that the results are quite sensitive for the value of K and that the permeability curves, from which K is derived, are not at all the same for the two systems considered[3,4]. When $[\eta]$ and f for system B are calculated on using K values derived from the permeability curve pertaining to system A the results are wrong by a factor of about 3.

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Proton spin–lattice relaxation in poly(vinyl acetate) in solution

In a recent paper[1], it was shown that proton–lattice relaxation measurements of polymers in solution were able to discriminate between various models for polymer motion which were equally successful in interpreting ^{13}C relaxation data[2]. It was found that the conformational jump dynamic model[3] of polymer motion combined with overall molecular tumbling[4] was the only model (of those considered) which explained all the experimental data consistently over a wide temperature range. The advantage of the ^1H relaxation measurements over ^{13}C measurements lay in their ability to sense spectral density functions at both low frequencies of the order of ^1H–^1H chemical shifts and high frequencies of the order of the instrumental frequency. It is desirable to test the validity of the conformational jump model further by making measurements at different operating frequencies. In this communication we therefore report proton relaxation data at 100 MHz for a solution of poly(vinyl acetate) in toluene-d_8 of concentration 134 mg/ml. Relaxation data at 300 MHz for this system has been reported earlier[1,5].

Two correlation times, τ_D and τ_0, determine the correlation function for the conformational jump model[3,4]. τ_D characterizes the local jumps of a chain on a tetrahedral lattice[3], and τ_0 characterizes the overall molecular tumbling[4]. Using procedures outlined previously[1], it is possible to obtain both correlation times, subject to certain restrictions, from the results of several types of relaxation experiments. These are[1]: (a) effective relaxation times of methine (A) and methylene (X) protons in the normal non-selective inversion recovery technique ($\pi-\tau-\pi/2$), denoted $T^{\rm eff}_{1A}$ and $T^{\rm eff}_{1X}$, (b) relaxation times for the A protons when X is decoupled (T_{AA}) and and *vice versa* (T_{XX}); (c) nuclear Overhauser enhancements of each type of proton when the other is saturated, η_A and η_X.

From the experimental data at 300 MHz, the values of τ_D and τ_D/τ_0 given in the second and third columns of *Table 1* have been derived[5]. At certain temperatures, a considerable range of values of τ_D and τ_0 fit the data satisfactorily. The remaining columns in *Table 1* compare the experimental parameters for the methine nucleus at 100 MHz with the corresponding values calculated[1] using these correlation times. Unfortunately at the lower frequency the overlap of methyl and methylene resonances is too severe to allow accurate measurement of the methylene relaxation times. The agreement between experimental and calculated values is quite good, allowing for respective uncertainties of the order of 10% and 30%. The two-parameter conformational jump model thus satisfies the frequency variation of relaxation times.

The temperature variations of τ_D and τ_0 for this sample parallel those for a less concentrated sample[1] of 17 mg/ml. τ_0 obeys an Arrhenius equation (within experimental error) with an activation energy of 12 ± 2 kJ/mol, while τ_D appears to undergo a rapid transition from values less than τ_0 to values greater than τ_0. At temperatures greater than about 10°C, the autocorrelation function decay is dominated by segmental motion, but at lower temperatures, the decay is dominated by overall tumbling. The values of τ_D at higher temperatures are essentially the same as those for the lower concentration[1], consistent with a local short-range reorientation process. The values of τ_0 are however significantly larger than those for the lower concentration, as expected for a large-scale motion likely to be more responsive to bulk solution viscosity.

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Table 1 Relaxation data for poly(vinyl acetate) in toluene-d_8, concentration 134 mg/ml. The correlation times are those obtained from data at 300 MHz[1,5]. The relaxation times predicted at 100 MHz for these correlation times are compared with the experimental values

			Calculated			Experimental		
T (°C)	τ_D (psec)	τ_D/τ_0	$T^{\rm eff}_A$ (msec)	T_{AA} (msec)	η_A	$T^{\rm eff}_A$ (msec)	T_{AA} (msec)	η_A
84	0.061	0.06	400	440	0.29	360	380	–
48	0.154	0.1	275	300	0.23	240	260	0.2
16	1.33	0.3	170	170	–0.05	190	190	0.0
	1.0	0.4	170	180	0.1			
5	4.22	1.0	160	150	–0.13	180	170	–0.1
	2.56	10.0	130	130	–0.06			
–23	56.2	10.0	160	120	–0.45	180	130	–0.55
	394.0	100.0	150	120	–0.35			
–40	700	100.0	200	100	–0.66	240	70	–0.75