Intermolecular cross-polarization nuclear magnetic resonance studies of the miscibility of poly(ethylene naphthalene dicarboxylate)/poly(ethylene terephthalate) blends

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Cross-polarization/magic-angle spinning ^{13}C nuclear magnetic resonance measurements on blends of poly(ethylene terephthalate) (PET), poly(ethylene naphthalene dicarboxylate) (PEN) and copolyesters of PET and *p*-hydroxybenzoic acid (PHB) were performed using different dephasing times of the dipolar decoupling. In the case in which the spectra of the two components of the blends are different, information on miscibilities is obtained by measurements with full dipolar decoupling. In the case of similar spectra, however, this method cannot be applied. It is shown that, under this condition, information on phase separation is obtained if the measurements are performed with delayed decoupling and no decoupling. While blends of PEN and copolyesters of PEN are miscible, phase separation is obtained if one component contains PEN and the other one PET.

(Keywords: blends; miscibility; poly(ethylene naphthalene dicarboxylate); poly(ethylene terephthalate); nuclear magnetic resonance; copolyesters)

INTRODUCTION

Cross-polarization/magic-angle spinning/dipolar decoupling (c.p./m.a.s./d.d.) ^{13}C n.m.r. has been established as a valuable tool for the determination of polymer–polymer miscibility on a molecular scale. The ^{13}C c.p./m.a.s./d.d. n.m.r. methods most used to study polymer–polymer miscibility are the following ones:

(1) Investigation of the perturbation of the isotropic chemical shift[1–5]. This method can be applied if there is a strong interaction between the molecules of the two components, as for example hydrogen bonding[1–3], molecular complexion[4] and charge-transfer interactions[5]. In this case changes in chemical shift of the resonance line of those carbon atoms which are involved in this interaction provide evidence that the segments of dissimilar chains are well mixed on a molecular basis.

(2) Investigation of intermolecular c.p. effect in a blend in which one of the components is deuterated[1,6–8]. This method is based on the short effective range of the dipolar interaction between carbon atoms and protons. If there is no miscibility a resonance line of the deuterated carbon atoms is not observed. In the case of miscibility cross-polarization between the deuterated carbon atoms of one component and the protons of the other component induces the resonance line. This intermolecular cross-polarization can occur only if the average proton–carbon distances in two different molecules are of the order of 10 Å or less, i.e. if the system is miscible on a molecular scale.

(3) Determination of the proton spin–lattice relaxation times T_1 through analysis of the average decay rate of the protons of all carbon atoms. In the case of phase separation the two values of T_1 of the single components are found. In contrast, if miscibility occurs a single relaxation time is found for the blend, lying in between the relaxation times of the two components[1,9–11]. In the same way one can also use the rotating-frame proton spin–lattice relaxation time $T_{1\rho}$.

In some polymer blends the chemical shifts and even the proton relaxation times of the two components are the same. Therefore it is not possible to use the three methods mentioned above. The purpose of this publication is to show that another method, namely delayed decoupling and no decoupling ^{13}C c.p./m.a.s. n.m.r., can be utilized to obtain information about the miscibility in such blends.

These methods, in particular the delayed decoupling n.m.r., have been used before in resonance line assignment of non-protonated carbon atoms[12,13] and to distinguish between a rigid and a mobile phase in semicrystalline polymers[14,15]. However, up to now no use has been made of this method to investigate the miscibility of different polymers.

DESCRIPTION OF THE NEW METHODS

There are two methods to distinguish between the resonance lines of the two components of a blend even

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if the chemical shift values of the two components are the same:

First, one can measure the ^{13}C c.p./m.a.s. n.m.r. spectrum without dipolar decoupling. Under this condition, the high-resolution cross-polarization resonance lines from protonated carbon atoms are not observed[16,17]. Magic-angle spinning by itself, however, is sufficient to produce the high-resolution cross-polarization resonance line from quaternary carbon atoms in protonated polymers. Obviously, the more distant protons, which are not connected to the carbon atoms by chemical bonds, enhance the intensity of the n.m.r. lines of the ^{13}C atoms without considerable broadening of the line. In the same way the line of deuterated carbon atoms is activated by more distant protons. As a consequence, if in a blend the first component is protonated while the second one is deuterated, the lines of the carbon atoms of the second component will only appear if the two components form a single phase, and they will not appear if phase separation takes place.

Secondly, one can measure the ^{13}C c.p./m.a.s. n.m.r. spectrum with delayed decoupling. This method is often also called the dipolar dephasing experiment. Following the contact time, an extra delay, T_{DD}, is inserted before acquisition. The delay, normally 50–100 μs, allows those carbon atoms to dephase which have strong coupling to protons, while the contributions from quaternary and deuterated carbon atoms remain unaffected. As a consequence, if in a blend the first component is protonated while the second one is deuterated, the lines of the carbon atoms of the second component will only remain if the two components form a single phase, and they will disappear with increasing delay if phase separation takes place.

Of course, one obtains information only on the miscibility of a deuterated and an undeuterated component from such a measurement. It is well known that deuteration of components of a blend influences their miscibility. However, the influence is usually comparatively small.

EXPERIMENTAL

The investigations were performed on different blends, each consisting of two of the following components: poly(ethylene naphthalene-2,6-dicarboxylate) (PEN); poly(ethylene terephthalate) (PET); and copolymers of PEN and poly(4-hydroxybenzoate) (PHB), namely PEN-*co*-PHB(80:20) and PEN-*co*-PHB(60:40), where the numbers in parentheses represent the composition in mole per cent of the copolymer. The different components and their intrinsic viscosities in hexafluoroisopropanol are listed in *Table 1*. The composition of the blends in weight per cent are shown in *Table 2*. The letter d indicates that the material is deuterated and the subscript number after d indicates the number of deuterons per monomer unit. Details on the synthesis of the polymers including their deuterated forms are given in previous papers[18,19].

In order to prevent transesterification reactions between the different components, the blending was performed in solution. The components were dissolved in hexafluoroisopropanol and precipitated by ethanol. The powder obtained was dried *in vacuo* at 40°C for 48 h before the n.m.r. measurement was performed. The samples of the pure components were prepared in a similar way.

Table 1 The intrinsic viscosities $[\eta]$ ($dl\,g^{-1}$) of the polymers used as components in the blends investigated. The numbers in parentheses represent the composition of the copolymer (mol%)

Polymers	$[\eta]$ ($dl\,g^{-1}$)
PET	0.7969
PET-d_8	0.6334
PEN	0.9909
PEN-*co*-PHB(80:20)	0.4198
PEN-*co*-PHB-d_{14}(80:20)	0.2489
PEN-*co*-PHB(60:40)	0.5999

Table 2 The investigated blends and composition (wt%). The numbers in parentheses represent the composition of the copolymer (mol%)

Polymers	Composition (wt%)
PET/PEN	50/50
PET-d_8/PEN	50/50
PEN/PEN-*co*-PHB-d_{14}(80:20)	50/50
PET/PEN-*co*-PHB-d_{14}(80:20)	50/50
PET-d_8/PEN-*co*-PHB-d_{14}(60:40)	50/50

The n.m.r. experiments were performed at room temperature on a Bruker MSL 300 n.m.r. spectrometer operating at 75 MHz. The proton 90° pulse length was 4 μs, the sample spinning frequency was 4.5 kHz, the contact time was 3 ms, and the recycle time of the pulse was 4 s. Spin sidebands were suppressed by using the pulse sequence TOSS[20]. Some 500 transients were accumulated for the normal spectra and relaxation spectra, 2000 for delayed decoupling spectra, and 5000 to 10 000 for the no-decoupling spectra.

RESULTS AND DISCUSSION

Blend of PEN and PET

In the first series of experiments we wanted to find out whether the methods 1 and 3 mentioned in the 'Introduction' can be applied to determine the miscibility. The curves a, b and c in *Figure 1* show the ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of PET, the blend PEN/PET (50/50) and PEN respectively. (Numbers in parentheses separated by a 'slash' represent the composition (wt%) of the blend, while numbers separated by a 'colon' indicate the composition (mol%) within the copolymer.) The assignment of the resonance lines follows from a previous paper[21] and is indicated by the numbers on each trace. The spectra show that the values of the chemical shift are almost the same for all three materials. Therefore, it is not possible to get information on the miscibility of the system by using method 1. Similarly, the values of the proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, have been found to be almost the same, namely 7.75, 7.70 and 7.55 ms for PEN, PET and the blend PET/PEN (50/50) respectively. This shows that method 3 is not applicable, either.

In order to try to apply method 2 we measured the spectra of the blends in which PET was deuterated. The curves d and e in *Figure 1* show the spectra of PET-d_8 and the blend PET-d_8/PEN (50/50). Because of the similarity of the spectra of PEN and PET it is not possible to decide whether the lines of PET-d_8 have been activated by the protons of PEN or not.

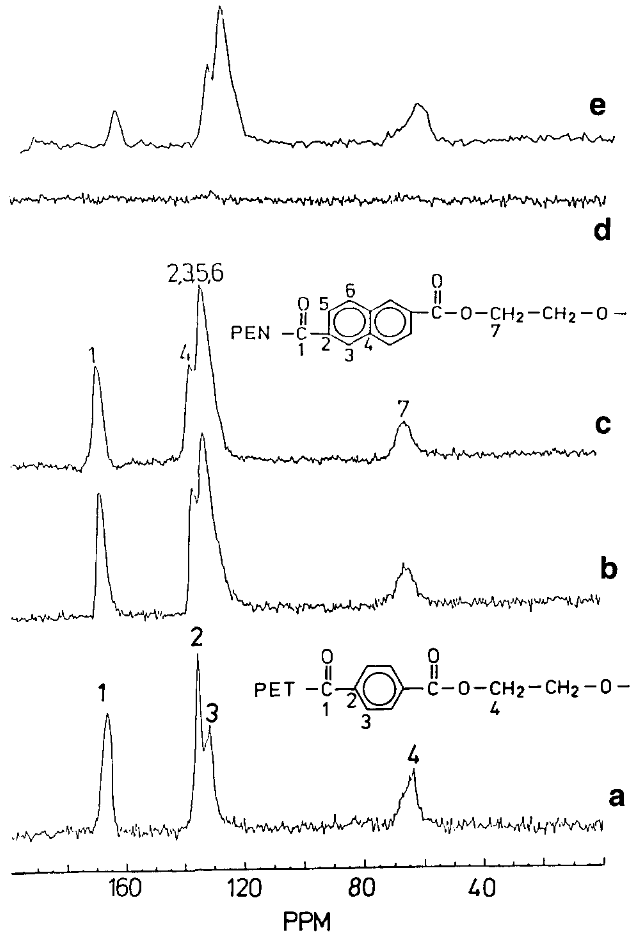

Figure 1 ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of (a) PET, (b) PEN/PET (50/50) blend, (c) PEN, (d) PET-d_8 and (e) PEN/PET-d_8 (50/50) blend

Let us next apply the new method of delayed decoupling and no decoupling. *Figure 2* shows the spectra of the PEN/PET blend under different decoupling conditions. As one can see, the spectrum clearly changes when the decoupling conditions are varied. The resonance lines of CH_2 completely disappear in the case of no decoupling. There only remain two very broad peaks of very small intensity, which arise from non-protonated carbon atoms, namely the carboxylic group and the quaternary carbon atoms. This shows that the lines of PET have not been activated by the protons of PEN, which proves tht PEN and PET are phase-separated.

*Blend of PEN and PEN-*co*-PHB(80:20)*

Let us first apply method 2. *Figure 3* shows the ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of protonated PEN, the protonated copolymer PEN-*co*-PHB(80:20), the corresponding deuterated copolymer and the blend of PEN and the deuterated copolymer. In the case of this blend, in the region between 120 and 140 ppm, there exist some characteristic differences in the spectra of the two components (see curves a and b). The copolymer shows some additional peaks. However, all peaks of PEN are also shown by the copolyester. As the copolyester was the deuterated species, it is not possible to recognize whether the peaks of the deuterated PEN in the copolymer have been activated by the protons of the protonated homopolymeric PEN or not.

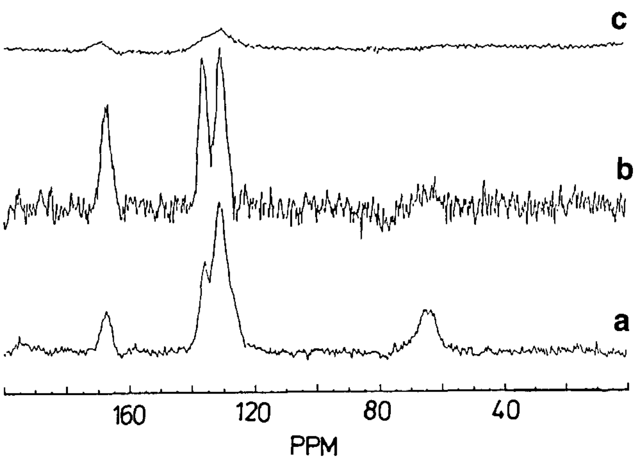

Figure 2 ^{13}C c.p./m.a.s. n.m.r. spectra of the blend of PEN/PET-d_8 (50/50) under various dipolar decoupling conditions: (a) full decoupling; (b) delayed decoupling (80 μs); (c) no decoupling

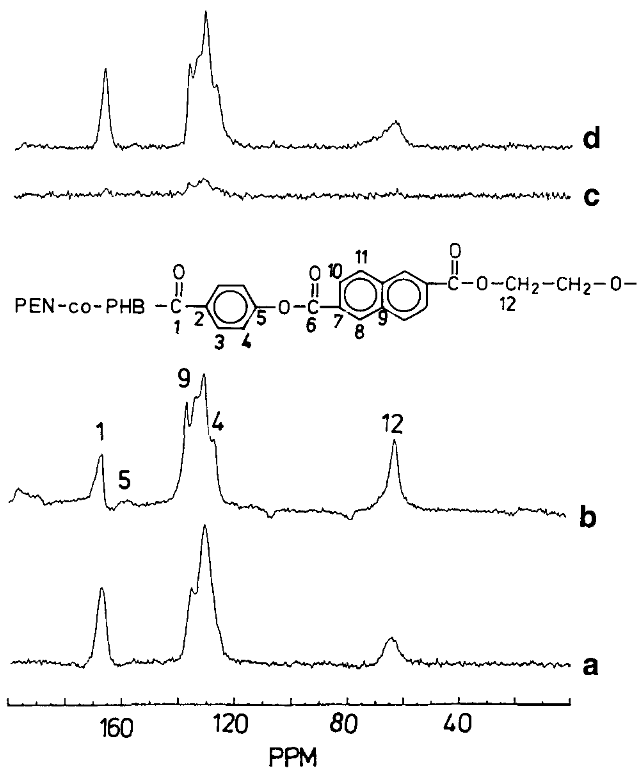

Figure 3 ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of (a) PEN, (b) PEN-*co*-PHB(80:20), (c) PEN-*co*-PHB-d_{14}(80:20) and (d) PEN/PEN-*co*-PHB-d_{14}(80:20) (50/50) blend

More information is obtained by using the method of delayed and no decoupling. *Figure 4* represents the corresponding spectra. One can clearly recognize the presence of the CH_2 line at 61 ppm in the no-decoupling spectrum, which is proof of miscibility. The broad line in the region from 120 to 140 ppm is a superposition of the resonance of the aromatic carbon atoms. The quaternary carbon atoms would give a contribution in any case (as for example in *Figure 3*) as the carboxylic carbon does. Therefore the resonance lines in the region from 120 to 180 ppm are not suitable to prove miscibility, in contrast to the CH_2 peak.

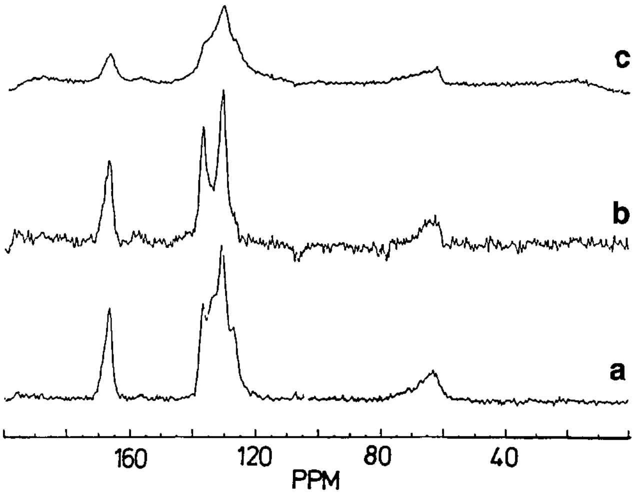

Figure 4 ^{13}C c.p./m.a.s. n.m.r. spectra of PEN/PEN-*co*-PHB-d_{14}(80:20) (50/50) blend under various dipolar decoupling conditions: (a) full decoupling; (b) delayed decoupling (80 μs); (c) no decoupling

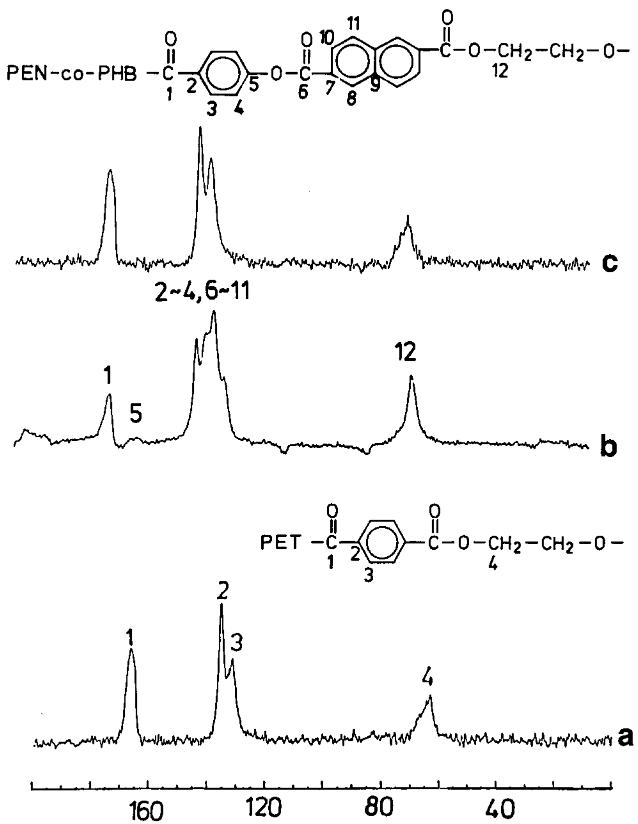

Figure 5 ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of (a) PET, (b) PEN-*co*-PHB-d_{14}(80:20) and (c) PET/PEN-*co*-PHB-d_{14}(80:20) (50/50) blend

*Blend of PET and PEN-*co*-PHB(80:20)*

Figure 5 shows the ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of protonated PET, protonated PEN-*co*-PHB(80:20) and the blend of the deuterated copolyester and protonated PET. In contrast to the results in *Figure 3*, the resonance lines of the copolyester (*Figure 5b*) do not appear in the spectra of the blend (*Figure 5c*). Therefore, we have to conclude that the two components are not miscible.

This result is supported by measurements using the method of delayed and no decoupling. *Figure 6* shows the corresponding spectra. In contrast to the result in *Figure 4*, the resonance line of the CH_2 groups in the copolyester is not activated by the protons of PET. This is proof of phase separation.

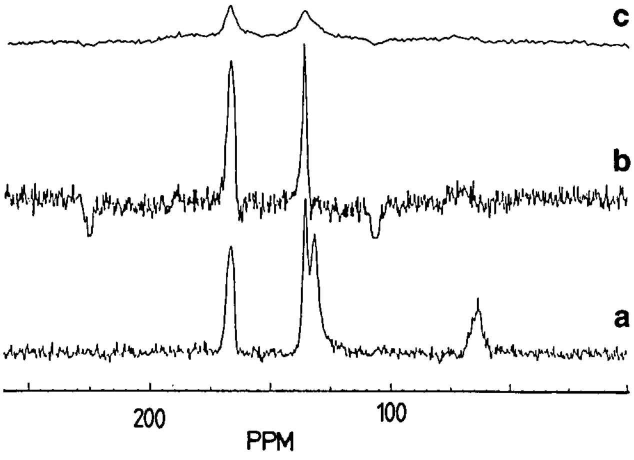

Figure 6 ^{13}C c.p./m.a.s. n.m.r. spectra of PET/PEN-*co*-PHB-d_{14}(80:20) (50/50) blend under various dipolar decoupling conditions: (a) full decoupling; (b) delayed decoupling (80 μs); (c) no decoupling

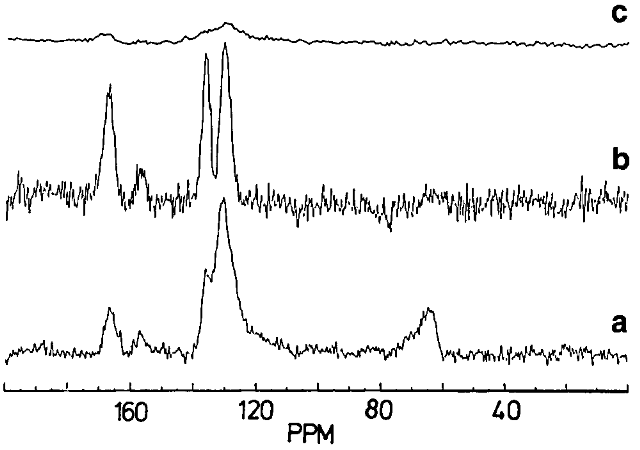

Figure 7 ^{13}C c.p./m.a.s. n.m.r. spectra of PET-d_8/PEN-*co*-PHB(60:40) (50/50) blend under various dipolar decoupling conditions: (a) full decoupling; (b) delayed decoupling (80 μs); (c) no decoupling

*Blend of PET and PEN-*co*-PHB(60:40)*

Finally, *Figure 7* represents the spectra of the blend of deuterated PET and protonated PEN-*co*-PHB(60:40) under different decoupling conditions. Let us first consider the spectrum obtained under full decoupling (*Figure 7a*). As in the case of the blend of PET with PEN-*co*-PHB(80:20) we cannot recognize whether a single phase is formed because PET has no characteristic line that is not also present in the copolyester. By inspecting the spectra obtained under delayed decoupling and no decoupling, however, we clearly see that the resonance lines of the CH_2 groups disappear, which proves that phase separation takes place.

In addition *Figure 8* represents the delayed decoupling spectra of the blend obtained by using different dipolar dephasing times. One can clearly recognize that the resonance line of the CH_2 groups has disappeared when the delay is longer than 30 μs. After this time, the lines of the quaternary carbon atoms and of the carboxylic groups in the copolyester are present while the lines of the deuterated PET are not activated.

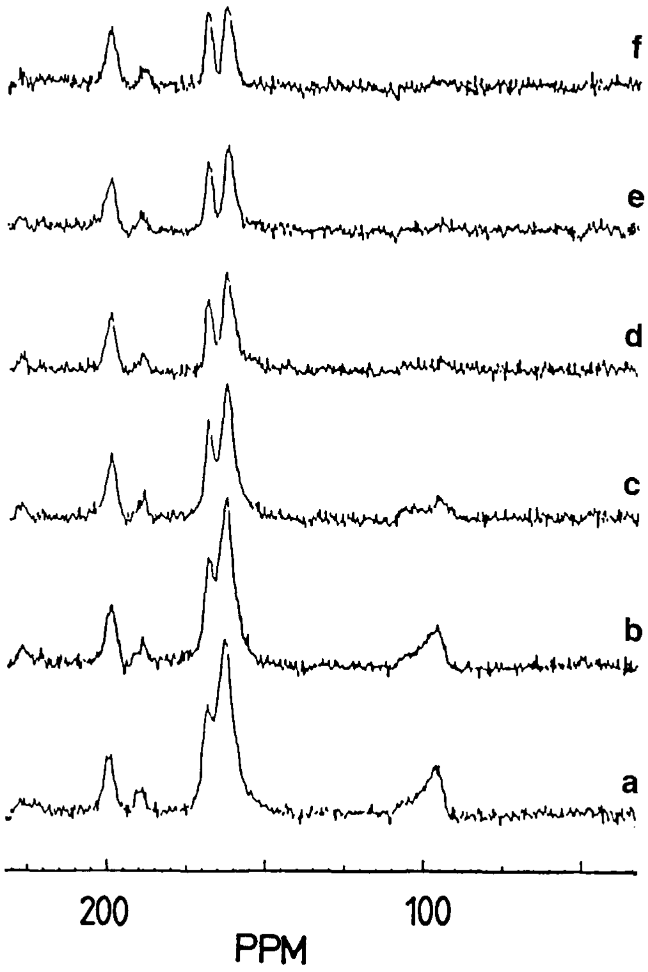

Figure 8 Delayed decoupling ^{13}C c.p./m.a.s./d.d. n.m.r. spectra of PET-d_8/PEN-*co*-PHB(60:40) (50/50) blend with different dipolar dephasing times: (a) 7 μs; (b) 10 μs; (c) 20 μs; (d) 30 μs; (e) 40 μs; (f) 50 μs

CONCLUSIONS

It is shown that the method of delayed dipolar decoupling and no dipolar decoupling yields important information on the miscibility of polymers on a molecular scale even in the case in which the resonance spectra of the two components are similar. Blends of PEN with the copolyester of PEN-*co*-PHB(80:20) are proved to be miscible, while blends of PET with PEN as well as of PET with PEN-*co*-PHB are phase-separated. It must be pointed out that no quantitative statement can be made concerning the extent of miscibility. From the measurements it can only be concluded that complete phase separation exists or not. Furthermore we want to emphasize that the measurements were performed on powder precipitated from solution. Therefore it cannot be excluded that phase separation is a consequence of fractionation during precipitation and that a single phase is formed after short melting. Further experiments on films melt pressed for different times will show if this is the case and they will also reveal the contribution of transesterification in the process of single-phase formation.

In order to find the extent to which phase separation takes place, investigations are in progress in which the dependence of the intensity of the resonance lines in the no-decoupling spectrum on the concentration of the protons is determined.

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REFERENCES

1 Yu, T. and Guo, M. *Prog. Polym. Sci.* 1990, **15**, 825
2 Cheng, C. and Belfiore, L. A. *Polym. Prepr.* 1989, **30** (2), 325
3 Zhang, X., Takegoshi, K. and Hikichi, K. *Polym. J.* 1991, **2**, 87
4 Qin, C., Pires, A. T. N. and Belfiore, L. A. *Macromolecules* 1991, **24**, 666
5 Simmons, A. and Natansohn, A. *Macromolecules* 1991, **24**, 3661
6 Zhang, X., Natansohn, A. and Eisenberg, A. *Macromolecules* 1990, **23**, 412
7 Parmer, J. F., Dickinson, L. C., Chien, J. C. W. and Porter, R. S. *Macromolecules* 1987, **20**, 2308
8 Belfiore, L. A. *Polymer* 1986, **27**, 80
9 Percec, S. and Hammond, T. *Polymer* 1991, **32**, 1252
10 Allen, P. E. M., Haglas, S., Simon, G. P., Williams, E. H. and Williams, D. R. G. *Polym. Bull.* 1986, **15**, 359
11 Dickinson, L. C. and Chien, J. C. W. *Polym. Prepr.* 1987, **28** (1), 112
12 Guo, M. and Zachmann, H. G. to be published
13 Clark, J. N., Jagannathan, N. R. and Herring, F. G. *Polymer* 1988, **29**, 341
14 Wilson, M. A., Pugmire, R. J., Alemany, L. B., Woolfenden, W. R., Grant, D. M. and Given, P. H. *Anal. Chem.* 1984, **56**, 933
15 Alemany, L. B., Grant, D. M., Pugmire, R. J. and Stock, L. M. *Fuel* 1984, **63**, 513
16 Schaefer, J., Stejskal, E. O. and Buchdahl, R. *Macromolecules* 1977, **10**, 384
17 Schaefer, J., Sefcik, M. D. and Stejskal, E. O. and McKay, R. A. *Macromolecules* 1981, **14**, 188
18 Jackson, W. J. and Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2043
19 Wu, W., Wiswe, D., Zachmann, H. G. and Hahn, K. *Polymer* 1985, **26**, 655
20 Dixon, W. T. *J. Chem. Phys.* 1982, **77**, 1800
21 Guo, M. and Zachmann, H. G. to be published