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Dielectric and NMR Relaxation of Poly(methyl vinyl ketone) in Dilute Solution

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ABSTRACT: Complex permittivities of poly(methyl vinyl ketone) in dioxane solution were measured at 20 °C over a wide frequency range extending from 1 MHz to several gigahertz by time-domain reflectometry. Two relaxation peaks were found, one at a frequency of 50 MHz and the other at 1 GHz. The lower frequency dispersion is assigned to a local conformational transition in the chain backbone, and the higher frequency dispersion to internal rotation of the side acetyl group. The backbone motions were also observed by ^{13}C spin–lattice relaxation.

I. Introduction

Solid amorphous polymers usually exhibit two (and occasionally more than two) regions of dielectric dispersion.[1-3] The slower (α) process becomes immeasurably slow in the glassy state, is thus related to motions of the polymer chain backbone, and accordingly follows WLF-type temperature dependence. In contrast, the more rapid (β) process is, at ordinary frequencies, usually observed below the glass temperature and follows Arrhenius temperature dependence. When the temperature is raised or the system diluted, the characteristic average relaxation times of the two processes approach each other, and frequently the two loss peaks merge into a single dispersion region, often dubbed $\alpha\beta$. If the polymer chains bear flexible polar side groups, it is natural and surely correct to relate[4] the β process to motions involving such side groups. However, the β dispersion has also been seen[1] in systems for which all dipoles are rigidly fixed to the main chain. Further, the relative strength of the two dispersions is not simply a function of the molecular geometry: for example,[1] for poly(methyl acrylate) $\Delta\epsilon_\alpha > \Delta\epsilon_\beta$, but under some conditions the reverse is true for poly(methyl methacrylate).

In dilute solution,[3] barring only those rare species carrying longitudinal dipoles within each repeat unit,[5-7] only a single absorption peak has been found (as far as we are aware) in all polymers, whether or not they have flexible polar side groups; it thus seems likely that in the latter case the backbone and sidechain motions are strongly enough coupled so that a merged $\alpha\beta$ type of process is being observed. The loss peak in solution usually falls in the frequency range from 1 MHz to 1 GHz, which in the past has posed relatively formidable experimental difficulties, and thus the existing data are both sparse and of limited precision. With the advent of recent improvements[8-10] of the time-domain reflectometry method, it seemed worthwhile to search anew for some evidence of a side-group dispersion, since absorptions with $\epsilon_{\max}''$ of the order of 0.01 can now be easily and accurately measured in just the previously difficult frequency range. In the present investigation, we elected to study a dilute dioxane solution of poly(methyl vinyl ketone), which according to semiempirical conformational energy calculations[11] should offer unusually low impedance to side-group motions. We indeed observe two partially overlapping dielectric loss peaks, one of which can confidently be ascribed to motions of the side acetyl groups. The main-chain motions have also been probed by ^{13}C spin relaxation measurements.

II. Experimental Section

The sample of PMVK was the same one used earlier[12] to determine the equilibrium dipole moment: presumably of atactic head-to-tail structure, it had a viscosity-average molecular weight of about 1×10^6. Dioxane was dehydrated and distilled before use. Dioxane-d_8 (99%, Aldrich) for the NMR measurements was used as received.

The TDR apparatus and the methods of making the measurements are described in detail in previous papers.[8-10] Here we applied the difference method, which is very useful for measurement of the small difference between a dilute polymer solution of permittivity ϵ_x^* and the reference solvent of permittivity ϵ_s^*. The relation between these quantities at a circular frequency ω is

$$\epsilon_x^* = \epsilon_s^* \frac{(v_0 - r_s) + (r_s - r_x)}{(v_0 - r_s) - i\omega(\gamma d_c/cf_2)(r_s - r_x)} \frac{f_x}{f_s} \tag{1}$$

where v_0, r_s, and r_x are the Laplace transform of the incident pulse, that of the reflected pulse from the known solvent, and that of the reflected pulse from the unknown solution, respectively; d_c is the length of cylindrical central conductor of the sample cell, γd_c the effective length of the conductor, and c the speed of propagation in vacuo (0.300 mm/ps). The function f is given by

$$f = z \cot z \tag{2}$$

where $z = (\omega d_c/c)\epsilon^{*1/2}$ and accounts for propagation and multiple reflection in the sample. The difference between the reflected pulse from the solvent and that from the solution was evaluated before transformation to give $r_s - r_x$ for precision measurements.

Equation 1 places a definite restriction on the choice of the cell length,[3] because f diverges at $|z| = \pi/2$ and eq 1 is hence useful only for $|z| < 1$. Therefore we chose d_c = 20 mm for the measurement from 1 MHz to 1 GHz and d_c = 5.0 mm for 0.1 GHz to several gigahertz.

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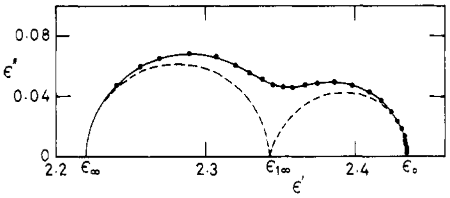

Figure 1. Dielectric dispersion and loss curves for a 4.21% (w/w) solution of PMVK in dioxane at 20 °C. The curves are calculated from eq 3 with the parameters given in Table I.

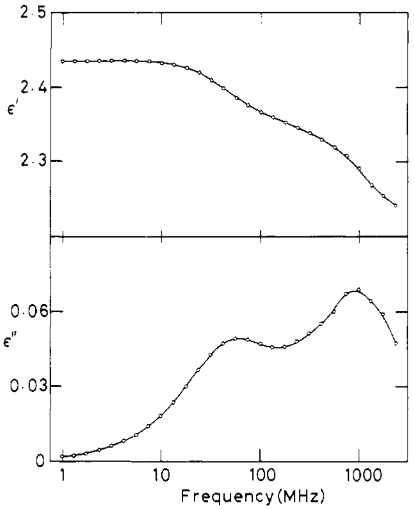

Figure 2. Complex permittivity plot corresponding to Figure 1. Dashed curves for the two separate relaxations are calculated from eq 3.

Spin-lattice relaxation times T_1 and nuclear Overhauser enhancements were determined at a frequency of 15.04 MHz in a JEOL 60Q spectrometer. The methods of preparing solutions and carrying out the measurements were conventional and have been described previously.[13] Estimated experimental uncertainties are 10% in T_1 and 15% in the NOE factor.

III. Results and Discussion

Dispersion and absorption curves for a 4.21% (w/w) solution of PMVK in dioxane at 20 °C are shown in Figure 1, and the corresponding Cole–Cole plot is given Figure 2. Two absorption peaks are evident, one at about 60 MHz and the other at 1 GHz, and each is not much broader than a simple Debye relaxation. For a quantitative treatment, the complex permittivity was assumed to be given as the sum of two Havriliak–Negami[14] contributions:

$$\epsilon^* = (\epsilon_s - \epsilon_m)[1 + (i\omega\tau_1)^{1-\alpha_1}]^{-\beta_1} + (\epsilon_m - \epsilon_\infty)[1 + (i\omega\tau_2)^{1-\alpha_2}]^{-\beta_2} + \epsilon_\infty \quad (3)$$

The corresponding real and imaginary parts were fitted to the experimental results by a nonlinear least-squares routine, producing the essentially quantitative agreement indicated by the full curves in Figures 1 and 2. The numerical constants are given in Table I. The parameters $\alpha_1 = 0.00$ and $\beta_1 = 0.82$ mean that the lower frequency dispersion corresponds to a not very broad Cole–Davidson process, while $\alpha_2 = 0.00$ and $\beta_2 = 1.00$ mean that the higher frequency process is Debye-like to within experimental error. The contributions from these two processes are shown as the dashed curves in Figure 2. It may be observed that the high-frequency limiting value, $\epsilon_\infty = 2.220$, is very close to the tabulated[15] static permittivity of pure dioxane at 20 °C, which is 2.218.

By analogy with the behavior of bulk amorphous polymers,[1-3] it is natural to assign the slower dispersion at 60 MHz to segmental motions of the main chain. This assignment is reinforced by the data for dilute solutions of vinyl polymers bearing only rigidly attached transverse dipoles, which are observed[3,16,17] to have a single loss peak at frequencies in the range 20–100 MHz at room temperature; for example, poly(vinyl chloride) in dioxane at 20 °C has[16] its maxium absorption at about 40 MHz. The faster observed process in PMVK at 1 GHz is then concluded to be due to the internal rotation of the side acetyl group.

Table I
Dielectric Properties of PMVK in Dioxane Solution (4.21% (w/w)) at 20 °C: Parameters of Eq 3

	ϵ_s		2.435
	ϵ_m		2.350
	ϵ_∞		2.222
	Lower Frequency Dispersion		
α_1	0.00	τ_1, ns	3.70
β_1	0.82	$\langle\mu_1^2\rangle^{1/2}$, D	1.02
	Higher Frequency Dispersion		
α_2	0.00	τ_2, ns	0.155
β_2	1.00	$\langle\mu_2^2\rangle^{1/2}$, D	1.25

The above assignment is also supported by the relative strength of the two dispersions. Effective mean square dipole moments *per repeat unit* may be calculated from the Onsager equation in the form

$$\langle\mu^2\rangle = (9k_BTM_0/4\pi N_Ad_1)(2\epsilon_s + \epsilon_u)(\epsilon_u + 2)^{-2}(\epsilon_s - \epsilon_u)/\epsilon_0 w \quad (4)$$

where M_0 is the molecular weight of the monomer unit, N_A the Avogadro number, k_B the Boltzmann constant, T the absolute temperature, d_1 the density of the solvent, and w the weight fraction of polymer. To find the effective component rigidly perpendicular to the chain backbone, $\langle\mu_1^2\rangle$, corresponding to the slower dispersion, we must take ϵ_m for ϵ_u in equ 4, while for the calculation of the effective side-chain contribution $\langle\mu_2^2\rangle$ we must use ϵ_m in place of ϵ_s and ϵ_∞ in place of ϵ_u. The dipole components thus obtained are listed in Table I, and their ratio is found to be $\langle\mu_2^2\rangle^{1/2}/\langle\mu_1^2\rangle^{1/2} = 1.2$. With a C–C–C bond angle of 116° (the value used by Suter[11]) at the carbonyl carbon atom, we should expect the ratio to be 1.6 if each acetyl group behaved independently, which is certainly far from the case. There is no simple way to take correlations into quantitative account, and we regard the fact that $\langle\mu_2^2\rangle$ exceeds $\langle\mu_1^2\rangle$ as ample confirmation of the assignment we have made.

The overall equilibrium dipole moment ratio is $D \equiv \langle\mu^2\rangle/\mu_0^2$, where μ_0 is the dipole moment of a repeat unit (taken as equal to that of methyl ethyl ketone) and $\langle\mu^2\rangle = \langle\mu_1^2\rangle + \langle\mu_2^2\rangle$. Our results give $D = 0.35$, which is in good agreement with a figure of 0.32 reported previously[12] for PMVK in the same solvent and satisfactorily explained by Suter[11] in terms of a two-state rotational isomeric model based on his semiempirical potential energy calculations. This rather low value of D indicates a high degree of negative directional correlation between neighboring dipoles.

It seems remarkable that each of the two observed dispersions is so close to being Debye-like, in view of the extensive correlations evident in the low value of D. It may also be recalled that in bulk polymers the β dispersion is usually rather broad and far from the Debye limit. In future work the effects of temperature and concentration on the dielectric behavior will be investigated, in hopes of gaining more understanding of this situation.

According to Suter's calculations,[11] hindrance to internal rotation of the side group is much greater in the higher

Table II
^{13}C Spin-Lattice Relaxation Times and Nuclear Overhauser Enhancements of PMVK in Dioxane-d_8 (15% (w/w))

temp, °C	T_1/ms (NOE)		
	CH	CH_2	CH_3
60	84 (2.4)	51 (2.4)	550 (2.9)
50	77 (2.4)	42	360
37	56 (2.3)	29 (2.3)	300 (2.4)
26	49 (1.9)	24 (2.2)	270 (2.2)

Table III
Harmonic Mean Correlation Times for Segmental Motions of PMVK in Dioxane[a]

temp, °C	τ_h/ns[b]	
	$s = 1$	$s = 3$
62	0.53	0.17
50	0.62	0.21
37	0.91	0.39
26	1.13	0.54

[a] Calculated from data of Table II with model of ref 18.
[b] Average of values for methine and methylene carbons.

poly(*n*-alkyl vinyl ketones) than in PMVK, and it seems likely that for these polymers only a single absorption would be detectable in dilute solution, as is the case with the polyacrylates, polymethacrylates, and poly(vinyl acetate).

Turning now to the NMR results, we show in Table II the observed ^{13}C spin-lattice relaxation times T_1 at various temperatures for the three types of carbon atom in a repeat unit of the polymer. The corresponding NOE factors are given in parentheses. Save possibly at the highest temperature, the T_1 values for the methine carbon are, within experimental error, twice as long as those for the methylene carbon, indicating equal participation of both groups in the important segmental rearrangements. The methyl-group results are of typical magnitude and are not of further concern here.

Mean correlation times for the backbone segmental motions have been evaluated from the data of Table II and are shown in Table III. The first set of times corresponds to a single-exponential time-correlation function, but with this model the observed NOE factors cannot be reproduced. A satisfactory fit can be achieved with a variety of models,[18] and for convenience we use the simple treatment with a sharp cutoff of intersegmental correlations ($s = 3$) that we have employed in previous work.[13,19] The derived harmonic mean times are the second set shown in Table III. It is seen that these are definitely shorter than the dielectric correlation time for the slower process 1 (see Table I). Simulation studies[20] predict a ratio of between 2 and 3 between the two times. The level of agreement obtained between the two techniques is not unlike that seen for other polymers.

From the temperature dependence of the calculated correlation times we obtain an Arrhenius activation energy of 20 ± 3 kJ mol^{-1}. Subtracting, as in the Kramers diffusion limit, a viscous-flow activation energy for dioxane of 11 kJ mol^{-1}, we derive an average barrier height of the order of 10 kJ mol^{-1} for the backbone process, a typical value for flexible chains.

Some years ago the ESR spectrum of a spin-labeled PMVK sample in dilute tetrahydrofuran solution was reported by Bullock, Cameron, and Smith.[21] The line shape, fitted with a single-exponential relaxation process, yielded a correlation time of 0.5 ns at 20 °C. If the correlation time is proportional to solvent viscosity,[17] this figure corresponds to a value of 1.3 ns in dioxane at 20 °C. The nitroxide spin label is larger than that for an acetyl group, so the extent of its rotational freedom about the connecting C–C bond is surely somewhat less than that of the acetyl group. Within this uncertainty, the agreement between ESR and dielectric results is regarded as satisfactory.

The ESR data yield[21] an activation energy in THF of 18.9 ± 0.6 kJ mol^{-1}, corresponding to a barrier height of 11.4 kJ mol^{-1}. This figure is in good agreement with our NMR result and lies among the several barriers to single-bond backbone rotations evident in the potential energy map of Suter.[11]

We plan to extend the dielectric study of PMVK to other temperatures and concentrations and also to investigate the dielectric properties of poly(*tert*-butyl vinyl ketone), a macromolecule whose conformational properties seem well understood.[22]

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Registry No. PMVK, 25038-87-3.

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