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Solid state ^{13}C n.m.r. cross-polarization studies of a poly(methyl methacrylate)/solution chlorinated polyethylene blend

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A partially miscible blend of deuterated poly(methyl methacrylate)/solution chlorinated polyethylene (dPMMA/SCPE) has been examined by cross-polarization magic angle spinning ^{13}C n.m.r. (CP/MAS). The polymer–polymer intermolecular distance has been calculated and shows very close interaction between the two homopolymers.

(Keywords: ^{13}C n.m.r.; cross polarization; CP/MAS; poly(methyl methacrylate); solution chlorinated polyethylene; blend miscibility)

Introduction

The miscibility and microscopic structure of polymer blends has been of intense interest both in industry and in academia[1-4]. This communication explores a new technique based on the use of cross-polarization magic angle spinning ^{13}C n.m.r. (CP/MAS), which is routinely used to acquire high resolution solid state spectra of polymers[5-8]. In a conventional CP/MAS experiment carbon intensity is due to transfer of magnetization via a through space CP step from adjacent protons. The dipolar interaction responsible for this process has a r^{-6} dependence, where r is the interatomic distance. This means that the rate of CP of non-protonated carbon atoms is relatively slow, resulting in low intensity[9]. The experiment can be easily extended to polymer blends if one blend component is fully deuterated[10]. This removes the possibility of intramolecular CP, which means that the intensity arising from the deutero component in the final spectrum will depend only on the extent of contact it has with the protons from the other polymer component. In this way calculation of the intermolecular polymer–polymer distances allows detailed assessment of the molecular interactions responsible for miscibility of the blend.

In this communication we present the results of an initial study using CP/MAS ^{13}C n.m.r. on a blend of deuterated poly(methyl methacrylate)/solution chlorinated polyethylene (dPMMA/SCPE).

Experimental

The dPMMA was prepared by radiation chopping of high molecular weight dPMMA to give a molecular weight, $M_w = 821\,000$ g mol^{-1} and polydispersity, $PD = 2.62$, with no appreciable crosslinking. Solution state ^{13}C n.m.r. of the dPMMA proved the polymer to be 99.9% deuterated with 61% syndiotactic, 36% heterotactic and 4% isotactic triad sequences. The SCPE had a $M_w = 10^6$ g mol^{-1} and $PD = 1.61$.

The dPMMA/SCPE blend samples were made by solution casting the polymer mixture from a 5% chlorobenzene solution. The samples were air dried until tacky and then placed in a vacuum oven at 40°C for a period of a few days until the film was completely dry. The cast film was then crushed to a powder and packed into the solid state sample rotor.

Solid state spectra of the blend were acquired using a CP/MAS accessory on a Bruker AC300 n.m.r. spectrometer (75.5 MHz) at a spin rate of 4 kHz. Chemical shifts were externally referenced to adamantane (based on TMS = 0 ppm). Cross-polarization times were determined using a variable contact time sequence, in which the CP pulse was incremented in 20 steps from 5 to 10 000 μs. The spin locking field had a corresponding resonance frequency of 48 kHz.

Results and discussion

The intensities of all resolvable peaks in the blend spectrum were measured as a function of CP time, the behaviour of the SCPE methylene and dPMMA carbonyl peaks being shown in *Figure 1*. The data for each peak were fitted to the equation:

$$I(t) = \frac{C[\exp(-t/T_{1\rho}) - \exp(-t/T_{\mathrm{CP}})]}{(1 - T_{\mathrm{CP}}/T_{1\rho})} \tag{1}$$

where T_{CP} is the CP time, $T_{1\rho}$ is the relaxation time under the Hartman–Hahn CP condition[9] and t is the contact time. The parameter C is equal to the maximum theoretical intensity of the peak in the absence of relaxation.

The fitting was achieved using a non-linear least squares regression analysis program (New Methods Research Inc., Syracuse, USA), with C, t and T_{CP} as variable parameters and $T_{1\rho}$ fixed by determination in a separate delayed contact time experiment. In *Figure 1* the much slower CP resulting from intermolecular transfer to the dPMMA carbonyl in the blend is quite

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Table 1 Cross-polarization times for carbons in a 75:25 dPMMA/SCPE blend cast from solution, and for an hPMMA reference homopolymer

Polymer	Carbon type	Chemical shift (ppm)	$T_{1\rho}$ (ms)	T_{CP} (μs)	Quantitative peak areas (arbitrary units)	Nearest[a] proton distance (Å)
SCPE	CH_2	35	8.0	25	0.29	1.09
SCPE	CHCl	62	8.0	33	0.30	1.09
SCPE	CCl_2	97	8.0	500	0.04	2.03
dPMMA	CD_3	18	8.0	11 000	0.72	3.4
dPMMA	-C-	45	8.0	17 000	1.07	3.6
dPMMA	OCD_3	52	8.0	10 800[b]	1.21	3.4
dPMMA	C=O	178	8.0	13 000	0.93	3.5
hPMMA[c]	CH_3	18	21	97	–	1.09
	-C-	45	21	245	–	2.03
	OCH_3	52	21	77	–	1.09
	CH_2	58	21	67[b]	–	1.09
	C=O	178	21	2 000	–	–

[a] Four equidistant protons are assumed to cross-polarize to dPMMA via the intermolecular route

[b] Partial overlap with methoxy peak makes fitting difficult. The peak is not resolved in the deuteroblend, which may lead to errors in OCD_3 intensity values

[c] Hydrogeneous PMMA was measured for comparative purposes

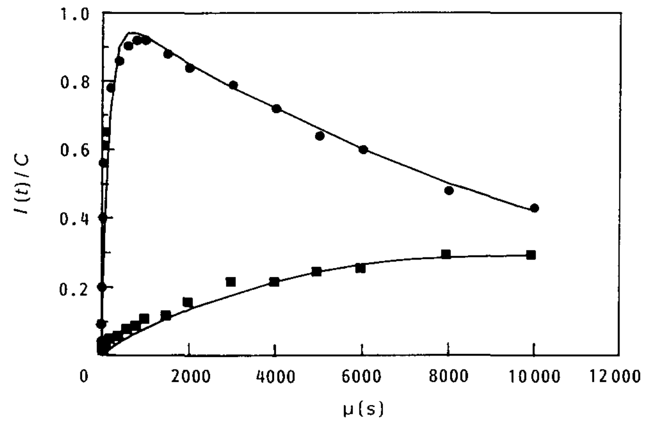

Figure 1 Plot of normalized intensity against contact time for the SCPE -CHCl- carbon (●) and the dPMMA carbonyl (■). The solid lines are fits to the data using equation (1)

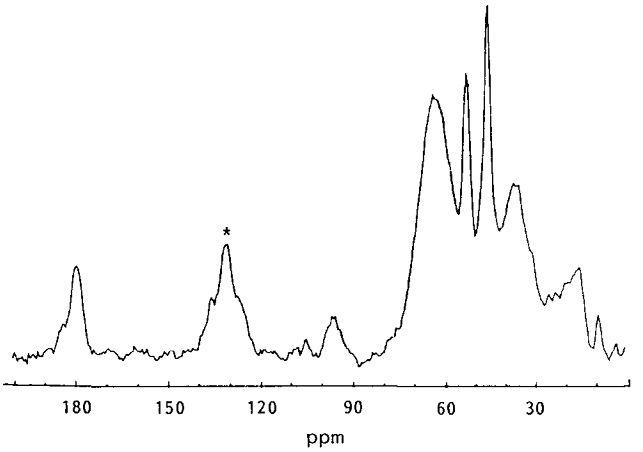

Figure 2 ^{13}C CP/MAS spectrum of the 75:25 dPMMA/SCPE blend, using a contact time of 1000 μs and a spin rate of 4 kHz. The feature marked with an asterisk is a superposition of the C=O spinning side band and a peak due to vinyl decomposition products

evident. The later fall in intensity of the SCPE methylene peak is due to $T_{1\rho}$ relaxation, which is observable because the rapid intramolecular CP results in full magnetization transfer at very short contact times.

In the blend spectra some dPMMA peaks are overlapped by SCPE peaks. In order to carry out accurate curve fitting these contributions were removed from all 20 spectra by subtracting a spectrum containing only SCPE features. A blend spectrum acquired at a short contact time ($t = 100$ μs) was used for this purpose. This was considered to be an acceptable procedure because all the SCPE peaks in the overlapped region had achieved constant ratios at this contact time whilst the slowly cross-polarizing dPMMA features were not visible. The resulting difference spectra showed only the dPMMA peaks, with intensities varying with contact time. *Table 1* summarizes the chemical shift and fitted T_{CP} data for the sample, and also for a reference hydrogeneous PMMA homopolymer measured under the same spin locking field conditions.

The ^{13}C CP/MAS spectrum of the blend shown in *Figure 2* was acquired using a contact time of 1000 μs. The peak areas of both blend components in this spectrum were determined by a cut and weigh method, taking into account the spinning side band contributions to the dPMMA carbonyl signal. The peak areas were then corrected for quantitative comparisons by multiplying by the ratio between the theoretical maximum intensities (C) and intensities after a contact time of 1000 μs. The appropriate ratios were provided from the fitted intensity *versus* contact time data. *Table 1* lists the corrected peak areas for all measured peaks. A full description of CP/MAS intensity *versus* contact time behaviour is beyond the scope of this communication and a detailed account is given in reference 9.

The corrected areas of the dPMMA peaks in the blend should all be the same, reflecting the molar ratios of the carbon types. The experimental spread of results is acceptable considering the overlap of peaks, and an average value of 0.9 area units was taken for the quantitative area corresponding to one dPMMA carbon. In the same way the area corresponding to one SCPE carbon was estimated to be 0.3 units. The comparison of the two values gives a measure of the amount of the dPMMA which is cross-polarizable and therefore intimately mixed with the SCPE.

In order to establish the mean internuclear distance between SCPE protons and dPMMA carbons it is necessary to make use of the T_{CP} of the well defined SCPE methylene carbon. Proton to carbon intramolecular T_{CP} values are proportional to r^6, where r is the internuclear distance, and also proportional to n^{-1}, where n is the number of protons attached to the carbon[9]. Thus, it can be seen that the two protons on the SCPE methylene at a distance of 1.09 Å give rise to a T_{CP} of 25 μs. It is not possible to know how many SCPE protons are involved in interchain CP to the dPMMA carbons, but an approximation can be made that on average four SCPE protons are near any one dPMMA carbon. Therefore, a T_{CP} of 11 000 μs for the dPMMA methyl is calculated to result from interaction with four protons ($n = 4$) at a mean distance of 3.4 Å. The values calculated from the experimental T_{CP} values of each of the dPMMA carbons are shown in *Table 1*. The above example can be used to illustrate the influence of the approximation in mean number of interacting protons, since $n = 3$ gives $d = 3.2$ Å, and $n = 5$ gives $d = 3.5$ Å. Cross-polarization times are also directly related to the motional rates of the corresponding C–H vectors[5], so this information would ideally be required in a rigorous comparison. However, in the blend case it was considered that the motional rate of the protons on the SCPE methylene would be similar to that influencing internuclear CP, eliminating this source of uncertainty from the above calculations.

The measured area ratio of 3:1 implies that all of the dPMMA component is accessible to the SCPE component in this partially miscible blend, based on an original 75:25 dPMMA:SCPE weight ratio. This suggests that the two components are very intimately mixed together. In addition the mean distance from SCPE protons to dPMMA carbons was calculated to be ~3.5 Å suggesting very close interaction between neighbouring polymer chains. Even the inner dPMMA quaternary carbon is cross-polarized at a rate comparable with the other more accessible protons. This is consistent with the view that the chlorine substituents will polarize the methine C–H bonds of SCPE, resulting in an attraction of the methine protons to the dPMMA ester oxygens. This would have the effect of bringing the protons sufficiently close to the dPMMA backbone to undergo intermolecular CP.

This technique is also currently being applied to other polymer blend systems, including an immiscible blend. It is hoped that the accurate measurement of CP data and ^{13}C peak areas will provide information about the extent of phase separation and the proportion of the interphase region. Further experiments are underway to explore the possibility that the high centripetal force samples experience during MAS may itself lead to phase separation over extended periods of time.

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