

Acoustic Relaxation and Infrared Spectroscopic Measurements of the Plasticization of Poly(methyl Methacrylate) by Water

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Synopsis

Measurements are reported on the acoustic attenuation and velocity of dry and wet samples of poly(methyl methacrylate) over a temperature range of 5° to 70°C and over a frequency range of 5 to 35 MHz. Lowering of the glass transition temperature with increase in water content was reflected in an increase in the acoustic attenuation and a lowering of the velocity at high temperature. Comparison of the infrared spectra of wet and dry thin films indicates that water exhibits spectroscopic characteristics of isolated rather than highly clustered molecules. A study of the temperature dependence of the diffusion coefficient of water into the polymer matrix provided an activation energy for the migration process. The data suggest that water plasticizes poly(methyl methacrylate) via specific local interactions with the backbone.

INTRODUCTION

The effects of plasticization on a polymer matrix by the addition of small molecules have been widely reported in the literature.¹⁻⁵ Measurements of the low-frequency mechanical properties of partially hydrated poly(methyl methacrylate) indicates that water can act as a plasticizer.⁶⁻⁸ It is, however, not very clear from these latter studies whether water undergoes specific bonding interactions, exists as clusters or as a single molecular entity, and to what extent single or groups of backbone units are involved in the polymer relaxation. This study of the acoustic relaxation, diffusion coefficients, and infrared spectra of dry and wet poly(methyl methacrylate) film was performed in an attempt to clarify the nature of the interactions between the water and the polymer.

EXPERIMENTAL

Materials. The polymers used in this study were commercial samples. The molecular weight of the polymers and their distributions were determined by gel permeation chromatography (Table I). The values are uncorrected for the finite resolving power of the columns, and the true distribution may be expected to be narrower than reported.⁹ The tacticities of the polymers were determined from the intensities of the hetero-, iso-, and syndiotactic peaks in the ¹H NMR spectrum. These latter data were obtained from solutions of the polymer in

TABLE I
 Characteristics of the Poly(methyl Methacrylate) Samples^a

	Molecular weight $M_n \times 10^4$	Distri- bution M_w/M_n	Crystal- linity, % ^c	Tacticity, %			Co- polymer % Acry- late ^b	$T_g, ^\circ\text{C}$
				s	i	h		
AI BDH	3.69	3.13	40	60	4.5	35.5	10	92
AII du Pont	1.57	2.16	33	52	6	42	—	—
AIII du Pont	14.5	3.59	50	50	5	45	2	103
AIV du Pont	3.76	2.21	50	48	12	40	4	101

^a s = Syndio, i = iso, and h = heterotactic.

^b Acrylate copolymer content estimated on the basis of the T_g shifts as determined by DSC (ref. 26). T_g estimated by scanning DSC measurements. The transition for sample AII could not be positively identified.

^c Crystallinity calculated from the measured densities.

CDCl_3 and were recorded at 100 MHz. The spectra were in good agreement with those reported in the literature.¹⁰⁻¹²

Sample Preparation. The poly(methyl methacrylate) was molded into disks of 5.0 cm diameter and approximately 5 mm thickness by pressing at 140°C for 8 hr at a pressure of 1.4 MN/m². Thin films used for the infrared studies were solvent cast from chloroform solution and were typically between 0.03 and 0.1 mm thick.

Diffusion Measurements. The disks prepared as indicated above were submersed in a thermostated container of deionized water held at the temperature of measurement. The disks were weighed to a precision of ± 0.0005 g, the sample having been carefully dried to remove excess moisture. The disks

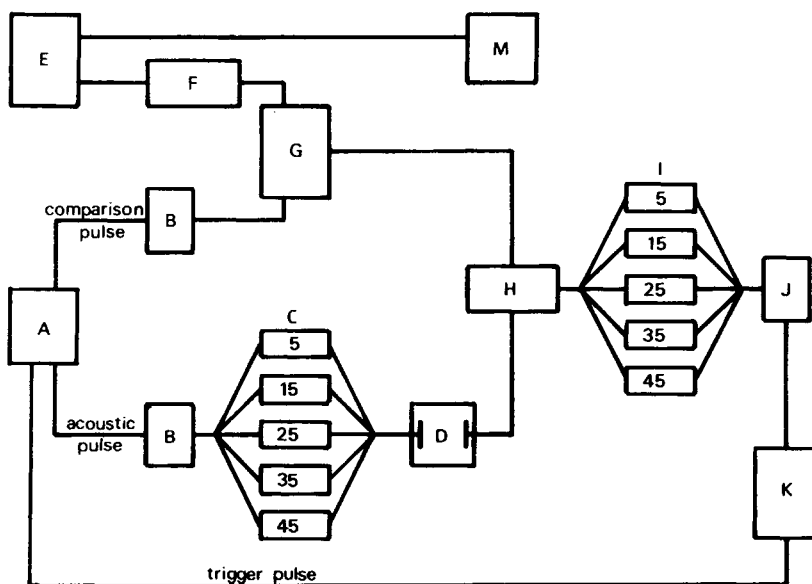


Fig. 1. Block diagram of the complete acoustic attenuation and velocity measurement system: (A) 1 KHz pulse generator; (B) pulse amplifier; (C) tuned oscillators; (D) acoustic cell; (E) reference oscillator; (F) calibrated attenuator; (G, H) impedance matchers; (I) tuned amplifiers; (J) video amplifier; (K) oscilloscope; (M) frequency meter.

weighed approximately 15 g, and an uptake of 2% water led to a change in weight of 0.3 g. Measurements were performed at 16°, 38°, 60°, and 100°C. Swelling of the disk was estimated to be less than 0.1% below 70°C. Above this temperature, equilibrium was difficult to achieve, and swelling accompanied by cracking and softening was observed.

Acoustic Measurements. The ultrasonic attenuation and velocity in the polymer disks were measured using a technique similar to that described by Waterman,¹³ Figure 1. The longitudinal waves from the 5-MHz quartz transducer were coupled to the goniometer-mounted sample by immersion in a bath of deionized water, thermostated to $\pm 0.2^\circ\text{C}$. Prior to measurement, the samples were vacuum dried for 16 hr at 30°C or until no further weight decrease was observed. The experiments lasted approximately 6 hr, and water immersion only occurred for the short period required to obtain the measurements. On no occasion was the sample left in the water for any appreciable period of time and the concentration of water was observed to change by less than 0.1% during the course of the complete temperature scan. The acoustic pulse was approxi-

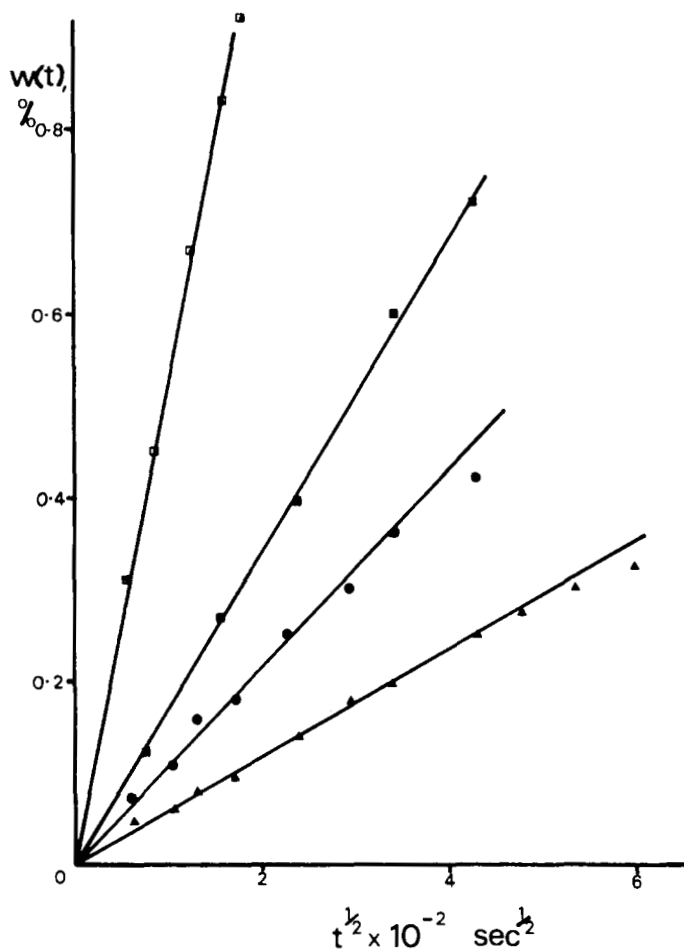


Fig. 2. Rate of water uptake in predried poly(methyl methacrylate) disks pressed from polymer AI: filled triangles, 289°K; filled circles, 311°K; filled squares, 333°K; open squares, and dots, 373°K.

mately 20 volts in amplitude and provided an elastic wave of intensity 0.05 watts/cm². The attenuation was determined by measurement of the rectified signal amplitude with and without sample, corrections being made for the reflections at the polymer-liquid interfaces.¹⁴ The velocity was determined using the critical angle technique.

Infrared Spectroscopic Measurements. The spectra of thin films and disks were recorded using Perkin-Elmer 125 and 257 grating spectrometers and an Optica UV/visible/near-IR grating spectrometer, the latter being used to avoid the effects of sample heating experienced with the other spectrometers. Attenuated total reflection spectra were obtained using an RIIC TR-9 attachment with KRS-5 plates.

RESULTS AND DISCUSSION

Diffusion Experiments

The diffusion data, Figure 2, were analyzed using Fick's law:¹⁵⁻¹⁷

$$\frac{W(t)}{W(t = \infty)} = \frac{4}{d} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (1)$$

where $W(t)$ and $W(t = \infty)$ are, respectively, the increase in weight at time t and time infinity; d is the sample thickness, and D is the diffusion coefficient. D was calculated from the initial slope of the graph of sample weight increase against square root of immersion time, and thus both it and the activation energy were averaged over the concentration range investigated.^{18a} D has shown to be independent of molecular weight for M_n between 45,000 and 1,615,000 at 37°C.¹⁸ The temperature dependence of D , Table II, gave an activation energy of 38.5 ± 2.2 kJ/mole. These data agree well with those previously reported in the literature for poly(methyl methacrylate).¹⁹⁻²²

Acoustic Measurements

The acoustic absorption and velocity measurements for dry and wet samples agree well with those reported in the literature.^{23,24} It is clear from Figure 3 that the temperature dependence of the attenuation depends on molecular weight, tacticity, and copolymer content. The increase in absorption of the 16,000 molecular weight sample against the 145,000 sample is indicative of the effects of endgroup rotation on the temperature-frequency position of the backbone relaxation process.²⁵ In a solid polymer, the chain ends are less constrained than the chain centers and thus undergo the comparatively large-scale motion associated with the glass transition at a lower temperature. If the ultrasonic at-

TABLE II
Diffusion Coefficients of Water in Poly(methyl Methacrylate)

Temperature, °K	Diffusion coefficient, (cm ² /sec) × 10 ⁹	Equilibrium composition, wt-% H ₂ O
289	4.41	2.15
311	16.1	2.15
333	43.9	2.15
373	150	7

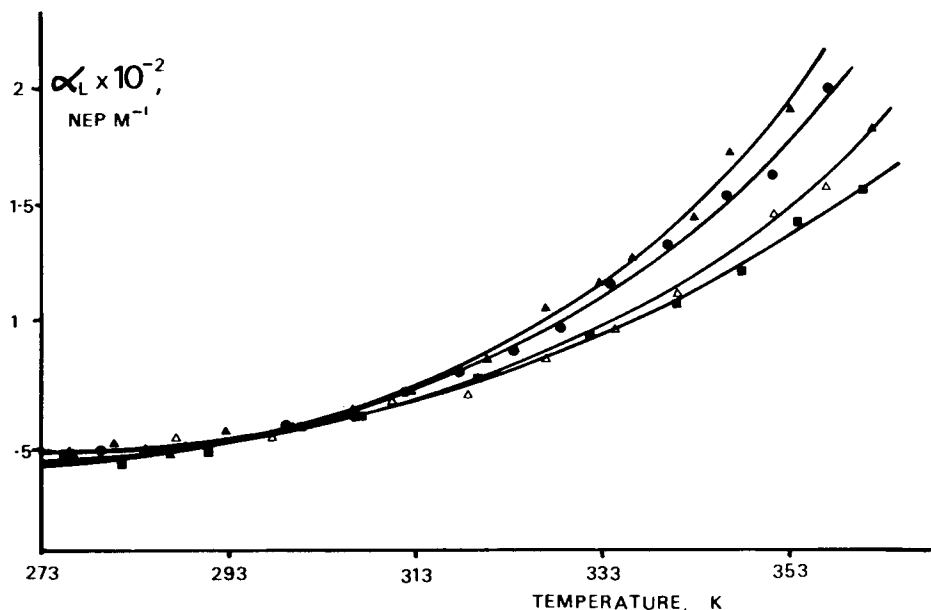


Fig. 3. Attenuation of longitudinal waves in predried poly(methyl methacrylate) at 5.0 MHz as a function of temperature: closed squares, AIII; open triangles, AII; closed circles, AIV; closed triangles, samples AI.

tenuation is due mainly to molecular motion, then the lower molecular weight polymer will show the attenuation changes associated with the glass transition at a lower temperature than the higher molecular weight material. Similarly, the more mobile methyl acrylate units and isotactic methyl methacrylate units will tend to lower the glass transition temperature of the polymer. In the case of the former, it is possible to estimate the methyl acrylate content from the magnitude of the T_g shift, Table I.^{26,27}

Dielectric studies²⁸⁻³⁸ have shown that side-group, backbone, and water relaxations can give rise to loss processes, but in the frequency-temperature range of this study, the methacrylate group motion or beta process is indistinguishable from that of the backbone or alpha process, and the relaxation corresponds to a coupled or cooperative motion. When studied separately, the beta process has an activation energy of 84 ± 6 kJ/mole, while that of the alpha process is 420 ± 100 kJ/mole.³⁶ The coupled or cooperative motion appears to have an activation energy close to that of the beta process. The observed increase in attenuation with temperature is associated with the low-temperature side of a broad loss peak centered around T_s and caused by the onset of large-scale motion. The observed first-power dependence of attenuation upon frequency has been reported previously,²⁴ and this can give rise to the erroneous impression that the loss peak shifts to a lower temperature with increasing frequency, implying a negative activation energy. This motion is responsible for the observed increase in attenuation with temperature at all the frequencies studied, Figure 4.

The increase in attenuation with water content, Figure 5, must be ascribed to a downward shift in the temperature of the main relaxation process since acoustic studies of pure water as a function of temperature and pressure³⁹⁻⁴¹ show that it alone will give rise to a negligibly small attenuation.

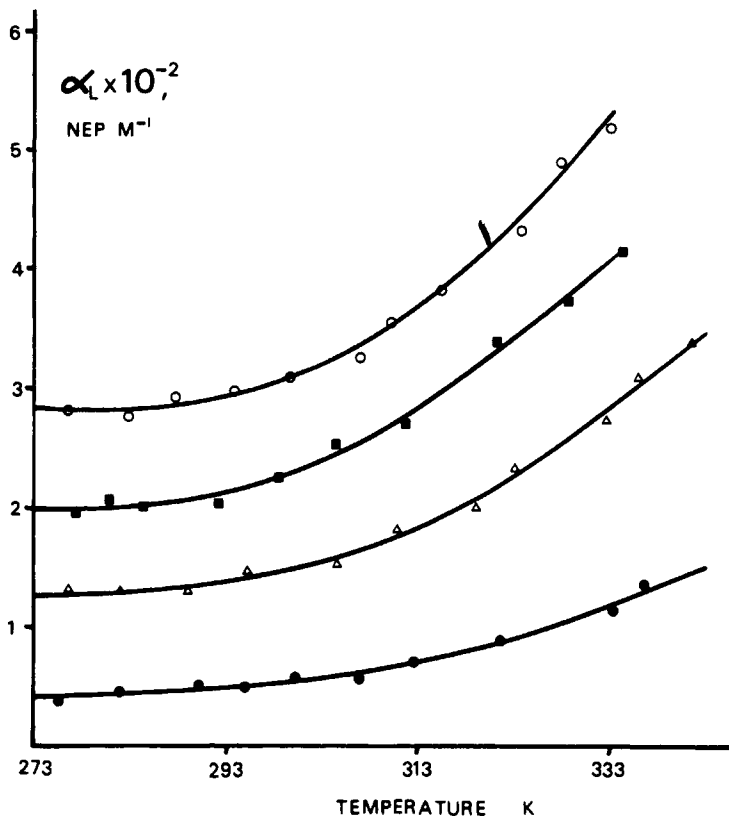


Fig. 4. Attenuation of longitudinal waves in predried poly(methyl methacrylate) (sample AI) as a function of temperature: closed circles, 5.0 MHz; open triangles, 15.0 MHz; closed squares, 25.0 MHz; open circles, 35.1 MHz.

It is well known that the modulus of a polymer changes from a value characteristic of a glassy solid to that of a rubber in the region of the glass transition, and that this is usually associated with the onset of molecular motion. Measurements of the limiting high frequency modulus of poly(methyl methacrylate) are not feasible, but can be estimated to within $\pm 4\%$ by extrapolation of values for similar systems to be 850 ms^{-1} .⁴² Allowing for the changes in modulus due to the addition of an equivalent quantity of water, it is possible to estimate the proportion of the polymer which is being plasticized, i.e., the weight fraction of the polymer with a modulus characteristic of the melt calculated on the basis of a two-phase model (Table III). It is evident that the effect of water is both a function of concentration and temperature. The uncertainty introduced by the extrapolation involved in the estimation of the infinite modulus leads to a possible error of 0.5% in the degree of plasticization.

The acoustic attenuation may be considered in terms of the function $\alpha_{\text{excess}}/x\alpha_{\text{polymer}}$, Table IV, where α_{excess} is the attenuation difference between wet and dry samples, x is the water concentration in weight per cent, and α_{polymer} the attenuation in the dry polymer. Since the excess is small at low concentrations and α_{polymer} is small at low frequencies, the values scatter somewhat; but it appears that this function is independent of temperature and only slightly dependent upon frequency. The principal difference appears in the magnitude

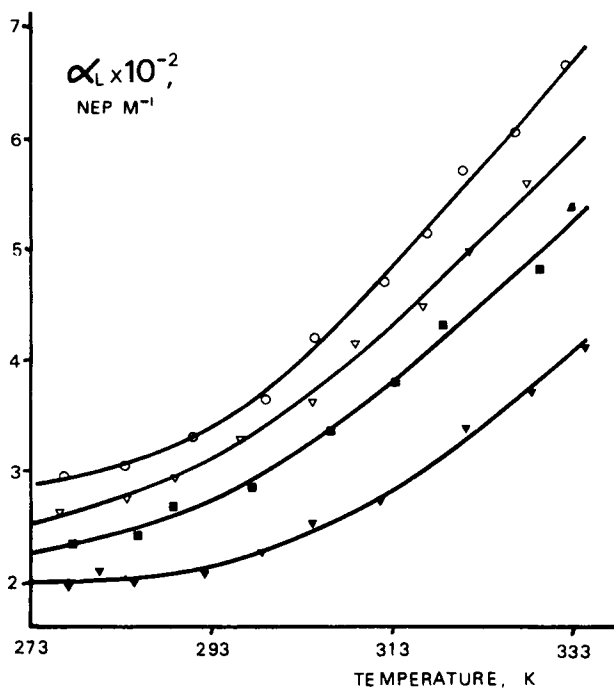


Fig. 5. Attenuation of longitudinal waves in poly(methyl methacrylate) (sample AII) at 25.0 MHz as a function of temperature: closed triangles, dry; closed squares, 0.73% water w/w; open triangles, 1.15% water w/w; open circles 1.76% water w/w.

TABLE III
Analysis of the Velocity Data in Wet and Dry PMMA

Temperature, °K	Velocity, m			Corrected difference values ^a		Plasticization, ± % of polymer ^b	
	0.0 ^c	1.1	1.8	1.1 ^c	1.8	1.1 ^c	1.8
273	2777	2777	2777	-15.5	-25.3	0.8	1.30
283	2766	2766	2763	-16.0	-29.0	0.83	1.49
293	2750	2750	2743	-16.3	-33.7	0.86	1.75
303	2725	2725	2714	-16.6	-38.2	0.88	2.00
313	2697	2695	2673	-18.9	-51.6	1.01	2.75
323	2676	2670	2632	-23.0	-71.8	1.25	3.89
333	2633	2622	2590	-28.1	-71.0	1.56	3.92
343	2597	2580	2540	-34.2	-85.1	1.94	4.79
353	2557	2530	2490	-44.2	-95.1	2.56	5.57
363	2515	2475	2430	-57.2	-113.2	3.40	6.69

^a The corrected difference values correspond to the difference between the observed value for the velocity and the velocity of dry PMMA corrected to allow for the presence of water, i.e.,

$$v = c_{\text{obs}} - (c_{\text{PMMA}} + x\% c_{\text{H}_2\text{O}})$$

where x is the % of water present. Note that this form of the equation is used since no swelling is observed in the temperature range studied, and therefore the properties are additive.

^b Calculated as

$$y = \frac{\text{corrected difference}}{c_{\text{PMMA(dry)}} - 850} \times 100\%$$

^c Water content, wt % H₂O.

TABLE IV
 Normalized Attenuation Data for Hydrated PMMA^a

Poly- mer	Fre- quency, MHz	Temperature, °K						
		0	10	20	30	40	50	60
AI	15	0.37	0.37	0.34	0.30	0.30	0.27	0.25
	25	0.25	0.27	0.31	0.34	0.36	0.35	0.34
	35	0.28	0.33	0.37	0.40	0.41	0.40	0.37
AII	15	0.14	0.10	0.08	0.09	0.10	0.11	0.09
	25	0.12	0.12	0.12	0.12	0.12	0.11	0.09
	35	0.06	0.06	0.10	0.13	0.12	0.12	0.12

$$^a \alpha = (\alpha_{\text{obs}} - \alpha_{\text{dry PMMA}}) / x \alpha_{\text{dry PMMA}}$$

of this function for samples AI and AII, which differ both in molecular weight and in acrylate content (Table V). The addition of water is more effective in plasticizing the motion of the segments in the more mobile solid. It may be concluded that this effect arises both from the degree to which the backbone motion is cooperative and also from the energy change associated with the moving group. A methyl methacrylate group next to a steric defect like a chain end or a methyl acrylate group will be more likely to absorb energy and move than the main chain. The nature of the moving moiety will determine the magnitude of the energy absorption process.

Infrared Spectroscopic Study

The vibrational spectrum of dry PMMA in the region below 4000 cm^{-1} has been thoroughly studied.⁴⁴⁻⁴⁶ Jones⁴⁷ observed the IR spectrum of wet PMMA above 4000 cm^{-1} under conditions of low resolution and found that the extinction coefficient of a band in the region of 5000 cm^{-1} varied linearly with water content up to 2% by weight. Details of spectra obtained for wet, dry, and ratioed samples are given in Table VI. A typical ratioed spectrum is displayed in Figure 6; it indicates that the absorbed water yields two major peaks at 5236 and 7046 cm^{-1} , each with a lower frequency side band. There appears to be no significant change in position or shape with varying water content, and the peak height absorbance of the stronger band was found to be roughly linearly dependent on water concentration. Heating the samples to around their T_g (100°C), by using the hot source of the Perkin-Elmer 125, shifted the band maximum and low-frequency contour upward by 18–20 cm^{-1} .

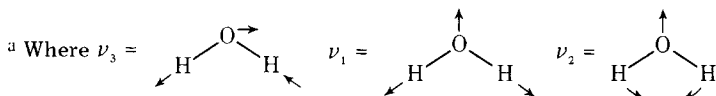
 TABLE V
 Temperature Shifts to Normalize Wet and Dry Attenuation^a

Poly- mer	Fre- quency, MHz	% Water				Poly- mer	Fre- quency, MHz	% Water		
		0.61	0.96	1.22	1.33			0.73	1.15	1.76
AI	5	—	—	15.2	16.5	AII	5	—	9.0	22.5
	15	5.6	5.2	7.2	9.0		15	12.5	20.0	26.7
	25	4.5	5.0	8.0	9.1		25	17.3	25.0	29.8
	35	9.2	7.5	9.6	12.4		35	17.7	24.5	33.2

^a The shift in temperature required to achieve superposition of the two curves.

TABLE VI
IR Bands from Absorbed Water

Room temperature		80–100°C		Assignment ^a
cm ⁻¹	$\Delta\nu_{1/2}$	cm ⁻¹	$\Delta\nu_{1/2}$	
7046	280	7100	240	$\nu_3 + \nu_1$
6832	60	6850	—	
5235	100	5260	80	$\nu_3 + \nu_2$
5080–5120	—	5120–5180	—	
3635	50			ν_3
3551	45			ν_1



Spectra observed in the mid-IR region are displayed in Figure 7. Two bands due to absorbed water occur respectively at 3551 and 3635 cm⁻¹. Only thin films could be used for transmission spectra in this region and lower frequencies; “thick” slabs were investigated using the attenuated total reflection technique. Unfortunately, because optical contact between sample and reflecting crystal deteriorates toward shorter wavelengths, only the region below 2000 cm⁻¹ yielded spectra of any strength. ATR did, however, allow the carbonyl absorption at 1725 cm⁻¹ to be studied, and no significant change in shape or position was observed with change in water content. The only difference observed between wet and dry spectra was an increase in absorption in the 1650–1630 cm⁻¹ region where the symmetric bending mode of the H₂O molecule can be expected to occur.

Due to its ability to form strong hydrogen bonds of ca. 20 kJ/mole, the water molecule is found largely unassociated only in the vapor or dispersed in very low concentrations in nonpolar liquids. In these circumstances, its IR spectrum is found to consist of a number of relatively sharp resolved absorption bands from fundamentals or combinations of the three vibrational modes or the isolated molecules, Table VII.^{48,49} It should be noted that the IR spectrum of the vapor is dominated by the free rotational structure and that the pure vibration modes are forbidden on symmetry grounds, though ν_1 can and has been observed from the vapor by Raman scattering.⁵⁰

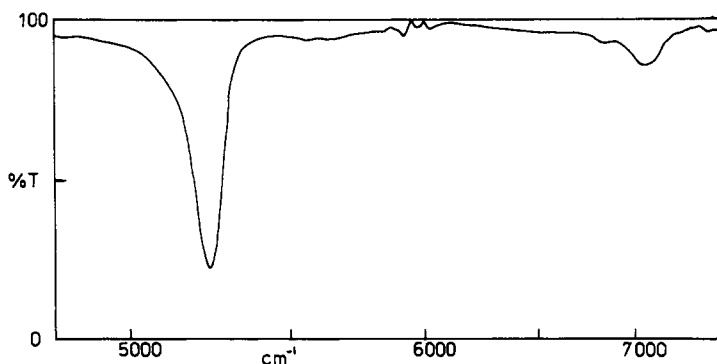


Fig. 6. Infrared transmission of wet ratioed against dry PMMA: thickness of samples, 3 mm.

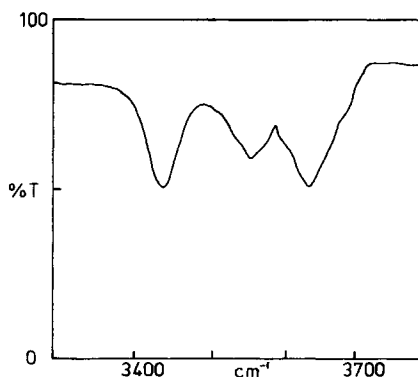


Fig. 7. Infrared transmission of a thin film of wet PMMA.

By contrast, water in its highly associated liquid form yields an IR spectrum consisting of very broad and diffuse absorption bands in which the stretching modes are not resolved as fundamentals, Table VII,^{49,51,52} and which are quite sensitive to changes in temperature. The stretching modes are reduced in frequency from values of the vapor, characteristic of the hydrogen bonding interaction.

The spectra reported here correspond to those of small concentrations of water in nonpolar or weakly polar liquids. The presence of the two side bands at 5080–5120 and 6832 cm^{-1} at positions similar to those from water indicates some degree of hydrogen bonding between water molecules though they appear to be rather narrower than would be expected, which implies that the extensive networks found in the liquid and responsible for the breadth of the absorption are absent. Taken as a whole, the spectra indicate that water molecules exist as very small clusters rather than as purely monomeric units and liquid water. A typical cluster might contain three water molecules and be weakly interacting with the polar regions of the polymer backbone.

Conclusions

It is clear that water interacts with the polymer either monomerically or, at the most, in trimer groupings. The change in activation energy which these

TABLE VII
IR Bands of H_2O Molecule in Various Environments^a

Vapor, cm^{-1}	Liquid (near fp)		Liquid (near bp)		CHCl_3		Assignment
	cm^{-1}	$\Delta\nu_{1/2}$	cm^{-1}	$\Delta\nu_{1/2}$	cm^{-1}	$\Delta\nu_{1/2}$	
7252	6880	600 ^a	7020	480 ^a	7165	80 ^a	$\nu_3 + \nu_1$
5332	5160		5220		5285		$\nu_3 + \nu_2$
	Liquid (room temp.)						
		cm^{-1}	$\Delta\nu_{1/2}$				
3756		(3490, 3280)	400		3690	38	ν_3
3657					3607	30	ν_1
1595		1654		75			ν_2

^a From refs. 48, 49, 51, and 52.

^b Our estimate.

interactions achieve is relatively small, at the most a lowering of 1 kJ/mole. It is evident that the observed change in the cooperative motion of the backbone with the side chain can be achieved by a combination of dielectric and hydrogen bonding interactions.⁵³ Through the Onsager local field interactions, the magnitude of the activation energy and the population distribution among the equilibrium isomeric states will be changed. Depending upon the nature of the states involved, the activation energy can be raised or lowered. The hydrogen bond is known to stabilize the ground state by intermolecular effects, but can lead to a lowering of the activation energy to internal rotation by modification of the electron distribution. The combination of these two effects appears to lower the glass transition temperature by approximately 5° to 33°C, corresponding to a lowering of the activation energy for the backbone motion of about 1 kJ/mole.

It is interesting to note that substituting the infrared shift between water vapor and absorbed water

$$\Delta\nu = \left\{ \begin{array}{cc} \frac{\nu_3 + \nu_1}{2} & - \frac{\nu_3 + \nu_1}{2} \\ \text{vapor} & \text{adsorbed} \end{array} \right\} = 114 \text{ cm}^{-1}$$

into the modified Badger-Bauer relationships⁵⁴ for normal and fluorinated alcohols yields values for the enthalpy of interaction (ΔH) of between 2.4 and 4.8 kJ/mole. This would suggest that the effects of plasticization of the poly(methyl methacrylate) by water are the result of changes of the order of 1–3 kJ/mole in the rotational profile. The observed diffusion activation energy is a measure of the scale of molecular motion necessary for the hopping of water molecules between trapping points in the polymer matrix. The observed value is considerably less than that found for segmental motion of the polymer and is evidence for the relatively small degree of interaction of the water with the polymer.

SUMMARY

Measurements of the acoustic attenuation and infrared spectra of wet and dry samples of poly(methyl methacrylate) suggest that water can act as a plasticizer for the cooperative motion of the polymer backbone. The water appears to exist either as isolated molecules or as small clusters.

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