The Points of Contact Between Poly(Methyl Methacrylate) and Absorbed Water as Indicated by PE/MAS ^{13}C NMR

P. E. M. Allen[1]*, S. Hagias[1], G. P. Simon[1], E. H. Williams[1]**, and D. R. G. Williams[2]

Departments of Physical and Inorganic Chemistry[1], and Chemistry Engineering[2],
University of Adelaide, Box 498 GPO, Adelaide, South Australia 5001

Summary

The development of the PE/MAS ^{13}C NMR spectrum of poly(d^8MMA) cross-polarized by the protons of water is used to follow the distribution of water as it is absorbed by the polymer. In the early stages, water is in contact with the backbone CD_2 and quaternary C. It makes contact with side-chain carbons later. A non-random distribution of close contacts between water and polymer molecules was also observed when P(d^8 MMA) was precipitated from d^8-acetone by water.

Introduction

The observation of a ^{13}C peak in a proton-enhanced, magic-angle-spinning, ^{13}C NMR experiment depends on the polarization of the ^{13}C nuclei by ^{1}H nuclei previously polarized in the ^{1}H rotating field. The cross-polarization interaction is dependent on the inverse sixth power of the interatomic separation (1) so the observation of a ^{13}C NMR signal is evidence of juxta-position of protons on the molecular scale. The technique can thus be used to identify the points of close contact between the components of a blend or solid-solution if one component is deuterated and the other is not.

PMMA can absorb up to 2 mass percent of water (2). Its presence affects the polymer: most notably the dynamic, mechanical properties where a water-induced transition can be observed between −100 and −80°C (3,4). The location of water molecules in PMMA glass is therefore of more than academic interest. The availability of good quality P(d^8MMA) in the form of a superannuated PE/MAS rotor induced us to investigate by determining which PE/MAS ^{13}C resonances appeared as the polymer absorbed water or was precipitated by water from a proton-free solution.

Experimental

P(d^8MMA) samples were prepared by dissolving a Brüker MAS rotor in chloroform, precipitating into methanol and drying under vacuum for 2 months at 80°C. Cast samples (~ 0.25 mm thick) were used for absorption experiments. For other experiments P(d^8MMA) in carefully dried d^6-acetone was run slowly into well stirred [1]H_2O, the precipitate collected and superficially dried.

PE/MAS ^{13}C NMR spectra were run on a Brüker CXP300 operating at 75.47 MHz with samples spun in DELRIN or KEL-F spinners at 2.6 kHz at

* To whom offprint requests should be sent
** Now at Varian Associates Inc., Palo Alto, CA 94303, USA

25±3°C. The transmitters were set to the Hartmann-Hahn condition using an adamantine sample. The magic angle was set using a duplicate of each sample with KBr added. PE/MAS spectra were obtained using a 90° ^{1}H pulse-width of 4.25 μs (59 kHz decoupling field), a 1 ms cross-polarization time and 5 s recycle times. A 20 kHz sweep was accumulated into a 1.25 K data-table and stored in a 4 K block.

Chemical shifts were measured from the DELRIN resonance taken as 90.0 ppm, or, in its absence, the methacrylate quaternary C (45.7 ppm on the DELRIN scale) taken as 45.0 ppm. Both standard PE/MAS and TOSS spectra were taken to identify and suppress spinning side-bands. The background spectrum of the dry P(d^{8}MMA) sample was taken to provide the basis for difference spectra of the wet samples.
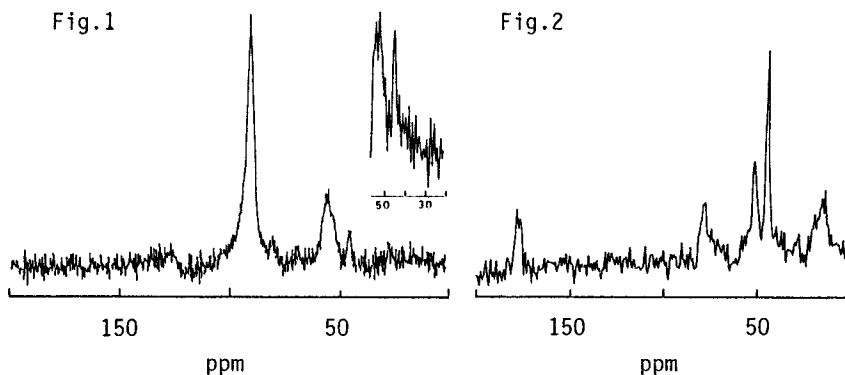
Fig.1   Fig.2

Fig.1   PE/MAS ^{13}C NMR spectrum of P(d^{8}MMA) exposed to ^{1}H$_2$O vapour for
        3 months at 30°C. Chemical shifts are relative to the Delrin-
        spinner resonance set to 90.0 ppm. The difference spectrum
        between this spectrum and that of a dry sample of P(d^{8}MMA) is
        shown in the inset.

Fig.2   PE/MAS ^{13}C NMR TOSS spectrum of sample shown in Fig.1 6 months
        later after storage in a sealed vessel at ambient temperature.
   Quaternary C is set to 45.0 ppm.

Results

A sample of cast sheet was held in a closed vessel above a water surface maintained at 30°C for 3 months. During this time it absorbed 0.8 mass percent of water. The PE/MAS spectrum of this sample is shown in Fig. 1. The most prominent feature is the DELRIN resonance (set to 90 ppm) and its spinning side-bands but P(d^{8}MMA) resonances are apparent in the CD$_2$ and quaternary C regions and, to a lesser extent, α-methyl. The first two are absent from the spectrum of the dry sample. The difference spectrum (inset Fig. 1) shows CD$_2$ at 54.1 ppm and quaternary at 45.7 ppm. The α-methyl resonance, present both before and after water-absorption, vanishes from the difference spectrum. It must arise from proton impurity at the α-CD$_3$ group in the sample.

The sample was left in contact with excess liquid water in a closed vessel and run again six months later. The spectrum (Fig. 2) was transformed to one showing all the features of that of $P(h^8MMA)$: CO at 178 ppm, the α-CD_3 multiplet at 14-20 ppm, OCD_3 at 52 ppm and quaternary C, set to 45 ppm. CD_2 has been engulfed by the growth of OCD_3 unless the shoulder at 55 ppm is significant.

The sample was dried to constant weight in a vacuum-oven at 80°C. The water content was reduced to 0.4 mass percent but there was no significant change in the PE/MAS spectrum.

Fig. 3 shows the PE/MAS spectrum of $P(d^8MMA)$ precipitated by ^1H_2O from d^8-acetone. The quaternary C resonance is prominent. Its downfield companion, by virtue of an 0.67 ppm shift, is likely to be OCD_3 rather than CD_2.

Fig.3 PE/MAS ^{13}C NMR TOSS spectrum of $P(d^8MMA)$ precipitated by ^1H_2O from d^8-acetone solution.

150   50

ppm
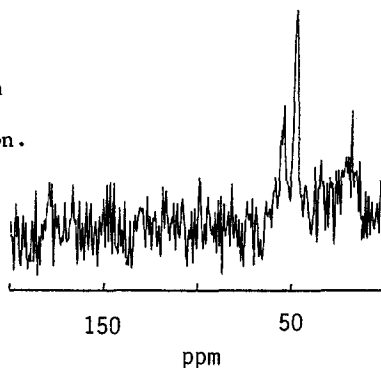
Discussion

Our experiments show that two different processes are involved in the absorption. A dual mechanism for the absorption of penetrants by glassy polymers is an old concept (5,6 and references cited therein). It is usually associated with the filling of voids, or microvoids, on one hand and 'ordinary solution' on the other (6). Turner (5) reported that the uptake by PMMA immersed in liquid water involved two processes: the faster proceeding with increase in density and no change of dimensions; the slower with swelling and relatively small density change.

To some extent our results are consistent with these concepts. We observed two processes: water molecules initially occupying somewhat specific sites relative to the repeating unit of the PMMA chain and then a near-random distribution, where close contacts were observed with all groups of the repeating unit. However the question whether the processes observed correspond to the concepts postulated previously requires closer examination.

The very nature of the cross-polarization interaction (1) means that the contacts observed are close - as close as those in a strong solute-solvent interaction in classical solution theory. A further requirement is that the water molecules involved have restricted mobility - free isotropic tumbling would have averaged the cross-polarization to zero. Two conclusions follow. Firstly the interactions observed in the initial uptake could arise from contacts which were isolated and randomly

distributed in space. Consequently the state of the system could be one of 'ordinary' solution just as it could be in the later stages when the close contacts were also random with respect to sites on the PMMA molecules. Secondly if water-filled voids were present in either state our experiments did not necessarily detect them. Water in voids sufficiently large for liquid-like tumbling to occur could have no influence on ^{13}C resonance intensities, except for those molecules in contact with the walls of the void and then only if their tumbling was constrained.

The points of contact in the initial uptake are not the sites where water-polymer interactions would be strongest. They must therefore be sites which occur along channels of easy penetration pre-existing in the polymer. The material is amorphous atactic PMMA and it may be assumed that the equilibrium, time-averaged conformation will be an unperturbed coil of dimensions similar to that in dilute solution in a θ-solvent (9,10). The detailed conformations of segments of the coil can only be surmised. In the case of it- and st-PMMA helical conformations with CH$_3$ and COOCH$_3$ pointing away from the axis are indicated both by X-ray diffraction measurements on the crystalline forms and by computation of the lowest energy chain conformation (11-14). The helix of crystalline st-PMMA is particularly interesting; a very loose coil enclosing non-stoichiometric amounts of the crystallization-inducing solvent (13). Our results suggest that amorphous PMMA contains chains coiled with substituent —CH$_3$ and —COOCH$_3$ pointing outwards and the main chain forming a channel of quaternary and CH$_2$ groups through which water percolates in the initial uptake. The eventual, more uniform distribution arises from a slower process which may be a redistribution or a second, slower absorption mechanism.

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