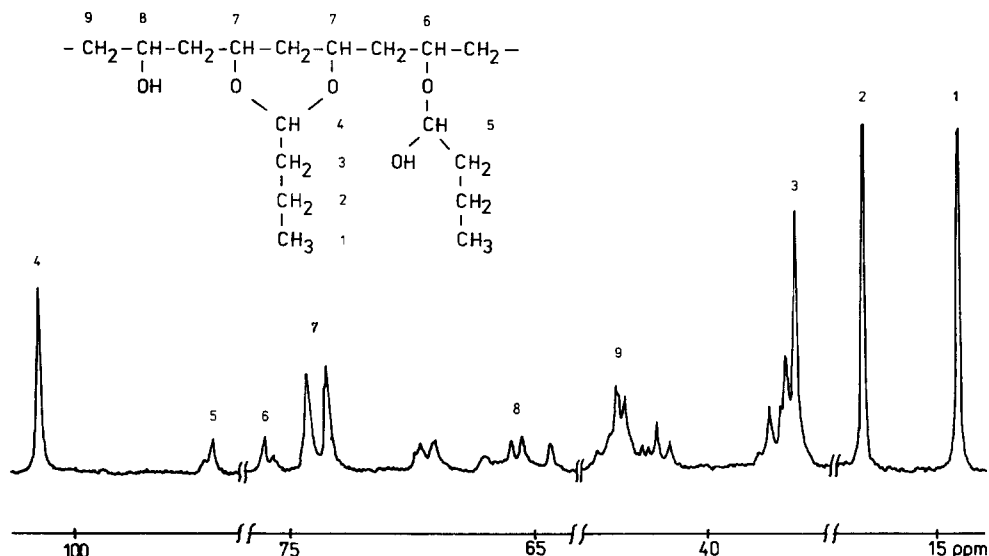


Figure 1 ^{13}C n.m.r. spectrum of PVB. The line assignment is shown on the chemical structure

distribution $\rho(\tau/\tau_0)$ by⁵:

$$\phi(t) = \int_0^\infty \rho(\tau/\tau_0) \exp(-t/\tau) d\tau \quad (3)$$

and $J(\omega)$ can be calculated by⁵:

$$J(\omega) = \int_0^\infty \rho(\tau/\tau_0) \frac{\tau}{1 + (\omega\tau)^2} d\tau \quad (4)$$

and, therefore, the decay of the longitudinal magnetization is purely exponential:

$$A_1(t) \sim \exp(-t/T_1) \quad (5)$$

An inhomogeneous correlation time distribution, i.e. a non-exponential decay of longitudinal magnetization, was not found and was therefore not considered.

For the fit of the experimental data, the symmetrical distribution of correlation times by Fuoss-Kirkwood (FK) has been chosen⁶:

$$\rho(\tau/\tau_0) = \frac{2\alpha}{\pi\tau} \cos\left(\frac{\pi}{2}\alpha\right) \frac{(\tau/\tau_0)^\alpha + (\tau_0/\tau)^\alpha}{(\tau/\tau_0)^{2\alpha} + (\tau_0/\tau)^{2\alpha} + 2\cos(\pi\alpha)} \quad (6)$$

where τ_0 and α are the most probable correlation time and the width parameter of the distribution, respectively. The corresponding $J(\omega)$ following from equations (4) and (6) is:

$$J(\omega) = \frac{\alpha}{\omega} \frac{(\omega\tau_0)^\alpha}{1 + (\omega\tau_0)^{2\alpha}} \quad (7)$$

Calculations with other symmetrical or unsymmetrical distributions like the modified FK distribution⁵ did not provide better results. This means that the distribution of correlation times by FK could describe the qualitative effects of the motional behaviour. Therefore this distribution has been chosen because of its simple expression for $J(\omega)$. Thus, using the phenomenological approach, the longitudinal magnetization decay can be calculated using equations (1), (5) and (7).

The second approach, is based on special models for the motion of each individual relaxator and permits the direct determination of an analytical expression for the correlation function. Because of the limited number of data, only simple models could be chosen. It was not

possible to use the model of Dejean de la Batie *et al.*⁷ which explains the ^{13}C relaxation behaviour of polymers in solution in terms of a defect diffusion model and rapid C-H vector 'libration' about a cone. Therefore a two-component conformation jump model (defect diffusion) has been applied⁸⁻¹⁰ which is characterized by relatively fast diffusion of defects, i.e. transport of orientation along the chain (τ_D) and by reorientation of larger parts of the chain (τ_0), e.g. under the influence of surroundings, without transport of orientation. The correlation function is then⁸:

$$\phi(t) = \exp(-t/\tau_0) \exp(t/\tau_D) \operatorname{erfc}(t/\tau_D)^{1/2} \quad (8)$$

where erfc is the complementary error function.

The corresponding $J(\omega)$ is^{10,11}:

$$J(\omega) = \frac{\tau}{1 + (\omega\tau)^2} \times \left\{ \left(\frac{\tau_0}{2\tau_D} \right)^{1/2} \frac{1}{K} [\omega\tau(K-1)^{1/2} - (K+1)^{1/2}] + 1 \right\} \quad (9)$$

where $\tau^{-1} = \tau_0^{-1} + \tau_D^{-1}$ and $K = (1 + \omega^2\tau_0^2)^{1/2}$.

Using this defect diffusion model, the longitudinal magnetization decay can be calculated using equations (1), (5) and (9). For the calculation of the NOE factor an analogous treatment can be applied.

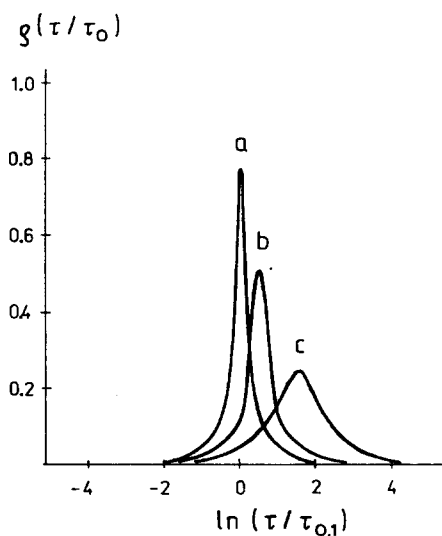
DISCUSSION

To fit the experimental data (T_1 , NOE) to the theoretical expressions [equations (1) and (2)] with fitting parameters τ_0 , α and τ_0 , τ_D , respectively, a function minimizing procedure involving the polyhedron deformation method¹² was used. In most cases the results were independent of initial conditions, so they may be considered as single sets of parameters describing experimental data with appropriate small errors. The results are given in *Table 1* together with some experimental data.

To characterize the motion of the CH_3 and CH_2 side chain groups, the correlation time distribution approach was chosen. It seems to be more appropriate than the defect diffusion model because of the relatively good

Table 1 Experimental data and calculated parameters

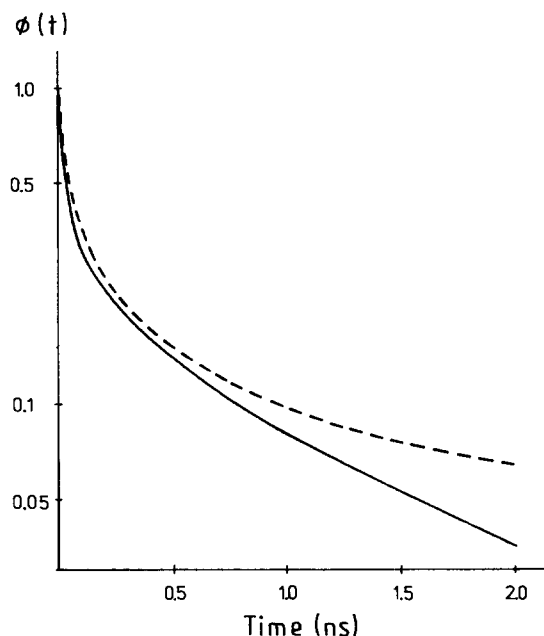
No.	Chemical shift (ppm)	Group	Experimental data			Correlation time distribution		Defect diffusion model	
			T_1^a (s)	T_1^b (s)	NOE ^b	τ_0 (ps)	α	τ_0 (ns)	τ_D (ps)
1	14	CH ₃	1.41	1.49	2.52	6.2	0.89	—	—
2	18	CH ₂	1.24	1.15	2.02	9.9	0.83	—	—
3	36	CH ₂	0.27	0.39	1.97	30.5	0.70	—	—
4	102	CH	0.22	0.33	2.01	78	0.51	2.4	49
5	95	CH	0.21	0.30	1.98	91	0.52	2.1	62
6	76	CH	0.20	0.31	2.20	102	0.58	1.7	69
7	74	CH	0.21	0.29	2.08	106	0.58	1.6	75
7 ^c	73	CH	0.18	0.29	1.93	107	0.47	3	71
8	66	CH	0.16	0.33	2.05	94	0.37	17	69
8 ^c	64	CH		0.34	1.91	99	0.32	13	66
9 ^c	45	CH ₂	0.11	0.17	1.96	64	0.45	2.8	42
9	44.6	CH ₂		0.18	2.11	61	0.47	2.8	45

^a At 22.6 MHz^b At 63 MHz^c Peak of the syndiotactic sequence**Figure 2** Distributions from the correlation time distribution model for (a) CH₃ (1 in Figure 1), (b) CH₂ (2 in Figure 1) and (c) CH₂ (3 in Figure 1). The parameters of the distributions are: (a) $\tau_{0,1}$ = 6.2 ps, α = 0.89; (b) $\tau_{0,2}$ = 9.9 ps, α = 0.83; (c) $\tau_{0,3}$ = 30.5 ps, α = 0.70

mobility of such groups. Some corresponding distributions are shown in Figure 2.

Figure 3 presents the two correlation functions of the CH side chain (4 in Figure 1) which have been calculated using two parameter sets derived from the same experimental data; τ_0 and α from equation (3) and τ_0 and τ_D from equation (8). It can be seen that there are some differences between the two functions, however, they are small enough to be indistinguishable in n.m.r. data analysis. This means that the determination of one of these two correlation functions is not possible in this case. Therefore a further investigation by an additional independent method, as in the following case, was not necessary.

The experimental data of main chain groups were fitted to both the defect diffusion model and the correlation time distribution approach. The parameters of correlation time distribution width α were very small ($\alpha \leq 0.6$). This means that a wide distribution of correlation times from

**Figure 3** Correlation functions of CH (4 in Figure 1). ---, Correlation time distribution model with τ_0 = 78 ps, α = 0.51; —, conformation jump model with τ_0 = 2.4 ns, τ_D = 49 ps

~0.01 ps to 1000 ns would exist in some cases. This seems to have no real physical significance. On the other hand, the description of the motion along the chain by a diffusional model seems to be physically reasonable. A comparison of the mean correlation functions of both approaches (calculated from the correlation functions of CH groups in the main chain according to the chemical composition of the polymer) shows that they differ strongly, especially for longer times (≥ 2 ns). To decide which of the approaches is better for main chain groups, an independent method would be useful. Here dielectric spectroscopy was used. The frequency range of dielectric spectroscopy (0.2 MHz–3 GHz) is wider than that of n.m.r. spectroscopy. This means that the form of the correlation function is better described up to longer times than in n.m.r. spectroscopy. So the comparison with the

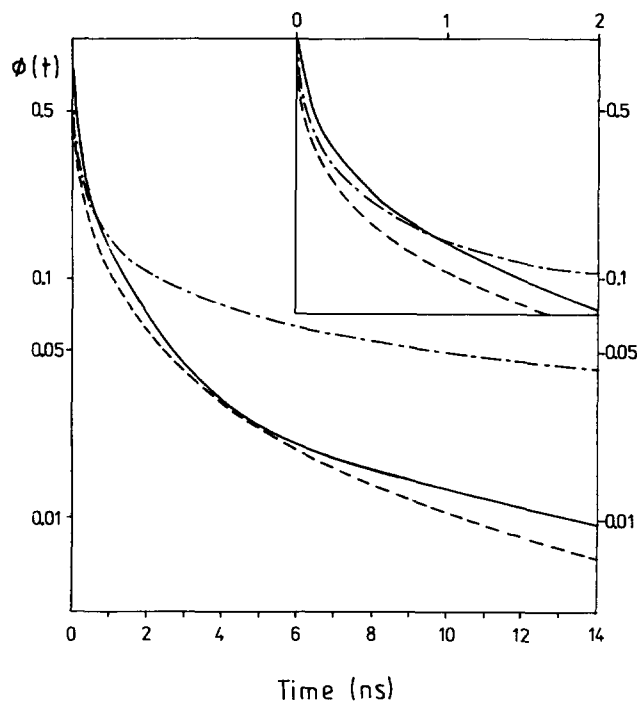


Figure 4 Mean correlation functions of the CH groups in the polymer backbone. —·—, Correlation time distribution model; ---, conformation jump model; —, correlation function from dielectric spectroscopy

behaviour of n.m.r. correlation functions at longer times (≈ 10 ns) could be a further criterion of the selection of one model. For a better comparison of the n.m.r. correlation functions with the behaviour of the dielectric correlation function the dielectric correlation times have been divided by a factor of 3 (because in dielectric spectroscopy first order spherical harmonics are used instead of second order as in n.m.r.¹³).

The three correlation functions are presented in *Figure 4*. The dielectric correlation function shows a similar course to the n.m.r. curve of the defect diffusion model, even for longer times. Therefore, the model of defect diffusion was chosen for the description of motional behaviour of backbone groups. The similar course of the time domain spectroscopy and defect diffusion correlation functions demonstrates that both methods yield equivalent information about the motional behaviour. The relatively small differences are caused by the different processes (motional behaviour of dipoles and internuclear vectors, respectively) investigated by the two methods. The main advantage of the n.m.r. method is the selectivity of information about the motional behaviour.

Molecular motion of side chain groups

The molecular motion of the two CH_2 and the CH_3 groups in the side chain of the acetals and the semi-acetals can be described by a correlation time distribution. Fitting parameters of this model show that the most mobile group, the group with the shortest correlation time and the narrowest correlation time distribution, is the CH_3 group (1 in *Figure 1*). With decreasing distance between the group considered and the backbone, the correlation time increases and the parameter of the correlation time distribution width, α , decreases, i.e. the distribution becomes wider (*Figure 2*). This means that the larger the distance of the considered group from the

polymer backbone the faster its molecular motion and the narrower its correlation time distribution. The reason for this behaviour is a progressive increasing of motional restriction by the neighbouring groups from the CH_3 end group to the backbone of the polymer. The result is not only a slower motion but also a more complicated type of motion which can be characterized by a broader correlation time distribution.

Molecular motion of CH and CH_2 groups in the polymer backbone

For the description of the local molecular motion of CH and CH_2 groups in the backbone the defect diffusion model was chosen. The correlation times, τ_D , characterizing the relatively fast anisotropic diffusion of defects, e.g. the transport of orientation along the chain, and τ_0 characterizing the reorientation of relatively large chain regions under the influence of surroundings are discussed. To estimate the error of calculated correlation times the correlation times for the experimental parameters with maximal errors were determined. It was shown that the error of correlation times is $\sim 20\text{--}30\%$. In those cases where only two experimental parameters (T_1 and NOE at 63 MHz) were determined because of the inadequate resolution of the spectra at 22 MHz for selective measurement of T_1 values, the parameter fitting does not yield unambiguous results and therefore these groups are not discussed. This includes all CH_2 groups with the exception of the CH_2 group of the vinyl alcohol unit (9 in *Figure 1*).

CH groups

The two CH groups in the side chain of the acetals (4 in *Figure 1*) and semi-acetals (5 in *Figure 1*) show interesting behaviour. It was found that the motion of these groups can be described by both models, by correlation time distribution with a broad distribution ($\alpha \approx 0.5$), and by the defect diffusion model (*Figure 3*). The fitting parameters of the two groups do not differ much; the mobility and the motional behaviour of the two groups are therefore comparable.

The correlation time τ_D of the CH groups in the backbone is nearly the same for all groups. This means that their local mobility is of the same kind. Remarkable differences were found for the correlation time τ_0 of these CH groups. The correlation time τ_0 of the CH group of the vinyl alcohol unit (8 in *Figure 1*) is much longer than that of the CH groups of the acetal (7 in *Figure 1*) and semi-acetal (6 in *Figure 1*). This distinction is caused by hydrogen bonds which are formed between the hydroxyl groups of the vinyl alcohol units and the solvent. This effect was not found for the hydroxyl group of the semi-acetal because the steric hindrance is too large for the formation of hydrogen bonds. The correlation time τ_0 of the CH groups of the acetal and the semi-acetal is of the same order. This means that the reorientations in the region of these groups under the influence of their surroundings are comparable. The reorientations in the vinyl alcohol region are more restricted because of hydrogen bonds. Two of the CH groups in the main chain show in the spectrum a tacticity splitting—the CH group of the vinyl alcohol unit (8 in *Figure 1*) and the CH group of the acetal (7 in *Figure 1*). The difference between the correlation times of the iso- and syndiotactic sequence of the vinyl alcohol are very small so that one can conclude that no tacticity effect exists. In the case of

the CH groups of the acetal (7 in *Figure 1*), the correlation time τ_D of the iso- and syndiotactic ring structures do not differ, but a difference between the correlation times τ_0 of the iso- and syndiotactic ring structures was found. This means that one of these structures is more rigid relative to a motion within the chain. The assignment of the tacticity splitting of this CH group was not clear till now. It is known that the isotactic ring is energetically favoured in comparison with the syndiotactic ring and that the syndiotactic ring is more strained¹⁴. Assuming a connection between the longer correlation time τ_0 and the greater rigidity of the syndiotactic acetal ring, the results of microdynamical measurements could be used to assign the tacticity splitting—the lines at 74 and 73 ppm correspond to the iso- and syndiotactic ring structures, respectively.

CH₂ groups

As mentioned above, the correlation times τ_0 and τ_D were determined for only one CH₂ group. This group, the CH₂ group of the vinyl alcohol (9 in *Figure 1*), shows a tacticity splitting in the spectrum. However, no tacticity dependence of the correlation times was found. The mobility of the CH₂ groups in iso- and syndiotactic sequences of vinyl alcohol is the same.

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