CP-MAS ^{13}C NMR Spectra of Poly(*N*-vinylcarbazole) Complexes with 2,4,7-Trinitro-9-fluorenone and 2,4,5,7-Tetranitro-9-fluorenone

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ABSTRACT: Charge-transfer complexes of poly(*N*-vinylcarbazole) (PNVC) with 2,4,7-trinitro-9-fluorenone (TNF) and 2,4,5,7-tetranitro-9-fluorenone (TENF) were prepared by slow evaporation of a common solvent and investigated by CP-MAS ^{13}C NMR spectroscopy. Parallel studies were performed on crystalline complexes of *N*-ethylcarbazole (NEC) with the same electron-acceptor molecules: TNF and TENF. Charge-transfer interaction is observed in the complexes by upfield shifts of various signals. In the PNVC complexes, only one signal can be assigned to the charge-transfer complex with TENF. All the other potential shifts are overlapped by the broad polymer signals. TNF and TENF are not proton-rich substances, and in their complexes almost all the magnetization arises from intermolecular interaction, transmitted from the electron-donor molecule, which is richer in protons. Charge-transfer interaction depresses the value of the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$H) of PNVC to a higher extent in its complexes with TENF. This allows selective observation of "uncomplexed" electron-acceptor molecules at longer contact times. The number of $T_{1\rho}$H values found for a particular complex is indicative of the homogeneity of that charge-transfer complex. It appears that PNVC-TENF is homogeneous for any sample containing less than 50 mol % TENF and becomes a mixture of at least two components at higher TENF content. Mixtures of PNVC with TNF, however, are not homogeneous at any composition.

Introduction

Poly(*N*-vinylcarbazole) (PNVC) is one of the most studied specialty polymers. The interest in this polymer was brought about by the discovery of its photoconductive properties. Its ability to form charge-transfer complexes with suitable electron-acceptor groups opened a whole new area of research. The most studied charge-transfer complex of PNVC had as the electron-acceptor compound 2,4,7-trinitro-9-fluorenone (TNF). A monograph published in 1981 by Pearson and Stolka[1] can still be considered the main reference in the field. Many papers have been published on charge-transfer interactions in polymer systems, and the polymers studied may or may not contain carbazole groups. The photoconductive properties of charge-transfer polymers are no longer the main point of investigation. Charge transfer, as part of a larger group of nonbonding interactions, can be considered as a model for transmission of information in living systems. A considerable amount of research is being done on the potential nonlinear optical properties of polymer materials containing electron-donor and -acceptor groups. These properties are generated by the alignment of such groups in strong electric fields, for example. Among a great number of systems under investigation, the PNVC-TNF complex was shown recently to possess third-order nonlinear optical susceptibility. The source of this property was charge-transfer excitation and not the free carriers responsible for photoconduction.[2]

Our research has been centered around resolving two problems of charge-transfer interactions in polymers. The first one was building intramolecular charge-transfer complexes by copolymerization of monomers containing donor groups and other monomers containing acceptor groups. The donor site was carbazole in most of the cases. A series of synthetic conditions were employed that affected the extent of charge transfer in the copolymer.[3] Some of these copolymers proved to be photoconductive, having a maximum photocurrent in the near-infrared region.[4-6] The second problem, and the more interesting one, was the measurement of the extent of charge-transfer interactions in the polymers. The most common way to do this is to run the electronic spectra of the polymers and to measure the maximum absorbance of the charge-transfer band in the visible range of the spectrum.[7] We used mainly NMR spectra. Some of the chemical shifts could be correlated with the changed electronic density of one or the other site. Proton[3] as well as carbon[5] shifts proved to be useful. Both these methods measure the charge-transfer interaction in solution. The charge-transfer interaction is found to depend strongly on solvent and concentration.

Measurements of charge-transfer interactions in the solid state are not very common. For blends of polymers containing donor and acceptor groups, respectively, Percec et al.[8] demonstrated that a decomplexation endotherm can be observed in differential scanning calorimetry (DSC) scans and can be used to measure the thermodynamic parameters of interaction in the solid state. Absorption and electroabsorption spectra of films of PNVC-2,4,7-trinitro-9-fluorenone (TNF) complexes have been previously analyzed in terms of complex composition by using certain limiting approximations.[9] We have started a series of investigations of charge-transfer interactions in polymer systems using solid-state high-resolution ^{13}C NMR spectroscopy (CP-MAS). It was first demonstrated in 1981[10] on small molecular charge-transfer complexes that CP-MAS ^{13}C NMR spectroscopy can give information on changes of electron densities due to complexation (by means of chemical shift changes) and on changes in the cross-polarization pattern. Changes in chemical shifts due to complex formation have been studied in clathrate complexes as well.[11]

In recent papers on an intramolecular complex (copolymer) containing a carbazole unit as the donor and a dinitrobenzoic ester unit as the acceptor, we demonstrated using model compounds and blends of the homopolymers the following: (1) Upfield shifts up to 5 ppm occur in such systems. From the change in the electron densities due to charge-transfer interaction one would expect an upfield shift of the acceptor (increased electron density around the carbon nuclei) and a downfield shift of the

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donor signals (decreased electron density). It is observed that both shift upfield, the acceptor signals to a greater extent than the donor signals. This is believed to be due to the predominant effect of aromatic shielding in the stacked structure formed by complexation.[12] (2) The $T_{1\rho}$H value (the spin–lattice relaxation time in the rotating frame), which is indicative of spin diffusion in the system, can be related to the degree of charge-transfer interaction between the donor and acceptor groups.[13] Also, the $T_{1\rho}$H value is very sensitive to the presence of minute amounts of solvent trapped in the polymer film.

More recent studies suggest that the use of $T_{1\rho}$H as an indication of charge-transfer complex formation can be extended to polymer blends containing interacting groups. $T_{1\rho}$H is one of the parameters used to determine if a polymer blend is compatible.[14] Its use in polymer blends containing charge-transfer interacting groups can demonstrate the phase structure of the blend and the "degree" of interaction between the components.[15]

In our opinion, the use of CP-MAS ^{13}C NMR spectroscopy to study charge-transfer interactions in polymer systems is extremely promising, generating information on spin diffusion and molecular motion in the kilohertz range (by $T_{1\rho}$H measurements) and on complex molecular geometry (mainly chemical shift effects). These are just two of the parameters that can be measured in the solid state by CP-MAS spectroscopy, and we are planning to extend our studies later. For the time being, measurement of these two parameters can be used to better our understanding of charge-transfer interaction in various polymer systems.

The subject of investigation in the present paper is the PNVC–TNF complex. It is probably one of the most intensively studied polymer charge-transfer complexes in the literature. Our CP-MAS ^{13}C NMR research began with this complex. However, it proved to be more complicated and took longer than expected. Both components needed preliminary studies just to assign the NMR spectra. A complete assignment of the PNVC spectrum in solution is presented in another paper.[16] TNF is an asymmetrical molecule, with 13 different carbon atoms that generate 13 different signals. Due to the difficulty of interpretation of the spectra, a parallel study was undertaken on a similar but simpler molecule, 2,4,5,7-tetranitro-9-fluorenone (TENF). TENF also forms charge-transfer complexes with PNVC.[17] The complete carbon assignments for the two acceptor molecules in solution are published elsewhere.[18]

Experimental Section

PNVC (Aldrich) was purified by reprecipitation in a TNF–water or an acetone–methanol system. No residual monomer was present before or after purification, and no differences could be noted in the NMR spectra of the purified product. TNF (Polysciences) and TENF (Aldrich) were dried under vacuum before use. Complexes were obtained by slow evaporation of THF from a solution of the mixed components, followed by vacuum drying at 40 °C. Residual solvent was monitored by DSC. Complexes of PNVC with TNF were dark brown-purple. Complexes of PNVC with TENF were dark green. All complexes containing more than 50 mol % PNVC exhibited a metallic shine. *N*-Ethylcarbazole (NEC, Aldrich) was recrystallized three times from ethanol. 1:1 complexes of NEC with TNF and TENF were obtained by coprecipitation from dilute solutions in acetone. The crystals were filtered and subsequently dried under vacuum at room temperature. NMR samples were packed as powders; this required the breaking down of some shiny metallike films of polymer complexes with excess PNVC. CP-MAS ^{13}C NMR spectra were obtained on a Bruker CXP-200 spectrometer operating at 50.307 MHz. The 90° proton pulse was measured as 3.7 μs. The relaxation delay was set to 15 s, and the acquisition time was 0.102 s. To measure the $T_{1\rho}$H values, a pulse sequence with cross polarization and proton decoupling was employed, and the contact time was systematically varied. Starting at low values of the contact time, the signal first increases, reaches a maximum value, and then begins to decrease.[14] For some assignments, a dipolar dephasing procedure was used, with the pulse sequence described elsewhere.[19]

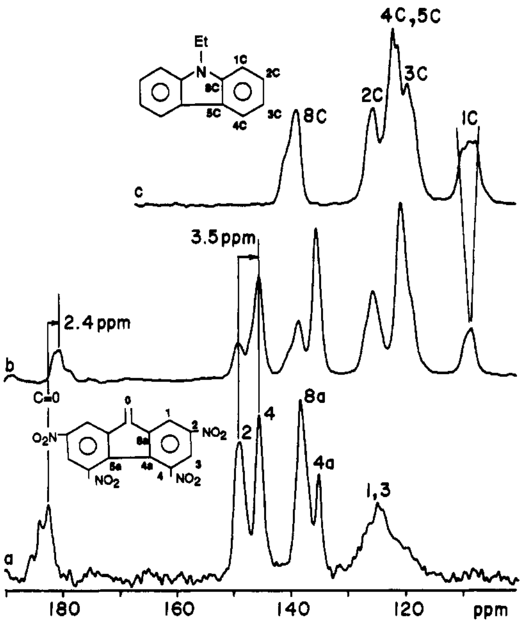

Figure 1. Aromatic and carbonyl regions of the CP-MAS ^{13}C NMR spectra of TENF (a), a crystalline 1:1 NEC–TENF complex (b), and NEC (c) obtained with a contact time of 80 ms.

Results and Discussion

Spectral assignments for PNVC in the solid state have been presented in earlier papers.[20,21] CP-MAS ^{13}C NMR spectra of TNF and TENF will be presented later on together with the spectra of their complexes. Two main points were kept in mind when analyzing the PNVC–TNF and PNVC–TENF complexes. The first was to identify any chemical shifts due to complexation and draw conclusions about the complex geometry; the second was to determine the composition of the charge-transfer complex resulting from mixtures containing varying amounts of the two components.

Chemical Shift Effects: Small Molecular Models. Small molecular charge-transfer complexes of hexamethylbenzene with certain electron-acceptor molecules revealed a downfield shift of the aromatic carbon signals of the donor, due to decreased electron density.[10] The acceptor was probably shifted upfield, but no evidence could be produced because of the nonprotonated nature of the molecule (no spectrum in the absence of a charge-transfer complex). For the system we studied previously, both the electron-donor and the electron-acceptor molecules had aromatic rings,[12] and all signals were shifted upfield due to the aromatic shielding effect. The same result can be expected for the PNVC–TNF and PNVC–TENF complexes. As in the previous case, however, the polymer signals are rather broad, and it is difficult to measure shifts of only a few ppm. Consequently we begin by presenting the chemical shift effects in small molecular complexes of NEC with TNF and TENF, respectively.

Figure 1 shows the aromatic regions of the CP-MAS ^{13}C NMR spectra of TENF (a), NEC (c), and the crystalline 1:1 NEC:TENF complex (b). All these spectra were obtained at a contact time of 80 ms. NEC has an unexpectedly complicated spectrum for a substance with only six nonequivalent carbons. It is obvious, especially from the signal around 110 ppm, which was expected to be a sharp singlet because it is due to carbon 1C, that NEC crystallizes in a such a manner that different molecules give different resonances because of their relative orientations. Attempts were made to obtained single crystals of NEC and to investigate its NMR spectrum in relation to its crystallinity, but the effort was abandoned after some unsuccessful initial results. Due to its abundance of protons, NEC gives a very strong spectrum at only a few scans and a minimal contact time (even 0.25 ms generated a good spectrum). For the same reason the relaxation mechanism is probably exclusively through protons, so the NEC spectrum is basically unchanged at contact times as long as 200 ms. Longer contact times were not tried due to hardware limitations.

TENF can be considered to be almost the opposite case. A large molecule containing only four protons, TENF generates an NMR spectrum only at longer contact times and a considerably greater number of scans. At longer contact times enough cross polarization is achieved to generate carbon signals. Subsequent increase of the contact time allows the signal to decay slightly due to the proton spin-lattice relaxation in the rotating frame. The 80-ms contact time used in Figure 1 has been chosen to allow comparison of the three spectra at the same contact time. The NEC-TENF complex has the same spectral characteristics as NEC because the complex contains a relatively large number of protons. A good spectrum can be obtained with a relatively small number of scans and at minimal contact times. Assignments for the TENF spectrum are relatively easy to make. The solution spectrum can be used as a guideline.[18] The signals are also rather broad, indicating some crystal effects (nonequivalent molecules in the crystal lattice), and the most obvious effect is felt by the carbonyl carbon, which seems to be split.

The spectrum of the crystalline NEC-TENF complex (Figure 1b) is quite different from the sum of the spectra of the two components. It is very difficult to assign all the signals in this spectrum, but there are a few obvious assignments. The carbonyl signals of TENF shift upfield by about 2.4 ppm; the exact figure is uncertain because of the splitting. The 1C signal of the carbazole ring narrows, indicating a change in the crystalline structure. The area between 143 and 150 ppm, assignable to the aromatic 2 and 4 carbons of TENF, suggests an upfield shift of the carbon 2 resonance of about 3.5 ppm, to resonate together with carbon 4. Not all the signals shift upfield, but the ratio of the intensities of the two signals is very different in TENF and in the complex. Probably the signals of carbons 8a and 4a behave similarly, but in this case there is interference from the 8C signal of NEC. The main NEC resonance area around 120-130 ppm narrows as well.

Figure 2 presents the spectrum of the NEC-TENF complex (b) together with the spectrum obtained by dipolar dephasing (a)—showing only nonprotonated carbons—and the spectrum obtained by difference (b) - (a) = (c)—showing only protonated carbons. The most important signal here is the nonprotonated carbon at 120 ppm, which belongs to carbon 5C of NEC. It is shifted 2 ppm upfield from the 122 ppm value in pure NEC, indicating charge-transfer complex formation. This signal is completely masked in the NEC-TENF complex spectrum by the intense protonated carbon signal.

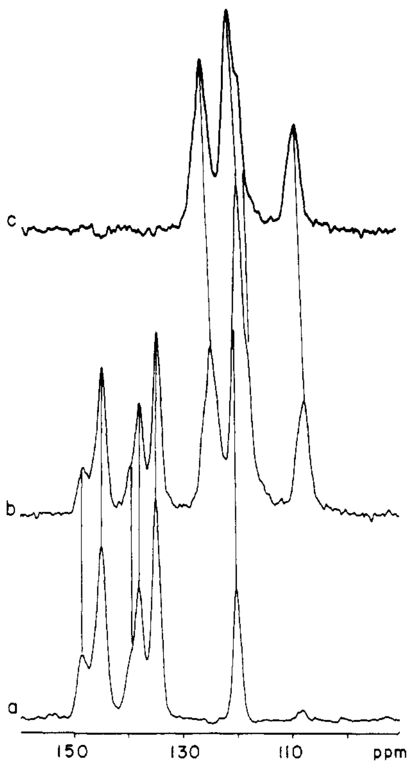

Figure 2. Aromatic region of the CP-MAS ^{13}C NMR spectra of a NEC-TENF complex obtained with dipolar dephasing (40-μs delay) (a), with a "normal" CP-MAS pulse sequence (b), and by subtracting (a) from (b) (c).

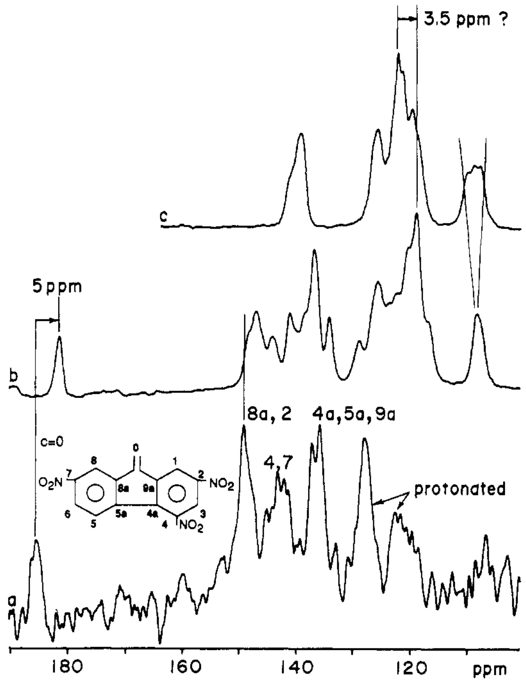

Figure 3. Aromatic and carbonyl regions of the CP-MAS ^{13}C NMR spectra of TNF (1500 scans) (a), a crystalline NEC-TNF complex (100 scans) (b), and NEC (100 scans) (c) obtained with a contact time of 80 ms.

Interpretation of the NEC-TNF complex spectra (Figure 3) is far more complicated. First, TNF takes many more scans than TENF to generate an acceptable spectrum. The spectrum shown in Figure 3a was obtained after 1500 scans, and the signal-to-noise ratio is much weaker than for the other two spectra, obtained after 100 scans. TNF gives a poorer spectrum than TENF, even though it has five protons, as compared with the four

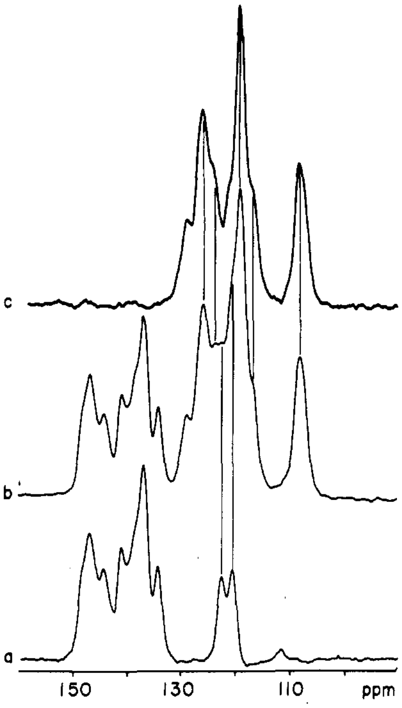

Figure 4. Aromatic region of the CP-MAS ^{13}C NMR spectra of a NEC–TNF complex obtained with dipolar dephasing (40-μs delay) (a), with a "normal" CP-MAS pulse sequence (b), and by subtracting (a) from (b) (c).

protons of TENF. A possible explanation is that maybe the two samples have different residual water content. The drying was performed under similar conditions, and different portions of the two samples were separately analyzed, but the results are always the same. Possibly TENF bonds water more strongly than TNF. Obviously, the carbon spectra do not give any indication concerning bound water or even if there is any. The assignments for this spectrum are approximate and presented in the figure. The spectrum of the crystalline NEC–TNF complex (Figure 3b) is more complicated than that of the NEC–TENF complex, mainly because TNF has 13 nonequivalent carbons. The only clear features are an upfield shift of the carbonyl carbon by about 5 ppm in the complex, together with upfield shifts of various magnitudes for the TNF carbons (the signals for carbons 2 and 8a have no counterparts in the complex spectrum) and the narrowing of the 1C carbon signal in NEC. It can be assumed that the most intense signal of NEC, at 123 ppm, now resonates upfield by 3.5 ppm in the complex. One of the most important features of the spectrum in Figure 3b is the remarkable intensity of the signals corresponding to the TNF carbons in the complex, as compared with the corresponding signal in TNF. It can be assumed that all the magnetization now comes from the protons of NEC, intermolecularly transmitted within the charge-transfer complex.

Complete assignments for the signals of the NEC–TNF complex are very difficult to make, even more so than those of the previously analyzed NEC–TENF complex. However, dipolar dephasing is of some assistance, and Figure 4 shows the nonprotonated carbon spectrum (a) and the protonated carbon spectrum obtained by difference (c) in comparison with the "normal" spectrum (b). The most interesting feature is the double signal at 122 and 120 ppm of the nonprotonated carbon 5C of NEC. If one imagines a sandwich complex between the two aromatic molecules, the two benzene rings of the carbazole can become nonequivalent because they are juxtaposed to the two different benzene rings of TNF (one mononitrated and the other dinitrated). This spectrum makes clear that one should expect double signals for each NEC carbon plus 12 aromatic carbon signals of TNF. Consequently, we have not attempted to assign it. As in the previous case, however, it is reasonable to assume that the signals between 143 and 150 ppm belong exclusively to TNF carbons.

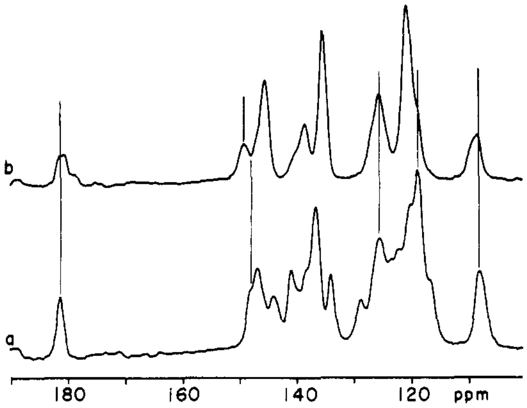

Figure 5. Aromatic and carbonyl regions of the CP-MAS ^{13}C NMR spectra of the NEC–TNF (a) and NEC–TENF (b) 1:1 crystalline complexes obtained at a contact time of 80 ms.

Comparison of the spectra of the two small molecular complexes (Figure 5) shows no significant differences between them in terms of chemical shifts. The carbonyl carbons resonate at about the same frequency for both, and only the next most shielded signal (carbon 2 of TENF) seems to be less shifted upfield than the corresponding signal of TNF. This difference might suggest a more favorable packing for the NEC–TNF complex, generating more aromatic shielding.

Chemical Shift Effects: PNVC Complexes. Poly(*N*-vinylcarbazole) has a $T_{1\rho}$H value of 112 ms. Two independent measurements were performed to confirm this value. One used the pulse sequence described in the Experimental Section, and the other used a different pulse sequence, which applies a 90° pulse to the proton reservoir followed by spin-lock of variable duration and then by cross polarization and acquisition while decoupling the protons.[22] The value of 112 ms means that the PNVC spectrum reaches a maximum intensity at about 2-ms contact and then maintains fairly intense signals for relatively long contact times. Figure 6e presents the spectrum of PNVC at 6-ms contact time. Figure 6b,c,d shows spectra of mixtures prepared with ratios of 6:4 (b), 4:6 (c), and 2:8 (d) of PNVC structural unit–TNF. The spectrum of the mixture obtained from a 8:2 ratio is not shown because it is identical with the spectrum of PNVC. All these spectra are obtained at a contact time of 6 ms. Figure 6a is the spectrum of TNF obtained at a contact time of 80 ms. The number of scans for Figure 6b–e is 200, while that for Figure 6a is 1500 scans. No chemical shifts can be observed in these spectra, mainly because the signals are very broad, and the area of interest (135–152 ppm) consists of a mixture of overlapping resonances. It is interesting to note, however, that in the sample with a great excess of TNF (Figure 6b), relatively sharp signals belonging to TNF can be resolved. As in the case of the small molecular complex, these signals are much more intense in the mixture than in TNF. This means that the excess TNF is intimately mixed with the PNVC and with some entity that could be considered to be a charge-transfer complex of PNVC and TNF and receives its magnetization from them.

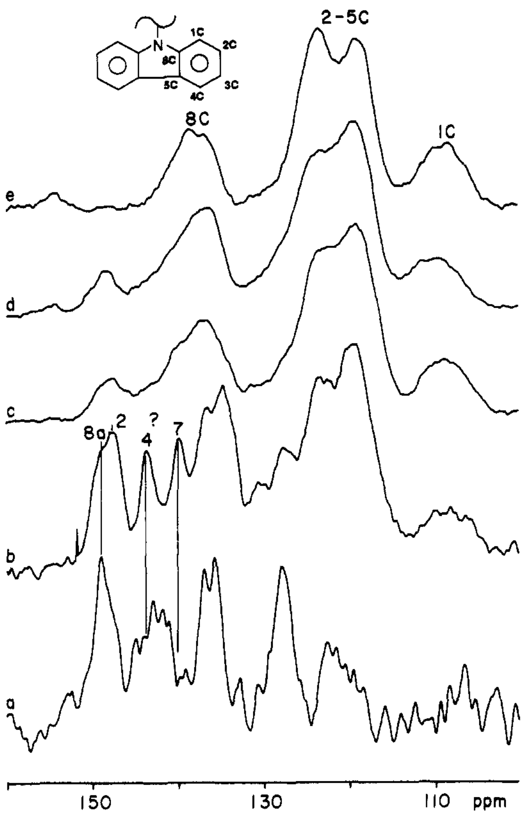

Figure 6. Aromatic region of the CP-MAS ^{13}C NMR spectra of TNF (contact time 80 ms) (a), a mixture of PNVC and TNF containing 20 mol % structural units of PNVC (b), a mixture with 40 mol % (c), a mixture with 60 mol % (d), and pure PNVC (e). Spectra (b)-(e) were obtained with a contact time of 6 ms.

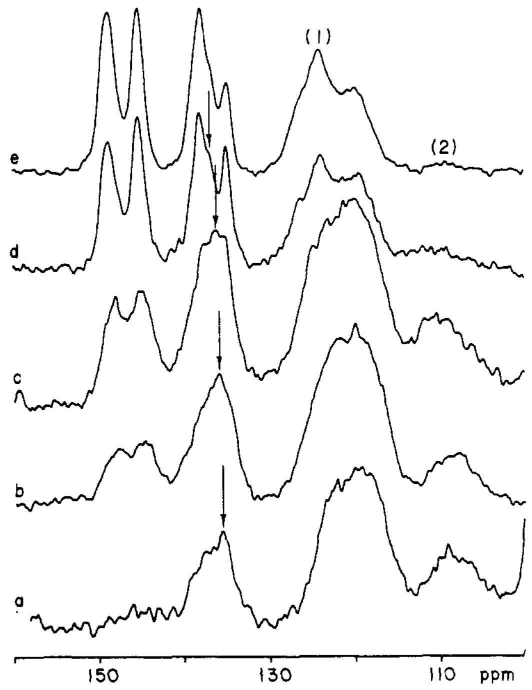

Figure 7. Aromatic region of the CP-MAS ^{13}C NMR spectra of mixtures of PNVC and TENF having various compositions: 85 mol % PNVC structural units (a), 66.7 mol % (b), 50 mol % (c), 33.3 mol % (d), and 15 mol % (e). All spectra were obtained at a contact time of 30 ms.

The spectra of PNVC-TENF mixtures are more informative. Figure 7 presents these spectra obtained from mixtures of PNVC with TENF containing 15 (a), 33.3 (b), 50 (c), 66.7 (d), and 85 (e) mol % TENF. All these spectra are obtained with a contact time of 30 ms. The spectrum of the sample containing 85 mol % PNVC is very similar to the spectrum of pure PNVC. Increasing the proportion of TENF in the mixture produces an increase of the signals between 143 and 150 ppm, which are due to complexed and uncomplexed TENF. There is another signal that is present in all spectra and appears to shift upfield with increasing PNVC content of the mixture, so that at 85% its position is the same as that observed for complexed TENF (135 ppm, Figure 1a). This signal is designated with an arrow on the figure. It is very difficult to distinguish it from the background noise, but it is a real signal and has a different relaxation behavior, as Figure 8 demonstrates. Figure 8 presents the spectrum of the mixture containing 33.3 mol % PNVC structural units and 66.7 mol % TENF. The "complexed TENF" signal is marked with an arrow and resonates at 137 ppm for this sample. One can clearly see that this signal is present at low contact times (1 ms, a), increases to reach a maximum between 2 (b) and 5 ms (c), then decreases by 10 ms (d), and has disappeared completely at 30 ms (e). This behavior is similar to that of some signals in this sample but differs from that of other signals. Hence, this signal could presumably be assigned to TENF molecules incorporated into some sort of charge-transfer complex with PNVC. The fact that it shifts upfield with decreasing TENF content in the mixture could indicate that this signal is an average of complexed and uncomplexed TENF, and at minimum amount of TENF in the mixture most of it is complexed and hence experiences the greatest upfield shift. Analysis of the evolution of these signals as a function of contact time is discussed in the last part of this paper.

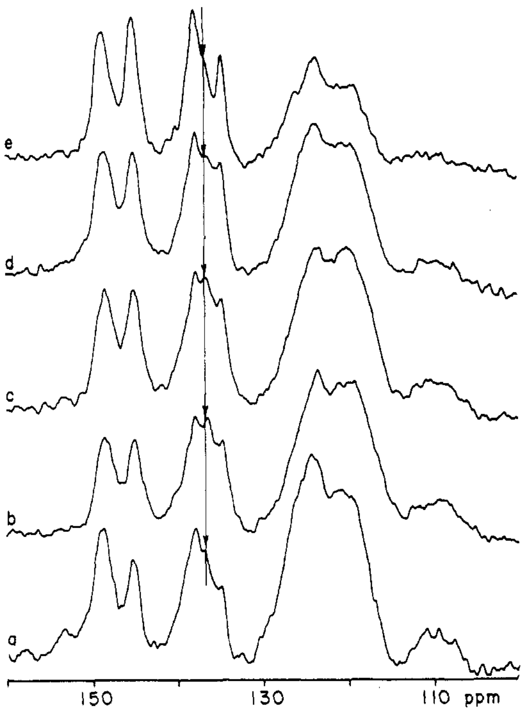

Figure 8. Aromatic region of the CP-MAS ^{13}C NMR spectra of a mixture of PNVC and TENF containing 33.3 mol % PNVC structural units obtained at different contact times: 1 (a), 2 (b), 5 (c), 10 (d), and 30 ms (e).

$T_{1\rho}$H Measurements in Polymer Mixtures. The curve of ln (signal intensity) as a function of contact time can be used to determine $T_{1\rho}$H at long contact times. For short contact times, valuable information about how the resonating carbons receive magnetization from the protons can be obtained. If a single $T_{1\rho}$H is being measured for all the components of a mixture, it usually means that the

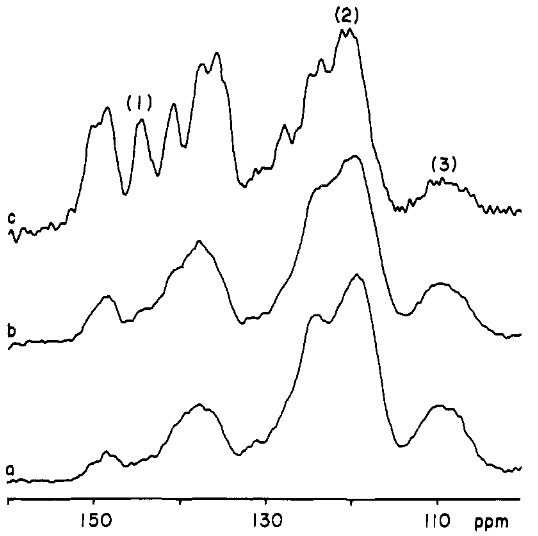

Figure 9. Aromatic region of the CP-MAS ^{13}C NMR spectra of a mixture of PNVC and TNF containing 40 mol % PNVC structural units obtained at 1- (a), 14- (b), and 200-ms (c) contact times.

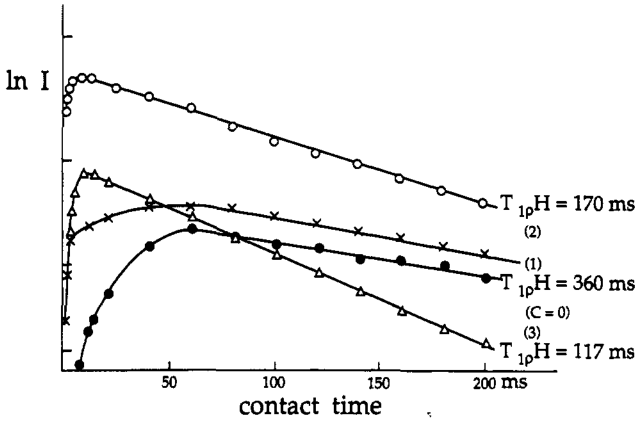

Figure 10. Evolution of magnetization as a function of contact time for a few signals (the numbers correspond to the signals shown in Figure 9) of the mixture PNVC–TNF with 40 mol % PNVC structural units.

mixture is homogeneous at the molecular level, i.e., the components are in close communication. For polymers, this principle applies to materials below their glass transition temperatures. This is definitely the case for PNVC, which has a T_g of 220 °C. Another interesting phenomenon is the buildup of magnetization for various components of the mixture. TENF and TNF alone build up very slowly, while in their complexes they receive magnetization from the electron-donor molecules.

Figure 9 shows the spectra of a mixture containing 40 mol % of PNVC structural units and 60 mol % of TNF. Though some signals belonging to TNF in its complexed form are obvious even at low contact times (1 ms, a) at around 150 ppm, they increase and become the main part of the spectrum at very long contact times (200 ms, c). Signal intensity was measured at various points in the spectrum and plotted as a function of contact time duration. Figure 10 shows such a plot for four signals: the carbonyl carbon of TNF, the signal marked with (1) in Figure 9c, arising mainly from TNF carbon 4, the signal marked (2) in Figure 9c, which is probably a combination of PNVC and TNF resonances, and finally the broad signal marked (3) in Figure 9c, belonging exclusively to carbon 1C of PNVC. Each signal generate a different $T_{1\rho}$H value, indicating inhomogeneity of the mixture. The fastest relaxing signal belongs to the polymer and has a relaxation time close to that of the pure PNVC. Everything else relaxes much slower, with the longest relaxation time for this sample of 360 ms (the carbonyl carbon of TNF). It is interesting to note that the carbonyl signal is composed of two parts. The one analyzed here is believed to arise exclusively from uncomplexed TNF, and the magnetization pattern can confirm this assignment, because it is very similar to that of pure TNF (reaches a maximum at ca. 60 ms). The other signal, shifted upfield by ca. 5 ppm but difficult to identify and measure because of some interfering spinning sidebands, is believed to belong to "complexed" TNF. Signal (1) is representative for the magnetization pattern of a resonance composed of both "complexed" and "uncomplexed" components. It grows fast at low contact times, comparably with signals belonging to the proton-rich polymer. After that it does not start decaying but still grows up to ca. 60 ms. One could conclude that the initial fast growth of the magnetization is that of TNF molecules, which form a charge-transfer complex with PNVC, while the second part of the growth period reflects only "free" TNF. This particular sample has an excess TNF and it is reasonable to assume that some of the TNF forms a separate phase in the mixture. For samples with higher TNF content the effects become more obvious because the excess TNF can be seen as a yellow powder mixed with the brown-black complex. However, no matter what the composition of the mixture, there are always some signals with slow relaxation behavior and some with intermediate values, and the fastest relaxing is the only signal that initially belonged to pure PNVC. Figure 11 presents a plot of $T_{1\rho}$H values as a function of mixture composition. These are only the minimum values of each sample, exhibited by the 1C carbon of PNVC. Each sample has a few measurable values that were not included in the figure. Because TNF is a crystalline substance with an unknown mechanism of relaxation, the value that could be measured for TNF was not included, because it does not have physical meaning.

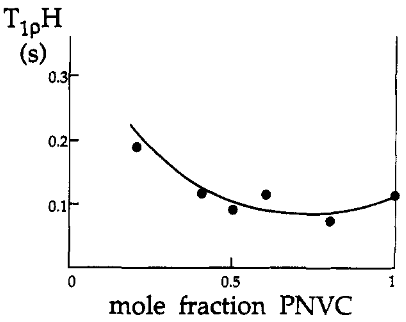

Figure 11. Plot of the minimum $T_{1\rho}$H value (measured on the 1C signal of PNVC) as a function of mixture composition in PNVC–TNF mixtures.

The value of $T_{1\rho}$H can be related to the distance required for spin diffusion,[23] and a depression of such values for charge transfer interacting systems was interpreted as a consequence of charge-transfer interaction (reduced mobility, hence increased efficiency of spin diffusion).[12,13] Figure 11 shows a continuous variation of $T_{1\rho}$H values, somewhat similar to the systems presented previously[13] but no real depression in comparison to the value of PNVC. It is important to emphasize that the points on Figure 11 represent *only* the $T_{1\rho}$H values measured for the 1C carbon of PNVC. Each sample analyzed had a few $T_{1\rho}$H values, all higher than the one in the figure, that were not included because of difficulties in assignments.

Mixtures of PNVC with TENF with an excess of TENF also show multiple relaxation behavior. An example is

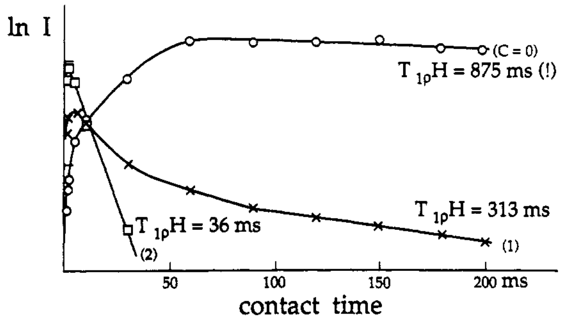

Figure 12. Evolution of magnetization as a function of contact time for a few signals (the numbers correspond to the signals shown in Figure 7) of the mixture PNVC–TENF with 15 mol % PNVC structural units.

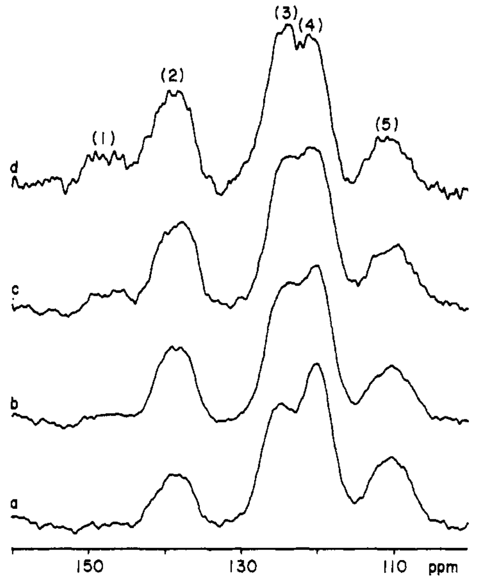

Figure 13. Aromatic region of the CP-MAS ^{13}C NMR spectra of a mixture of PNVC with TENF containing 85 mol % PNVC structural units obtained at 1- (a), 5- (b), 15- (c), and 25-ms (d) contact times.

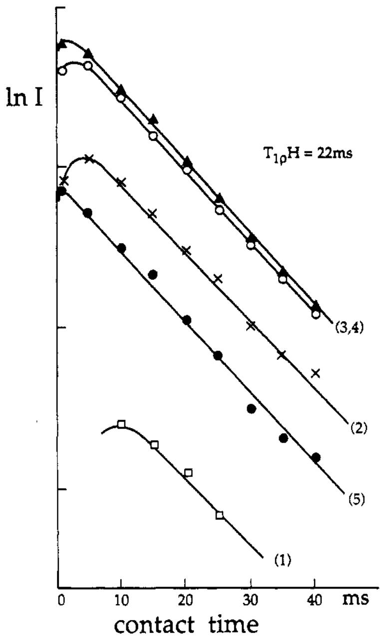

Figure 14. Evolution of magnetization as a function of contact time for a few signals (the numbers correspond to the signals shown in Figure 13) of the mixture PNVC–TENF with 85 mol % PNVC structural units.

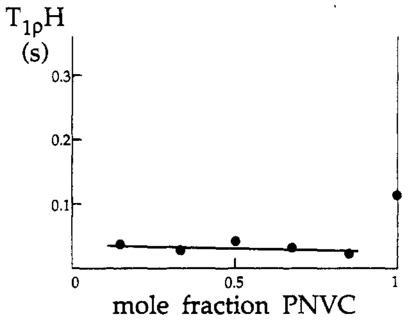

Figure 15. Plot of the minimum $T_{1\rho}$H value, measured on the 1C signal of PNVC, as a function of composition for mixtures PNVC:TENF.

presented in Figure 12 for a sample with 85 mol % TENF (see Figure 7e for an explanation of signals (1) and (2)). The "uncomplexed" TENF is shown by the relaxation behavior of the carbonyl signal and is similar to that of uncomplexed TNF. Signal (1) is a combination of the two components and it clearly has a nonexponential decay except at long contact times. Signal (2) belongs only to carbons 1C of PNVC and has almost completely disappeared by 30 ms. The $T_{1\rho}$H value of this signal (36 ms) is much smaller than any of the values read for the PNVC–TNF system.

Mixtures of excess PNVC with TENF however, behave as a single phase. Figure 13 shows the spectrum of a mixture containing 85 mol % PNVC structural units at a few contact times. The most notable characteristic of these spectra is the fact that the TENF-only signals (around 150 ppm) start appearing only at relatively longer contact times. Measuring the relaxation behavior anywhere in the spectrum (there are five points illustrated here) give a very consistent relaxation time constant (see Figure 14). This would suggest that mixtures of PNVC with TENF containing 50 mol % PNVC and less are perfectly homogeneous and that only excesses of TENF generate a multiphase system. A similar plot of $T_{1\rho}$H values as a function of the composition of the mixture (Figure 15) shows a fairly constant value of the charge-transfer complex $T_{1\rho}$H, independent of composition. It seems that no matter how little TENF is added to PNVC, a strong complex is formed and the two components are in very intimate contact. When TENF exceeds the 1:1 molar ratio, the excess is excluded from the charge-transfer complex and has a different relaxation behavior. For the first part of the graph in Figure 15, there are several experimental $T_{1\rho}$H values for each sample analyzed; they are not presented in the figure.

Comparing Figures 11 and 15, one can draw some conclusions concerning the composition and strength of charge-transfer interactions in PNVC–TENF and PNVC–TNF complexes, under the assumption that the depression in the $T_{1\rho\text{H}}$ value is associated with charge-transfer interaction. PNVC and TENF interact strongly and form a charge-transfer complex over a wide composition range. TENF is accommodated into the complex up to 50 mol %; at higher ratios it forms a separate phase. TNF forms a charge-transfer complex with PNVC, but it also exists separately in the mixture, independent of the initial composition. The depression of the $T_{1\rho}$H value in this case is much smaller than in the case of TENF, suggesting poorer communication between the components of the complex.

Conclusions

The results presented here, which are preliminary in nature, reveal that the CP-MAS ^{13}C NMR spectra of PNVC charge-transfer complexes convey a significant amount of information. Chemical shifts indicate charge-transfer complexation and are easily observable in the small molecular model compounds. Broad polymer spectra preclude observation of such chemical shift effects in most cases. However, one signal has been observed for the PNVC–TENF complex. In their complexes, both TNF and TENF acquire their magnetization from the more proton-abundant PNVC. Longer contact times, however, generate spectra that selectively observe "uncomplexed" small molecular acceptor molecules. This is due on the one hand to a slower polarization of such molecules and on the other hand to the decay of the charge-transfer complex signals (lower $T_{1\rho}$H value). Analysis of the magnetization behavior as a function of contact time indicates that the complexes PNVC–TNF are composed of a spread of chemically separate identities, possibly having different PNVC–TNF ratios in their charge-transfer complexes. The communications between the two components in PNVC–TNF is poorer than in PNVC–TENF. This last complex gives a single low $T_{1\rho}$H value for any composition with more than 50 mol % PNVC structural units. More TENF in the mixture generate a multitude of $T_{1\rho}$H values.

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References and Notes

(1) Pearson, J. M.; Stolka, M. *Poly(N-vinylcarbazole)*; Gordon and Breach Science Publishers: New York, 1981.
(2) Ghoshal, S. K.; Chopra, P.; Singh, B. P.; Swiatkiewicz, J.; Prasad, P. N. *J. Chem. Phys.* **1989**, *90*, 5078.
(3) Natansohn, A. *Polym. Bull.* **1983**, *9*, 67.
(4) Natansohn, A. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3161.
(5) Natansohn, A.; Flaisher, H. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 579.
(6) Natansohn, A. U.S. Patent 4,562,133, 1985.
(7) See, for example, the excellent review: Pearson, J. M.; Turner, S. R.; Ledwith, A. In *Molecular Association*; Foster, R., Ed.; Academic: New York, 1979; Vol. 2.
(8) Percec, V.; Schild, H. G.; Rodriguez-Parada, J. M.; Pugh, C. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 935.
(9) Weiser, G. *J. Appl. Phys.* **1972**, *43*, 5018, 5028.
(10) Blann, W. G.; Fyfe, C. A.; Lyerla, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 4030.
(11) (a) Lee, F.; Gabe, E.; Tse, J. S.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6014. (b) Komoto, T.; Ando, I.; Nakamoto, Y.; Ishida, S. *J. Chem. Soc., Chem. Commun.* **1988**, 135.
(12) Natansohn, A.; Simmons, A. *Macromolecules* **1989**, *22*, 4426.
(13) Simmons, A.; Natansohn, A. *Macromolecules* **1990**, *23*, 5127.
(14) The first paper suggesting the use of $T_{1\rho}$H as a probe for polymer-polymer compatibility was published in 1981: Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275. Tens of papers have appeared since then. The last one at the time of this writing is: Marco, C.; Fatou, J. G.; Gomez, M. A.; Tanaka, H.; Tonelli, A. E. *Macromolecules* **1990**, *23*, 2183.
(15) Simmons, A.; Natansohn, A. *Macromolecules*, in press.
(16) Natansohn, A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4257.
(17) Li, G.; Zhao, Y.; Liu, C. *Acta Phys. Chim. Sin.* **1987**, *3*, 551.
(18) Natansohn, A. *Polym. Bull.* **1989**, *21*, 217.
(19) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.
(20) Natansohn, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 21.
(21) Natansohn, A. In *Multiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Plenum: New York, 1989; p 401.
(22) Voelkel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468.
(23) McBrierty, V. J.; Douglass, C. J. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 295.

Registry No. PNVC·TENF, 109181-00-2; PNVC·TNF, 9020-74-0; TENF·NEC, 86807-37-6; TNF·NEC, 41481-16-7.