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Detection of Polymer Miscibility by $^{1}H/^{13}C/^{14}N$ Triple Resonance Solid State Nuclear Magnetic Resonance

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ABSTRACT: $^{1}H/^{13}C/^{14}N$ triple resonance has been used to verify the existence of a template complex formed by poly(methacrylic acid) and poly(*N*-vinylimidazole). The proximity of the imidazole ring and the carbonyl group of poly(methacrylic acid) leads to a significant loss of carbon-13 spin-echo intensity when ^{14}N is irradiated. This means that the internuclear distances in this template complex between the carbons of poly(methacrylic acid) and the nitrogen of poly(*N*-vinylimidazole) are less than 5 Å, as confirmed by a numerical model. Such an intimate mixing of the two components can also be concluded from proton $T_{1\rho}$ measurements.

1. Introduction

Polymer blends have gained great technical and economic interest since the development of the first polymers. Above all, the homogeneity of polymer blends plays an important role, because the intimacy of mixing and the phase structure determine many mechanical properties.[1]

Traditionally, the miscibility of polymers is characterized by differential scanning calorimetry: a single glass transition with a composition-dependent temperature T_g defines a miscible blend. When single component domains exist, they have domain sizes of maximally 100−200 Å.[2]

The NMR technique, however, offers information about miscible polymer blends on a molecular scale. A much used technique is the determination of the proton relaxation times T_1 and $T_{1\rho}$.[3] In a polymer blend one has the following possibilities. If the blend shows two different proton T_1 and two different proton $T_{1\rho}$ relaxation times, the single domain sizes are larger than about 500 Å. If there is just one proton $T_{1\rho}$, but two T_1's, the domain sizes are between 50 and 500 Å. Only one proton $T_{1\rho}$ and one proton T_1 represent domain sizes smaller than about 50 Å.[4]

In reality this method has some experimental limitations to detect the miscibility of a polymer system, especially if the proton relaxation times $T_{1\rho}$ of the pure components show no significant differences. Therefore other techniques may have to be employed to determine the miscibility of polymer blends on a molecular scale.

An alternative technique is the observation of a dipolar coupling between nuclear spins in the two components that form the blend. Here we want to show that the novel $^{1}H/^{13}C/^{14}N$ triple resonance technique[5−7] (TRAPDOR) can be used for this purpose.

The $^{1}H/^{13}C/^{14}N$ triple resonance pulse sequence is shown in Figure 1 and consists of a standard cross polarization experiment between ^{1}H and ^{13}C, followed by a rotor synchronized spin-echo sequence on the ^{13}C spins. The ^{14}N spins are irradiated during the first half of the echo period and the effect of ^{14}N irradiation is detected indirectly via the ^{13}C spins. Two experiments are performed, (a) without ^{14}N irradiation and (b) with ^{14}N irradiation. The first experiment is used as a reference for the second, the triple resonance experiment.

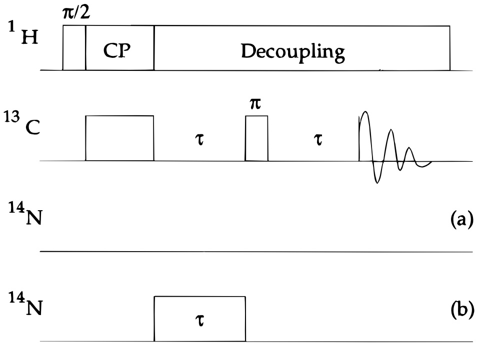

Figure 1. Triple resonance pulse sequences used in this work. Both the ^{13}C π pulse and the start of the acquisition are synchronized with the rotor echoes. The ^{14}N spins are irradiated during the first half of the echo period in (b); sequence a depicts the control experiment.

The resonances of ^{13}C, which have a spatial proximity to nitrogen, lose intensity in the triple resonance experiment, as is shown in the difference spectrum of (a) and (b).

The triple resonance technique was previously successfully applied to glycine,[5,6] polyamide-6,[6] and *N*-acetyl-D,L-valine.[7]

Especially the experiments with *N*-acetyl-D,L-valine provide important consequences for experiments on polymer systems, because they indicate that even in systems with large ^{14}N electric field gradients (EFG), it is still possible to alter the dipolar evolution of the ^{13}C spins coupled to ^{14}N. Therefore the $^{1}H/^{13}C/^{14}N$ triple resonance technique can be used to study the miscibility of polymer blends, when one component contains nitrogen, as we will show for a system of poly(methacrylic acid) (PMAA) and poly(*N*-vinylimidazole) (PVIm), prepared by template polymerization.[8] Detailed information about this polymer system is given by van de Grampel and Challa.[9−14] In these papers interactions between the carbonyl group of PMAA and the imidazole ring of PVIm[12] are reported.

2. Experimental Section

The solid state NMR spectra were obtained by using a Bruker CXP 300 at operating frequencies of 300.13, 75.47, and 21.69 MHz for ^{1}H, ^{13}C, and ^{14}N. A Bruker triple resonance MAS NMR probe which was tuned to provide a 90° pulse length of 5 μs for ^{1}H and ^{13}C and 10 μs for the ^{14}N nucleus was used. The third frequency channel was provided by a Bruker CXP 200 console and a Bruker high-power amplifier

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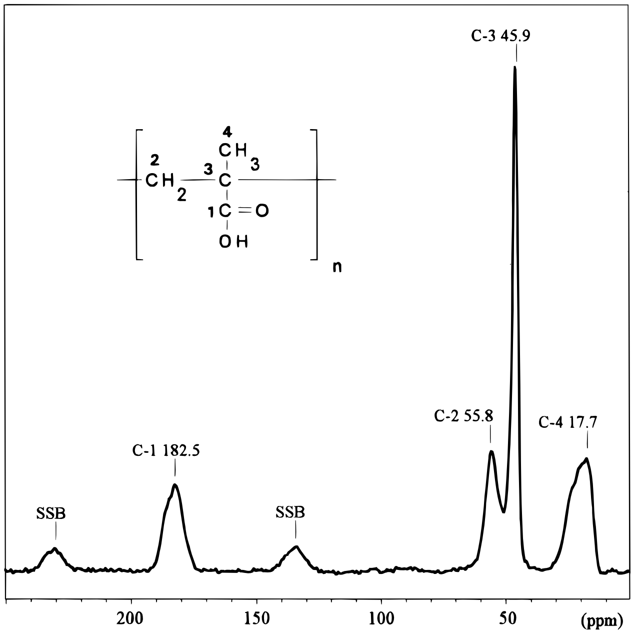

Figure 2. ^{13}C CP/MAS NMR spectrum of poly(methacrylic acid), PMAA. Spinning rate: 3.6 kHz. The numbers on the peaks correspond to those on the structure; spinning sidebands are denoted by SSB.

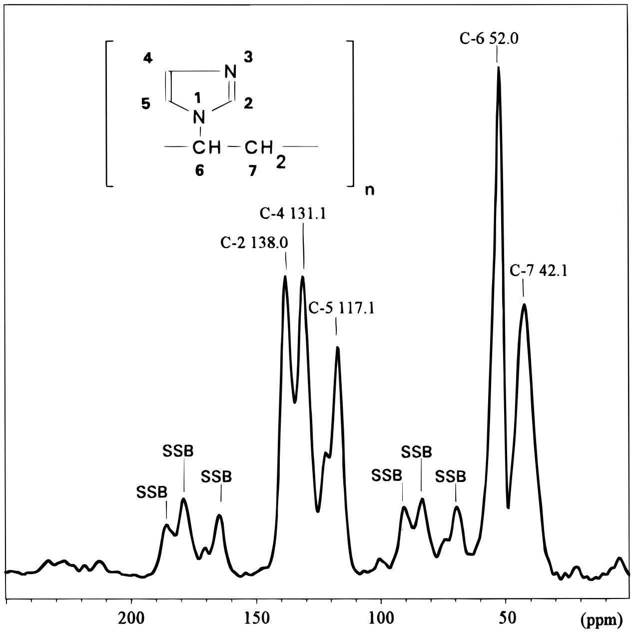

Figure 3. ^{13}C CP/MAS NMR spectrum of poly(*N*-vinylimidazole), PVIm. Spinning rate: 3.6 kHz. The numbers on the peaks correspond to those on the structure; spinning sidebands are denoted by SSB.

tuned to 21.686 MHz. The ^{14}N pulse lengths were determined with solid ammonium chloride, which resonates at approximately −5 kHz relative to the ^{14}N carrier frequency of 21.686 MHz. The stability of the two combined spectrometers was checked by using solid ^{13}C-enriched glycine.

Experiments were performed with the pulse sequence shown in Figure 1. The FID's (**f**ree **i**nduction **d**ecay) were collected by alternating between the control experiment (a) and the triple resonance experiment (b); 200 scans were added for each experiment before switching to the next. Between 4000 and 6000 scans were recorded for each experiment.

The proton $T_{1\rho}$ experiments with carbon-13 detection were performed by using the standard pulse sequence.[4] Variable delay times up to 20 ms have been used.

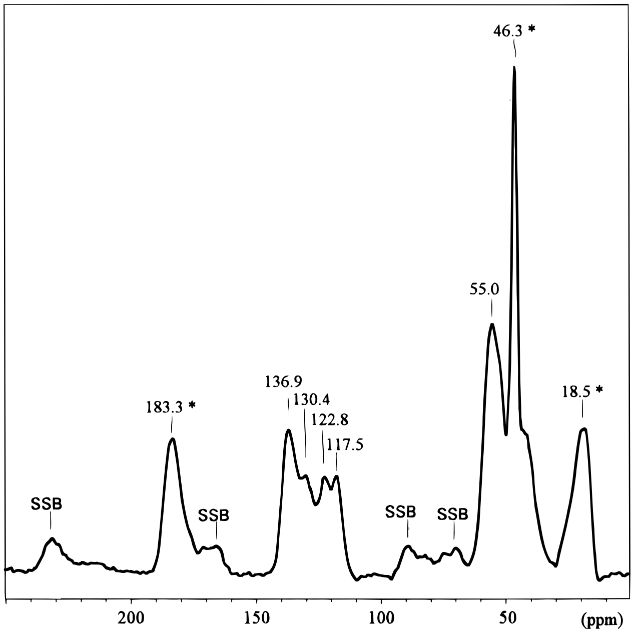

Figure 4. ^{13}C CP/MAS NMR spectrum of the template complex. Spinning rate: 3.6 kHz. The peaks arising from PMAA are marked with a cross. Spinning sidebands are denoted with SSB.

Table 1. Values of Proton $T_{1\rho}$'s for the Pure Components and the Template Complex[a]

isotropic peak [ppm]	PMAA $T_{1\rho}$(H) [ms]	PVIm $T_{1\rho}$(H) [ms]	template complex $T_{1\rho}$(H) [ms]
183.3	3.1		4.3
136.9		7.3	4.6
131.1		7.3	4.8
117.5		7.4	4.7
55.0	3.1	7.5	5.0
46.3	3.2	7.5	4.0
18.5	3.1		4.5

[a] The relaxation times were acquired with the standard pulse sequence. Proton spin lock times up to 20 ms have been used.

3. Results

3.1. CP/MAS Spectra. The CP/MAS spectra of PMAA, PVIm, and the template complex are shown in Figures 2 to Figure 4. The resonances are assigned to the different carbons in PMAA and PVIm, as shown. Spinning sidebands are marked with SSB.

One can clearly assign the resonance lines in the template complex and the pure components. In Figure 4 the carbonyl group at 183.3 ppm and the methyl group at 18.5 ppm are due to PMAA, the resonances between 136.9 and 117.5 ppm can be assigned to the imidazole carbons of PVIm. The resonances around 55 ppm result from overlapping lines from both components. The resonance line at 46.3 ppm is due to the PMAA quaternary carbon. The line shape of the resonances of the template complex and the pure components are very similar, except for the PMAA methyl group, which is narrower for the complex. Only the resonances of the imidazole ring are broadened and not as well resolved as in the spectrum of pure PVIm.

3.2. Proton $T_{1\rho}$ Measurements. To compare the triple resonance experiment results with a miscibility determination of this polymer system via proton relaxation times we first determined the proton $T_{1\rho}$'s of the pure components and the template complex. These results are presented in Table 1.

It is shown that the proton $T_{1\rho}$ relaxation times of the pure PMAA are different from the proton $T_{1\rho}$'s in

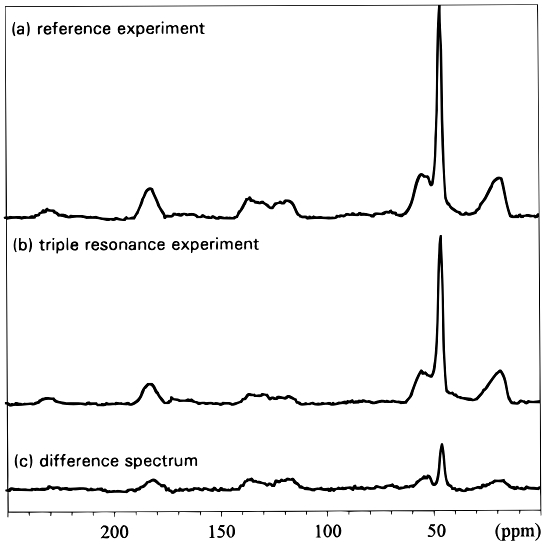

Figure 5. ^{13}C MAS spectra of the template complex, obtained with the pulse sequence shown in Figure 1. Spectrum a was recorded without ^{14}N irradiation; b, with ^{14}N irradiation at the frequency of 21.686 MHz. A spinning speed of 3.6 kHz and a spin-echo delay of 3.33 ms (i.e., 12 rotor periods) were used. The assignments of the resonances are given in Figure 3.

Table 2. Results of the Triple Resonance Experiment, Using the Pulse Sequence Presented in Figure 1[a]

isotropic peak	assignment	ratio I/I_0	intensity loss in %
183.3	PMAA	0.693	30.7
136.9	PVIm	0.467	53.3
131.1	PVIm	0.576	42.4
117.5	PVIm	0.388	61.2
55.0	PMAA + PVIm	0.753	24.7
46.3	PMAA	0.824	17.6
18.5	PMAA	0.823	17.7

[a] The ratio I/I_0 means the ratio of the triple resonance experiment to the reference experiment. ^{14}N irradiation was performed at 21.686 MHz, the spin-echo delay amounts to 3.33 ms (i.e. 12 rotor periods).

pure PVIm. For the template complex all protons have a $T_{1\rho}$ between 4.0 and 5.0 ms, between the values for the pure PMAA and PVIm. This points to intimate mixing of the two polymers in the complex.

3.3. $^1H/^{13}C/^{14}N$ Triple Resonance Experiments. Figure 5 shows the results of the triple resonance experiments. Spectrum a was acquired without ^{14}N irradiation; spectrum b, with irradiation. The difference spectrum is shown in (c) and indicates the loss of refocused ^{13}C intensity during ^{14}N irradiation for all resonances. Table 2 lists the relative decreases, relative to the control experiment (a).

The largest intensity decrease, about 50%, is seen for the imidazole ring, where the carbons are adjacent to the ring nitrogen. The PMAA resonances at 46 and 18 ppm show the smallest change (17%). The loss of ^{13}C intensity at 183.3 ppm (30%), the resonance of the PMAA carbonyl group, is the largest for PMAA.

This suggests a specific interaction between the carbonyl group of PMAA and the imidazole ring of PVIm.

4. Discussion

The triple resonance results and the proton $T_{1\rho}$'s of the polymer complex of PMAA and PVIm provide information about the mixing within this polymer complex.

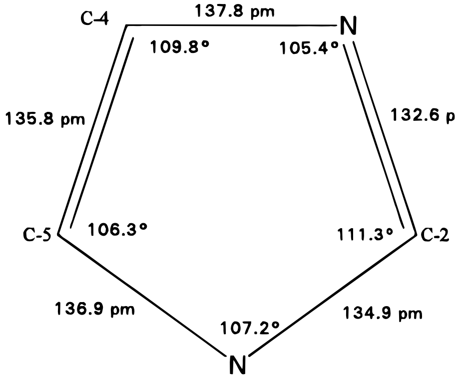

Figure 6. Exact geometry of the imidazole ring in PVIm.[15]

Table 3. Results of the Distance Calculation (Å) with the Two Different Models for the Internuclear Distances between PMAA and PVIm

model 1 $A = 9337.8 \pm 2801$	model 2 $A = 6373.6 \pm 598$, $B = 29776.9 \pm 7572$
C_6—N_1 = 1.55 ± 0.58	C_6—N1 = 1.37 ± 0.12
C=O—(N_1,N_3) = 1.44 ± 0.44	C=O—(N_1,N_3) = 2.13 ± 0.29
CH_3—(N_1N_3) = 1.74 ± 0.79	CH_3—(N_1,N_3) = 2.56 ± 0.42
quart C—(N_1,N_3) = 1.74 ± 0.79	quart C—(N_1,N_3) = 2.56 ± 0.42

The loss of ^{13}C-echo intensity is dependent on the distances between carbon and nitrogen, because the dipolar coupling between a carbon and a nitrogen spin are proportional to the inverse third power of the distance. With the known geometry of the imidazole ring as shown in Figure 6, we can estimate the internuclear distances between PMAA and PVIm.

For our model calculation we assume that the loss of carbon echo intensity in the experiment with nitrogen irradiation depends on two factors: (1) the distance r_i between the carbon under consideration and nitrogen i; (2) an interaction parameter that takes into account the magic angle spinning speed and the size of the nitrogen quadrupole interaction.

The last parameter describes how adiabatic the passages through the nitrogen resonances are.[4] In such a description the influence of the relative angles of the C−N dipolar tensor and the nitrogen quadrupolar tensor principal axes is neglected.

In model 1 we assume that both nitrogens can be described by the same interaction parameter, so that the relative decrease of the spin-echo intensity of a certain carbon is

$$\frac{I - I_0}{I_0} = -A\left(\frac{1}{r_1^{\,3}} + \frac{1}{r_3^{\,3}}\right) \tag{1}$$

where r_i is the distance from the carbon under consideration to nitrogen i (see Figure 6).

In model 2 we offer this relation

$$\frac{I - I_0}{I_0} = -\frac{A}{r_1^{\,3}} - \frac{B}{r_3^{\,3}} \tag{2}$$

For three carbons in the imidazole ring, carbons C_2, C_4, and C_5, we know the carbon−nitrogen distances and we can use these carbons to determine A and A and B, respectively; see Table 3. It shows that for these three carbons the spread in A and B values is only ±25%, which is not bad taking into account the crudeness of the models. We can now use the two models to calculate for PVIm carbon C_6 the distance to the imidazole nitrogen N_i and compare it to the known value. We find for the C_6-N_1 distance 1.55 Å with model 1 and 1.37 Å with model 2. Especially the value calculated with model 2 is close to the literature value of 1.32 Å,[16] and therefore we have some confidence in applying these models to determine the intermolecular distances.

Table 3 shows the results for the PMAA C=O, CH_3, and quaternary carbon. These results are calculated with an averaged C_{PMAA}—nitrogen distance for the two nitrogens. The indicated error ranges result from the error in *A* and *B* values and should not be considered as a real error range.

As mentioned above, the model used for Table 3 completely neglects that the *A* and *B* factors depend on the local geometry and are not really transferrable from the PVIm ring to the PMAA carbonyl carbon. However, since the local geometry in the blend is not known, we cannot easily refine the model.

In spite of the crudeness of this model we believe that the results indicate that the majority of the PMAA carbons are within ~3 Å from the imidazole ring, supporting the existence of a polymer complex as reported by Challa et al.[9-14]

5. Conclusions

The capability of the TRAPDOR triple resonance technique to detect polymer miscibility has been demonstrated. With a simple model we can approximate the distances between PMAA and PVIm from the resulting loss of ^{13}C-echo intensity.

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