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Solvent effects on the miscibility of PMMA/PVAc blends
II. Using two-dimensional NMR method, NOESY

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Abstract

The influence of solvent on the miscibility of poly(methyl methacrylate)/poly(vinyl acetate), PMMA/PVAc, and the interpolymer interactions responsible for their miscibility were investigated. 2D nuclear overhauser effect spectroscopy, NOESY, experiments were performed with pure polymers and also with 50/50 blend. Under conditions of blend miscibility, chloroform at 40°C and toluene at 30°C, NOESY results indicated the presence of two different types of intermolecular interactions between (i) methoxy protons of PMMA and methyne protons of PVAc; (ii) methoxy protons of PMMA and methyl protons of PVAc. In immiscible conditions, in DMF and in benzene, both at 40°C, only type (ii) interactions were detected. These results indicate that intermolecular interactions between the methoxy protons of PMMA and the methyne protons of PVAc are responsible for the miscibility of the blends in chloroform and toluene. The interactions between the methoxy protons of PMMA and the methyl protons of PVAc do not contribute to the miscibility of the blend and were explained as originating from contacts of unlike polymers in the interphase. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Solvent effects in the miscibility; Polymer blends; 2D NMR spectroscopy

1. Introduction

The use of 2D NMR methods, like nuclear overhauser effect spectroscopy (NOESY), in the investigation of specific interpolymer interactions is of great fundamental interest [1,2]. Specifically, the utilisation of NOESY in the investigation of the miscibility of polymers has gained importance because this technique allows, in principle, examination of polymer–polymer interactions in detail [3,4]. In solution, dipole–dipole interactions, which is proportional to the inverse sixth power of the interproton distance, $1/r^6$, give rise to transient NOE [5]. Specific interactions may be detected by use of the ^{1}H NOESY if the interacting groups are ca. 5 Å from each other or less [5].

In comparison with the solid state, the NOESY technique in solution presents several advantages. One advantage is the fact that the resonance is narrower than in the solid state due to high chain mobility, which enables to investigate specific interactions [6–9].

Mirau et al. [7,8] and Crowther et al. [6] applied NOE experiments to PS/PVME blends in concentrated solution. It was pointed out that interpolymer NOE becomes appreciable only when the polymer concentration is more than 25 wt.%. Above 40 wt.% concentration the interpolymer NOEs between the aromatic protons of PS and the methoxy protons of PVME, which indicate the existence of intermolecular specific interactions, are the same magnitude as intrapolymer NOEs. Crowther et al. [6] also used NOEs experiments to examine the solvent dependent compatibility of the PS/PVME blends in concentrated solutions. Since interpolymer cross-relaxation was observed in toluene solution, they concluded that the polymers were intimately mixed. However, no intermolecular NOE was observed for the opaque (separated phase) blend in chloroform solution. Zhang et al. [10] showed that even in a phase separated solution, NOEs between PMA and PVPh appear. Thus, NMR is an appropriate technique for examining miscibility at the molecular level in solution and may be applied to investigate the influence of solvent on the miscibility between polymers in a blend.

From the DSC and FTIR data, as reported by Song et al. [11], and the viscometric and DSC results, reported in the preceding article of this series [12], it was concluded that the solvent influences the miscibility of PMMA/PVAc blends. When obtained by casting from chloroform, films of 50/50 PMMA/PVAc are transparent and attractive interactions

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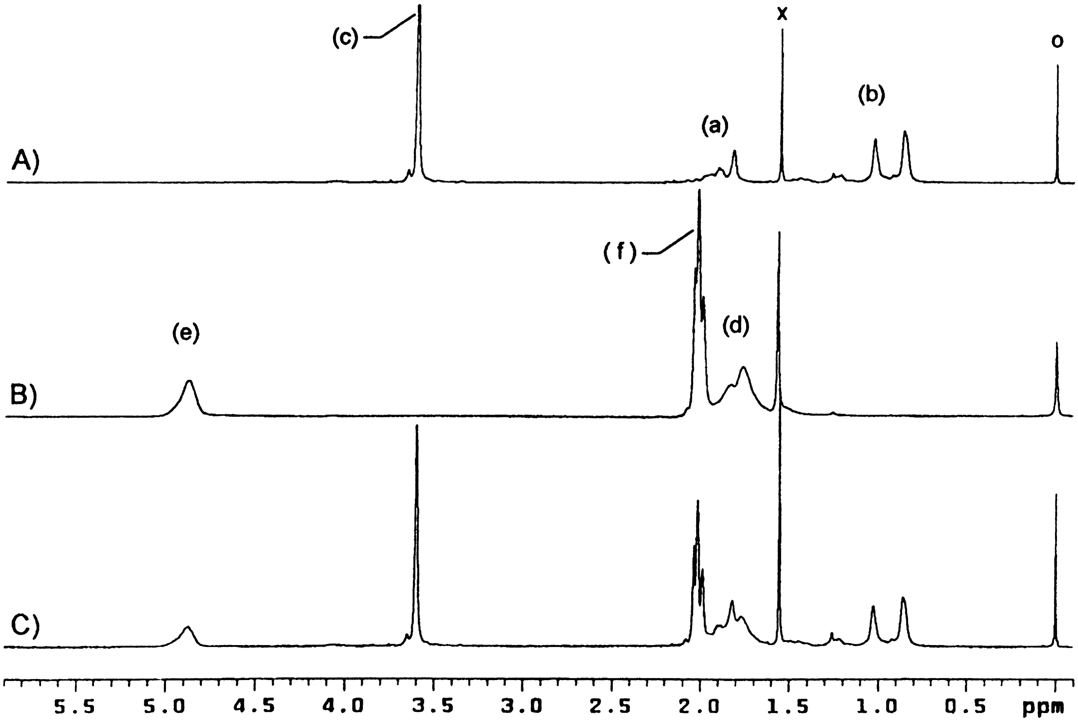

Fig. 1. ^{1}H spectrum of: (A) PMMA at 1% (w/v), (B) PVAc at 1% (w/v); and (C) 50/50 PMMA/PVAc blend at 3% (w/v), obtained in $CDCl_3$ at 40°C. The letters (a)–(f) indicate the protons as in Fig. 5. X and O indicate the peaks of H_2O and TMS, respectively.

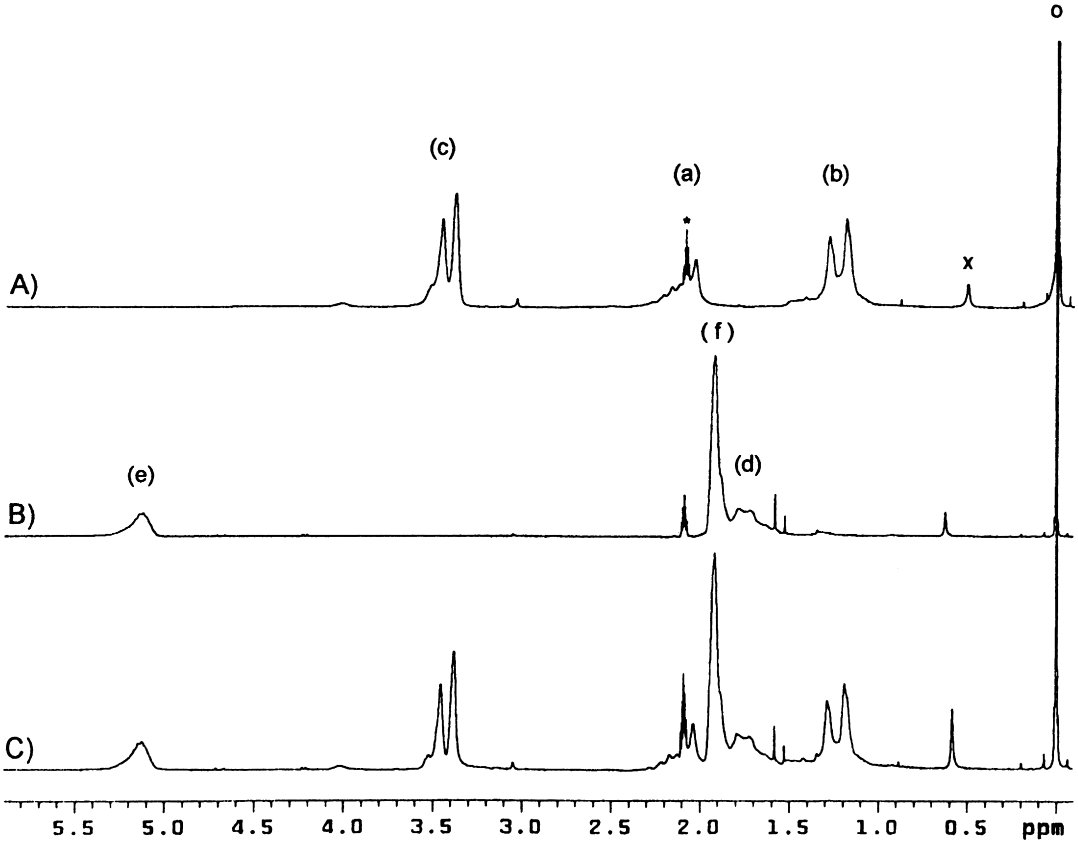

Fig. 2. ^{1}H spectrum of: (A) PMMA at 1% (w/v); (B) PVAc at 1% (w/v); and (C) 50/50 PMMA/PVAc blend at 3% (w/v), obtained in toluene-d_8 at 30°C. The letters (a)–(f) indicate the protons as in Fig. 5. X and O indicate the peaks of H_2O and TMS, respectively and * indicate the solvent peaks.

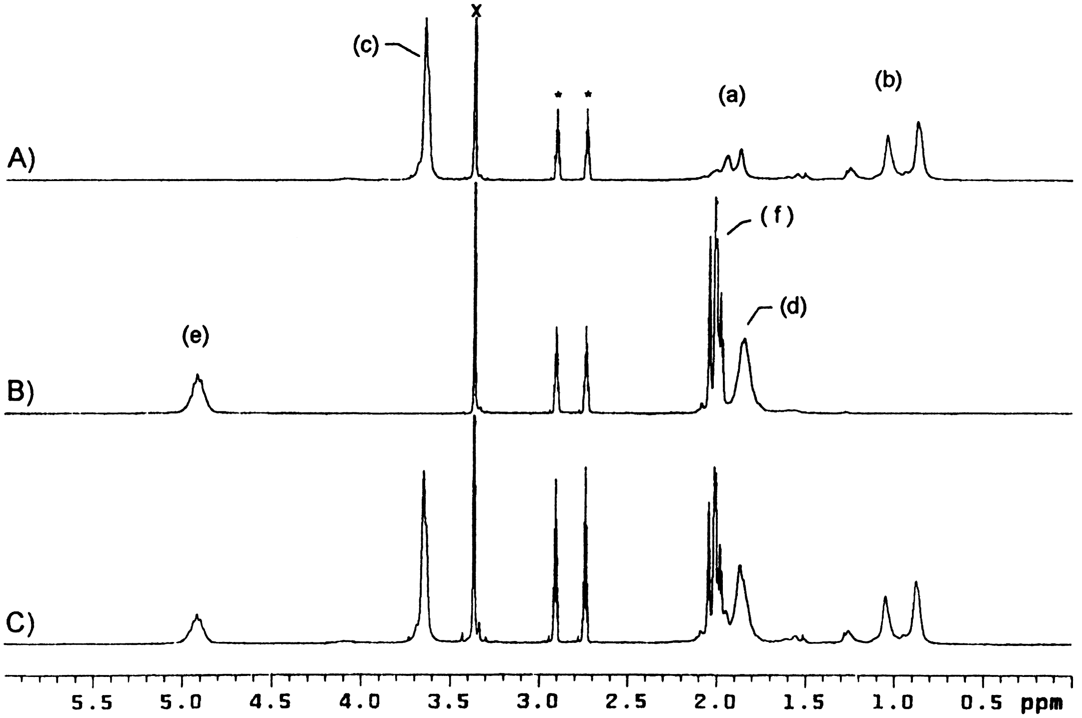

Fig. 3. ^{1}H spectrum of: (A) PMMA at 1% (w/v); (B) PVAc at 1% (w/v); and (C) 50/50 PMMA/PVAc blend at 3% (w/v), obtained in DMF-d_7 at 40°C. The letters (a)–(f) indicate the protons as in Fig. 5. X indicate the peaks of H_2O and * indicates the solvent peaks.

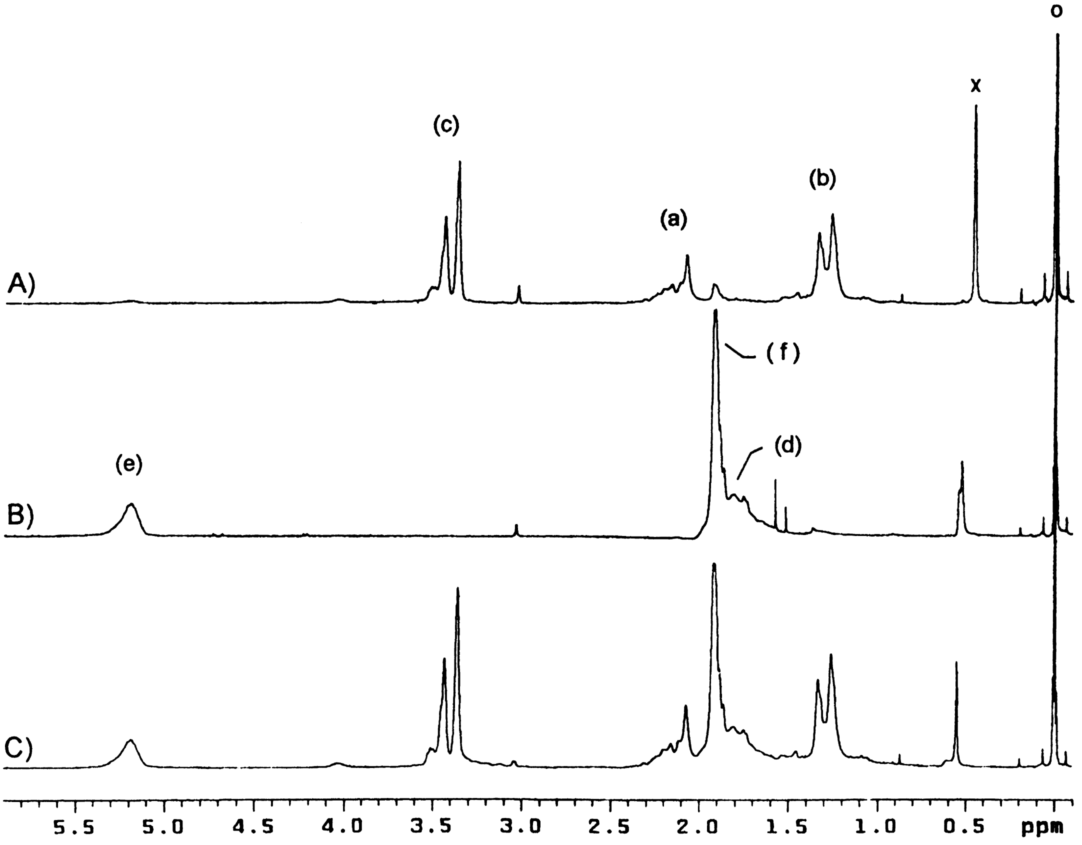

Fig. 4. ^{1}H spectrum of: (A) PMMA at 1% (w/v); (B) PVAc at 1% (w/v); and (C) 50/50 PMMA/PVAc blend at 3% (w/v), obtained in benzene-d_6 at 40°C. The letters (a)–(f) indicate the protons as in Fig. 5. X and O indicate the peaks of H_2O and TMS, respectively.

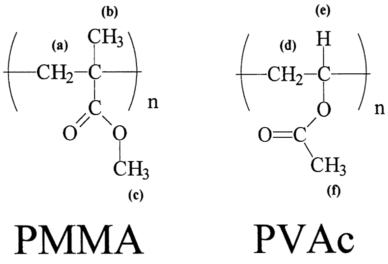

Fig. 5. Structures representing the various protons in the PMMA and PVAc polymers.

involving polymer-A/solvent/polymer-B were detected by viscometry measurements. When obtained by casting from DMF, the films were opalescent and repulsive interactions of unlike polymer coils seem to exist. In toluene, an intermediate situation was observed [12]; films of the blend showed transparency when cast at 30°C and opalescence when cast at 50°C. Based on these observations and on the viscometry results, it was suggested that attractive interactions prevail in toluene at 30°C but not at 50°C, whose viscometric properties of the system are closely similar to those presented in DMF. Thus, it was suggested [12] that in toluene at 50°C, each component would exist in their own coils.

This article reports results about the influence of the solvent on the miscibility of PMMA/PVAc blends using NOESY, 2D NMR spectroscopy. The purpose of the present study is to correlate the miscibility of PMMA/PVAc blends in different solvents, studied by DSC and viscometry [12], and the specific interactions between the polymers in solution, characterised by NOESY. These techniques are important and there is a little of study concerning this comparison.

2. Experimental

Poly(methyl methacrylate), PMMA (Aldrich 18,224-9, $M_v = 105.0\ \mathrm{kg\ mol^{-1}}$) and poly(vinyl acetate), PVAc (Aldrich, 18,949-9, $M_w = 83.0$; $M_v = 73.4$, both in $\mathrm{kg\ mol^{-1}}$) were used without prior purification.

All NMR measurements were performed at 300 MHz on a Varian spectrometer, model Gemini 2000. ^1H spectra were obtained from solutions at 1 wt.% for pure polymers and at 3 wt.% for 50/50 PMMA/PVAc blend in $CDCl_3$ 99D% (Aldrich), benzene-d_6 99D% (Aldrich), DMF-d_7 99.5D% (Aldrich) and toluene-d_8 99.5D% (Aldrich). Phase sensitive 2D NOESY experiments were performed from solution at 30 wt.% for pure polymers and at 40 wt.% for 50/50 PMMA/PVAc blend in $CDCl_3$, benzene-d_6, DMF-d_7 and toluene-d_8. The temperature was maintained at 40°C, except for the NOESY spectra obtained in toluene-d_8 for which the temperature was maintained at 30°C. The $(90°-t_1-90°-\tau_m-90°-\text{acquire})_n$ pulse sequence, according to the States et al. [13] method, was used. For each experiment, 256 1K complex spectra were acquired at several mixing times ranging from 25 to 750 ms. After zero filling in the t_1 dimension, the final data matrix size was 1K × 1K (real points). Apodization was used in both dimensions. The delay between acquisitions was 5 s.

Table 1
Chemical shifts of protons of PMMA and PVAc, determined in $CDCl_3$ and toluene-d_8 in 1 wt.%

^1H	δ (ppm)	
	$CDCl_3$	Toluene-d_8
(a)	1.82; 1.90; 1.94; 1.96	2.04; 2.11; 2.17
(b)	0.86; 1.03; 1.22	0.88; 1.05; 1.26
(c)	3.60	3.37; 3.46
(d)	1.76; 1.83	1.72; 1.74; 1.79
(e)	4.87	5.12; 5.15
(f)	1.99; 2.01; 2.03	1.92

Table 2
Chemical shifts of protons of PMMA and PVAc, determined in DMF-d_7 and benzene-d_6 in 1 wt.%

^1H	δ (ppm)	
	DMF-d_7	Benzeno-d_6
(a)	1.87; 1.94; 2.01; 2.08	2.07; 2.16; 2.20; 2.25
(b)	0.88; 1.05; 1.26	1.26; 1.33; 1.46
(c)	3.64	3.36; 3.44
(d)	1.85; 1.86	1.75; 1.81; 1.82
(e)	4.90; 4.92; 4.94	5.16; 5.21
(f)	1.97; 1.98; 1.99; 2.00; 2.01; 2.04	1.87; 1.89; 1.91; 1.92

3. Results and discussion

3.1. ^1H NMR measurements

In Figs. 1–4 the ^1H NMR spectra, at 300 MHz, of pure polymers (PVAc and PMMA) and their 50/50 blend in $CDCl_3$ (Fig. 1), toluene-d_8 (Fig. 2), DMF-d_7 (Fig. 3) and benzene-d_6 (Fig. 4) are shown. Peaks of different protons, according to the scheme of Fig. 5, are assigned in the spectra of the pure polymers. In Tables 1 and 2 the chemical shifts of each kind of proton as presented in the spectra of Figs. 1–4 are summarised. The existence of characteristic chemical shifts of different configurations of methyl protons *b* and methylene protons *a* of PMMA, can be observed in the different solvents. They were attributed to the presence of triads of several tacticity [14]. Except in toluene, a splitting in the signals of methyl protons *f*, of PVAc can be observed. A splitting of methylene protons *d*, also of PVAc was observed in the four solvents. This behaviour, according to the Ramey et al. [15] and Fugiwara et al. [16], is due to the presence of triads of different tacticity. In $CDCl_3$ and in DMF-d_7, the methylene protons *a*, of PMMA, and protons *d*, of PVAc, show very similar chemical shifts and, thus, peak overlapping is observed in the blend spectrum. In toluene

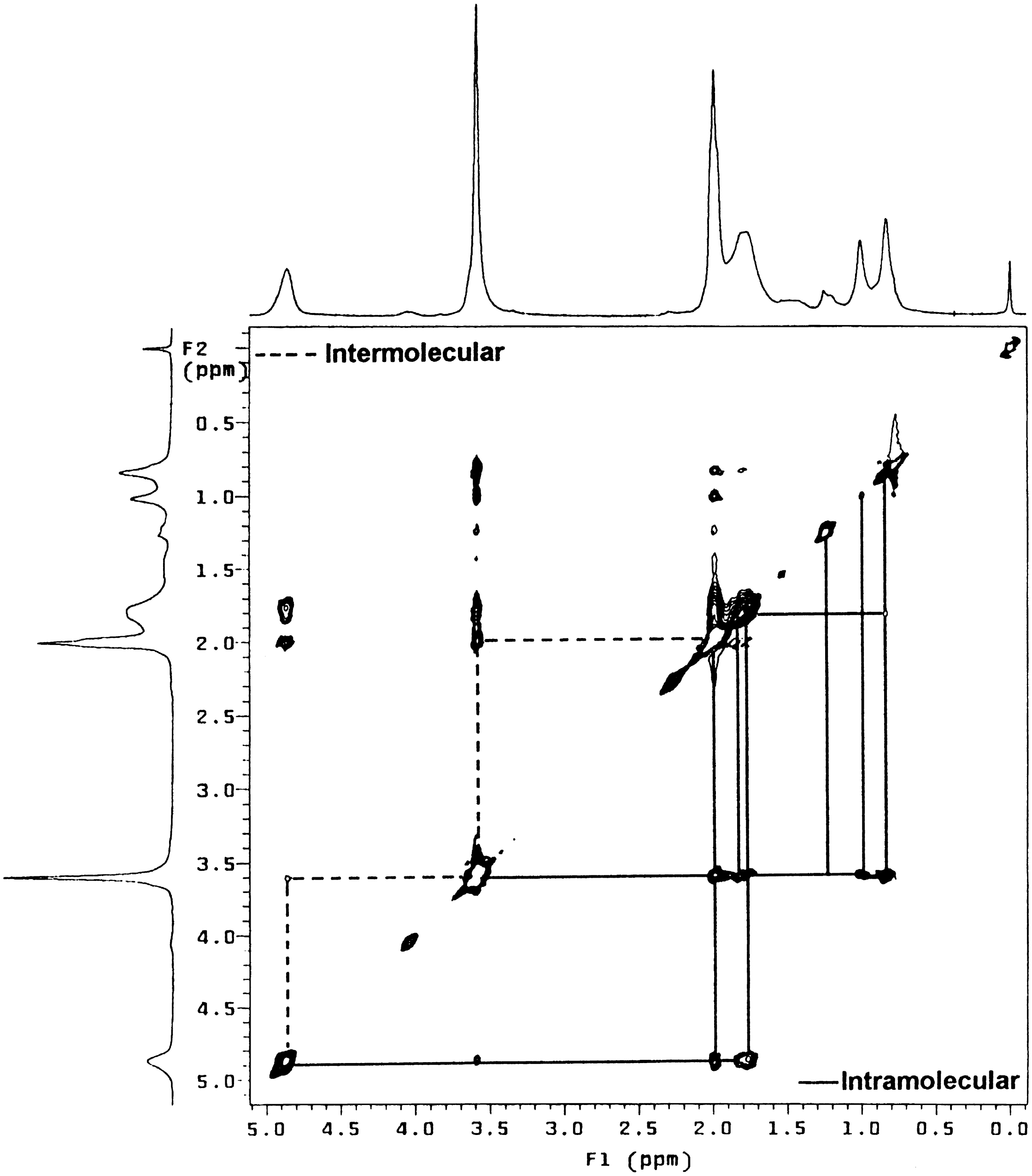

Fig. 6. ^{1}H NOESY spectrum of the 50/50 PMMA/PVAc obtained in $CDCl_3$, at 40% (w/v), at 40°C.

and benzene these peaks are not so close and overlapping in the blend spectra is not observed. The unambiguous assignment of signals referring to methylene protons *a*, of PMMA, in toluene, was hampered due to overlap with the signal of the residual methyl protons of the solvent. As will be shown later, these signals were suppressed in the NOESY spectrum due, mainly, to the high concentration of the blend solutions. However, in DMF the methylene protons *a*, of PMMA, and methylene and methyl protons, *d* and *f*, both of PVAc, overlap in the spectrum of the blend.

The spectra obtained in benzene-d_6 presented a close similarity to the ones in toluene, where a splitting in the peaks of methoxy protons *c*, of PMMA, can be observed. This is probably due to anisotropy effects of solvent [14]. In the $CDCl_3$ and DMF-d_7 spectra the signal of the methoxy protons *c*, of PMMA, appear as only one singlet.

3.2. 2D NOESY experiments

Two-dimensional experiments were performed in concentrated solutions to determine the intermolecular interactions that accompany the formation of a compatible blend. These measurements were also expected to confirm the solvent dependent compatibility of the 50/50 PMMA/PVAc blend that was observed previously [12]. PMMA/PVAc (50/50) blends were studied in four different solvents

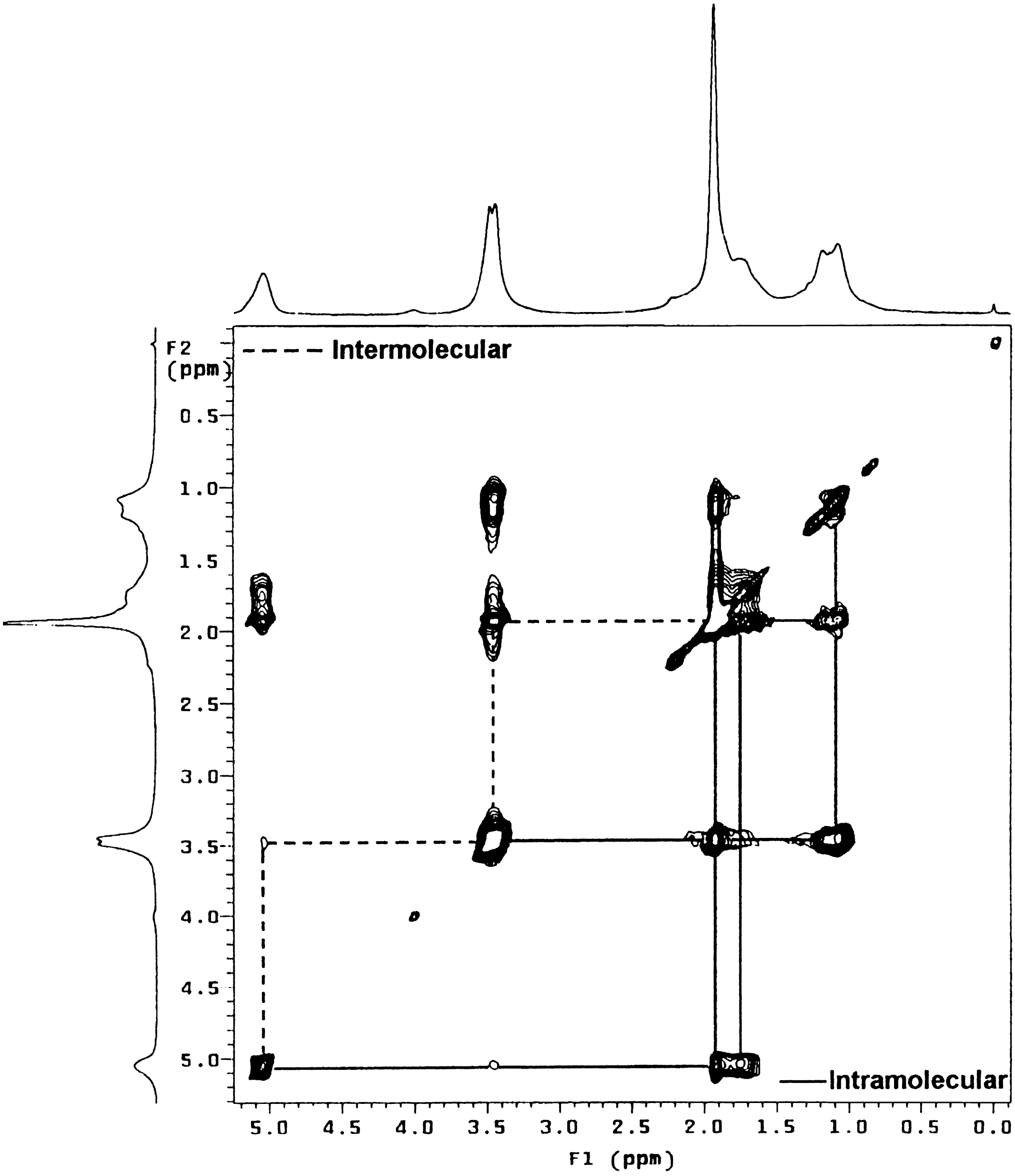

Fig. 7. ^{1}H NOESY spectrum of the 50/50 PMMA/PVAc obtained in toluene-d_8, at 40% (w/v), at 30°C.

at 40 wt.% in: (i) $CDCl_3$, at 40°C, and toluene-d_8, at 30°C, where homogeneous solutions were obtained; (ii) DMF-d_7 and benzene-d_6, both at 40°C, where heterogeneous solutions (phase separated) were observed.

In Figs. 6 and 7 the NOESY spectra from the homogeneous solution systems, $CDCl_3$ and toluene-d_8, obtained at mixing time 750 ms, are presented. Cross peaks, representing both intra- and intermolecular exchange of magnetisation during mixing time, can be observed. The lower portion of the 2D spectra traces out the connectivities due to the intra-molecular interactions. The upper dashed traces of diagonal show the intermolecular cross peaks. There appear intermolecular NOE cross peaks between the methyl protons *f*, of PVAc, and the methoxy protons *c*, of PMMA. A weaker intermolecular NOE cross peak can also be observed between the methyne protons *e*, of PVAc, and the methoxy protons *c*, of PMMA. The intra-molecular interactions could be easily attributed since appear in the NOESY spectra of the pure polymers (see Appendix A).

In Figs. 8 and 9 the NOESY spectra of immiscible solutions system obtained in DMF-d_7 and in benzene-d_6 at mixing time 750 ms, are presented. There, intra-molecular cross peaks not only appeared but also intermolecular ones between the methyl protons *f*, of PVAc, and the methoxy protons *c*, of PMMA. As in the case of the spectra in $CDCl_3$ and in toluene-d_8, connectivities for the intra-molecular interactions are showed in the bottom portion of spectra and the upper dashed traces show the intermolecular cross

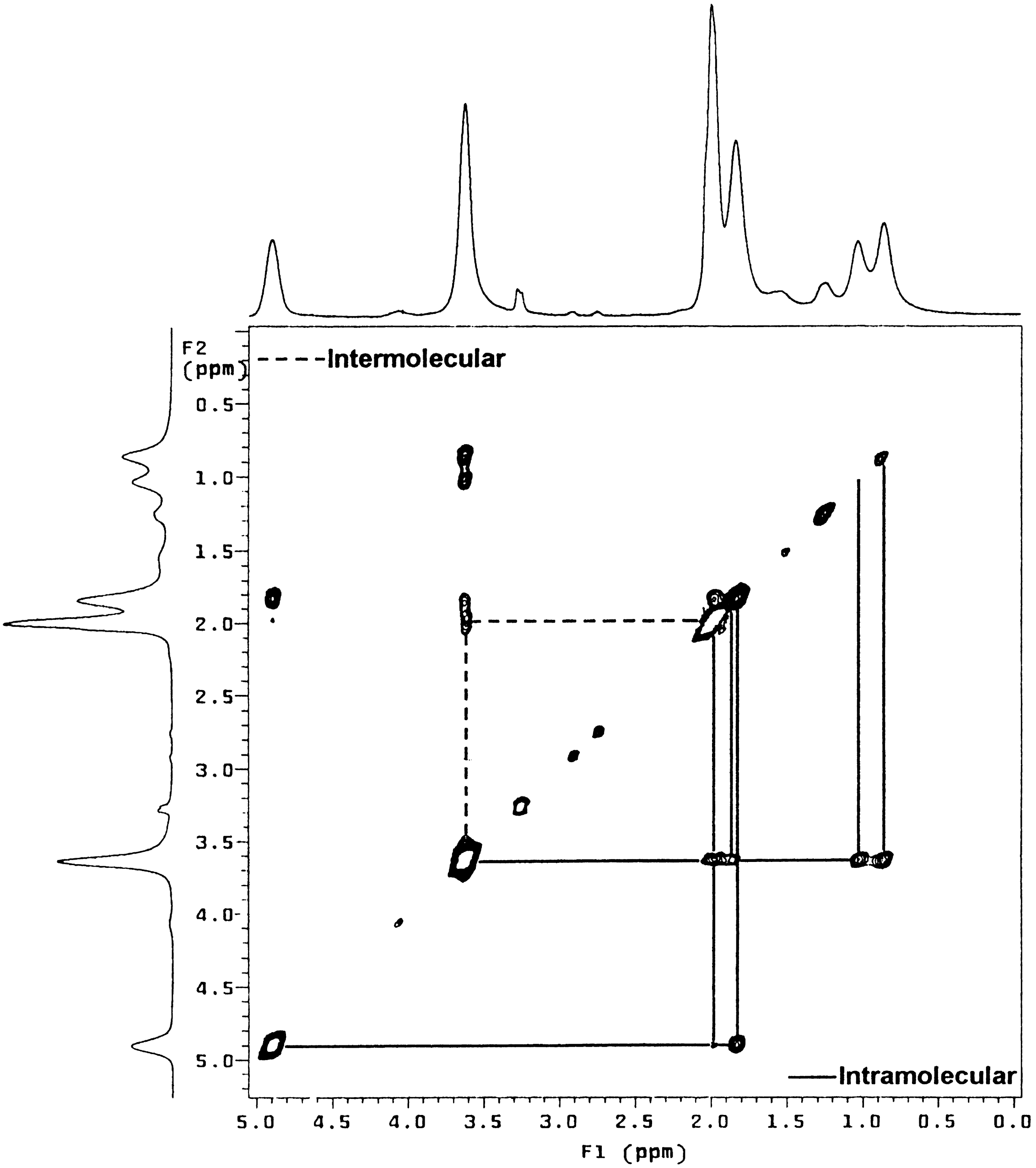

Fig. 8. ^{1}H NOESY spectrum of the 50/50 PMMA/PVAc obtained in DMF-d_7, at 40% (w/v), at 40°C.

peaks. There is a possibility that the intermolecular cross peak between *f* and *c* protons to be raised by the intra-molecular cross peak between *a* and *c* protons, of PMMA. This occurs because overlapping between protons *f*, of PVAc, and protons *a*, of PMMA. As shown in spectrum of the Fig. 4, in benzene-d_6 the methyl protons, *f*, of PVAc, do not overlap the methylene protons, *a*, of PMMA. Three different cross peaks involved the methoxy protons *c*, of PMMA may be observed in the NOESY spectrum presented in Fig. 9, obtained in benzene-d_6. Two of them are related to the intra-molecular interaction referring to the interactions between *a* and *c* and also between *a* and *b* protons, all of PMMA. In the same region, but just among the a/c and a/b signals the cross peak relative to the intermolecular interaction between methyl protons *f*, of PVAc, and methoxy protons *c*, of PMMA can be observed. It is suggest that in the NOESY spectra of blend obtained in $CDCl_3$, toluene-d_8 and in DMF-d_7, the overlapping may have caused, at maximum, a raising in the signal of the *f*/*c* cross peak.

The NOESY results indicate that the intermolecular correlation between the methyne protons *e*, of PVAc, and the methoxy protons *c*, of PMMA, is an interaction responsible for the miscibility of PMMA/PVAc blends in $CDCl_3$ and in toluene at 30°C. The proximity of the methyne protons *e*, of PVAc, and the methoxy protons *c*, of PMMA, therefore, suggests interpolymer hydrogen bonding.

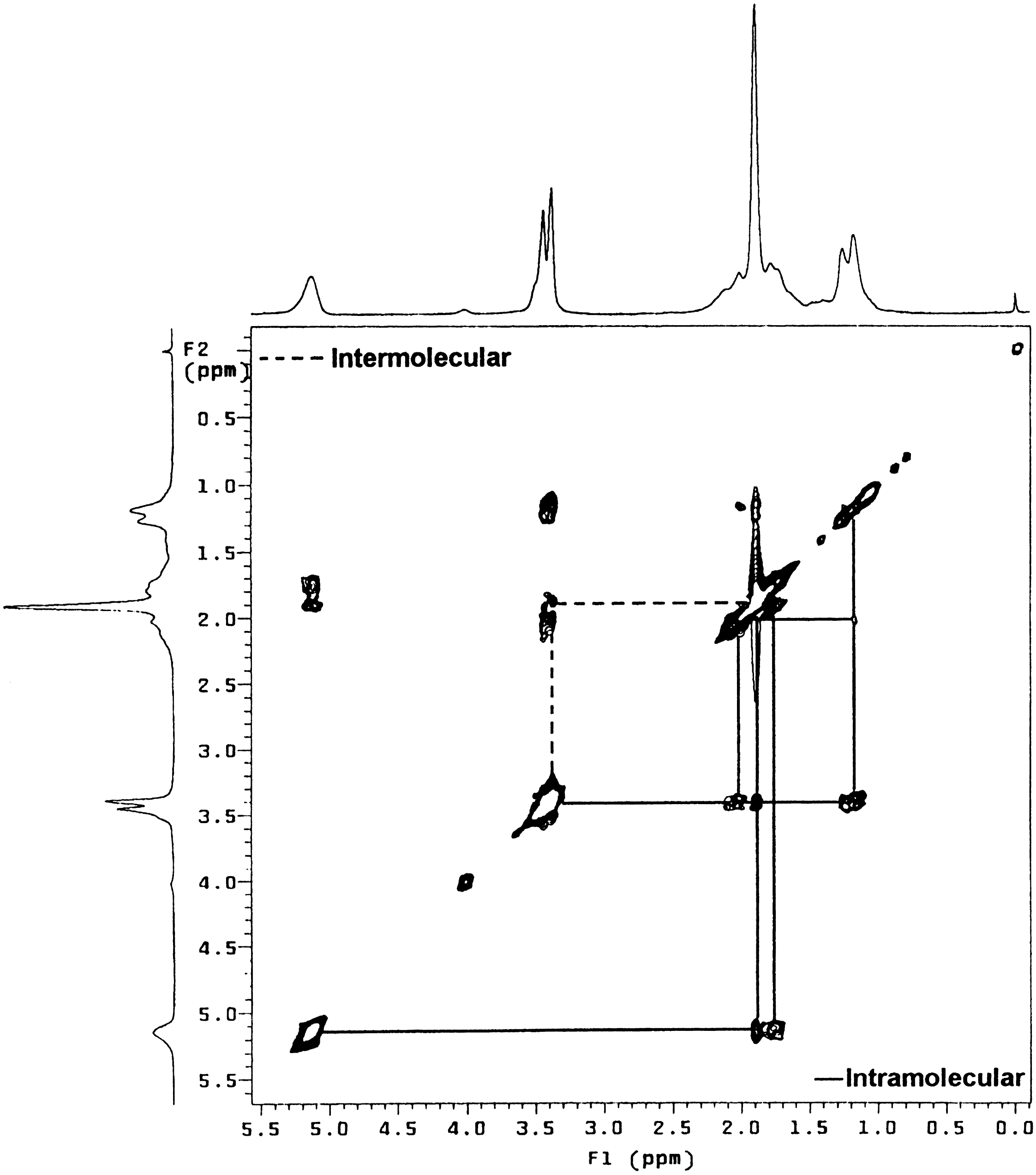

Fig. 9. ^{1}H NOESY spectrum of the 50/50 PMMA/PVAc obtained in benzene-d_6, at 40% (w/v), at 40°C.

Takegoshi et al. [9] applied NOE experiments to investigate the miscibility and inter-polymer interactions in poly(methyl acrylate) and poly(vinyl acetate), PMA/PVAc, film blends obtained by casting from acetone solution. Their PMA/PVAc system is very similar to our PMMA/PVAc blend system. An intermolecular NOE between the methyne protons *e*, of PVAc, and the methoxy protons of PMA was observed by those researches. This suggests that such specific interactions be probably due to hydrogen bonding interactions.

The motional properties of molecules may affect the cross peak intensities of NOESY [17]. If molecules have high mobility, spin diffusion becomes rapid and intermolecular NOE cross peak could be resultant from the exchange of magnetisation between spins in the same chain [18,19], causing the NOESY to be less useful to detect specific interactions. Variation of the mixing time is indispensable to minimise such effects and thus, to do an unambiguous interpretation and in particular for a quantitative analysis of the NOESY spectra [17]. If cross peak is mainly due to spin diffusion, the respective signal will not be detected at short mixing times. Then short mixing times are of most direct interest [17].

In Fig. 10 the dependence of relative area of NOESY cross peaks between metoxy protons, *c*, of PMMA and methyne protons, *e*, of PVAc, as a function of mixing

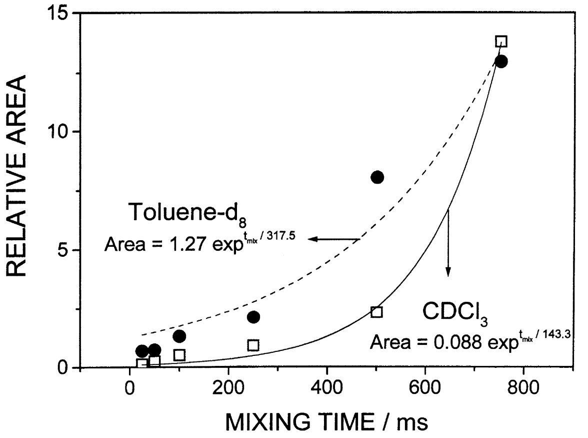

Fig. 10. Relative area of cross-peak of methoxy protons *c*, of PMMA and methyne protons, *e*, of PVAc as function of mixing time for 50/50 PMMA/PVAc blend in $CDCl_3$ at 40°C and toluene-d_8 at 30°C.

time is presented for 50/50 PMMA/PVAc blend in $CDCl_3$ and toluene-d_8. The areas of cross peaks *e/c* were normalised in relation to the area of methyne protons *e*, of PVAc. The normalised area of *e/c* cross peak grow exponentially with the mixing time in toluene-d_8 as well as in $CDCl_3$. In short mixing times the intensity of cross peak is almost the same in both solvents but at long mixing times the intensity in toluene is higher. The results presented in Fig. 10 indicate that the cross-peaks, observed in miscible conditions, are time-dependent effects, because its intensities increases with the mixing time. The results also indicates that the cross-peaks are not only due to the spin diffusion but may be properly connected to a close association process because the cross-peaks were detected in a large range of mixing times. In the same way we observed in our experiments that the intensity cross peak relative to the interaction between protons *f*, of PVAc and protons *c*, of PMMA (or *f/c*) could not be detected in short mixing times. Only at mixing times higher than 250 ms the cross peaks between *f* and *c* protons could be visualised, but their intensity were always smaller than cross peak between *c* and *e* protons.

In this work the intermolecular interaction between the methyl protons *f*, of PVAc, and the methoxy protons *c*, of PMMA was observed in NOESY spectra of the four solvents studied, i.e. at miscible and also at immiscible conditions. This result indicates that these interactions do not contribute to the miscibility of the PMMA/PVAc 50/50 blend in $CDCl_3$ and in toluene-d_8. The existence of those interactions at the immiscible condition, in DMF and in benzene, could be explained as originating from intermolecular contacts in the interphase region.

Blends of PMMA/PVAc were studied by Schenk et al. [20] using NMR solid state, in cast films from benzene or toluene. Intermolecular interactions were observed in cast films from benzene although the films were inhomogeneous. They suggested that interactions could have originated from the interphase regions. In contrast, these authors also observed that the blends prepared from toluene solutions, at ambient temperature, are more compatible than those from benzene solutions. They pointed out that in toluene solutions specific interactions seem to induce smaller sizes of domains which results in a higher compatibility level than in benzene solutions. Schenk showed that films prepared by casting from toluene at ambient temperature have domains so small that the films are transparent to the eye. By using X-ray scattering measurements, Schenk et al. [20] detected domains in PMMA/PVAc (opalescent) films whose dimensions could be larger than 100 nm when the films are obtained by casting from benzene. But when cast from toluene, the films are transparent and the domains lie in the 10–20 nm range.

From the results observed in this work can be inferred that in toluene solutions there are analogous intermolecular contacts as observed by Schenk et al. [20]. These intermolecular contacts may be detected by viscometry [21,22], as discussed previously [12]. The specific responsible interactions for these contacts may be characterised by the NOESY technique.

The results presented in this article are very consistent with the results obtained by viscometry and DSC presented in the preceding article of this series [12]. In these two articles, the miscibility of the 50/50 PMMA/PVAc blend was investigated in three different concentration conditions: in dilute solution, by viscometry; in concentrated solution, by NOESY; and in the solid state, by DSC. There is a correlation between the viscometry and 2D NOE results, both in solution, despite the difference in the concentration: in chloroform the blend is miscible, in DMF immiscible, and miscibility in toluene depends on the temperature. These results are also consistent with the DSC results, despite the difference of physical state. By our knowledge the comparison between NOESY and viscometry results is no already mentioned on the literature. By viscometry, the presence of interactions in dilute solutions of PMMA/PVAc, in toluene and in chloroform, was detected. By NOESY these interactions were characterised and it was concluded that not all contribute to the miscibility.

4. Conclusions

We used NOESY experiments to investigate the intermolecular interactions in the 50/50 PMMA/PVAc blend in several solvents. Under miscible conditions, chloroform at 40°C and toluene at 30°C, the results indicate the presence of two different types of intermolecular interactions: (i) between the methoxy protons of PMMA and the methyne protons of PVAc; and (ii) between the methoxy protons of PMMA and the methyl protons of PVAc. Under immiscible conditions (DMF and benzene, both at 40°C) only intermolecular interactions type (ii) were detected. These results indicated that the intermolecular interactions of type (i) are responsible for the miscibility of the blend in chloroform and toluene, at 30°C. The interactions of type (ii) did not contribute to the miscibility of the blend and were explained as originating in the interphase by contacts of unlike polymers.

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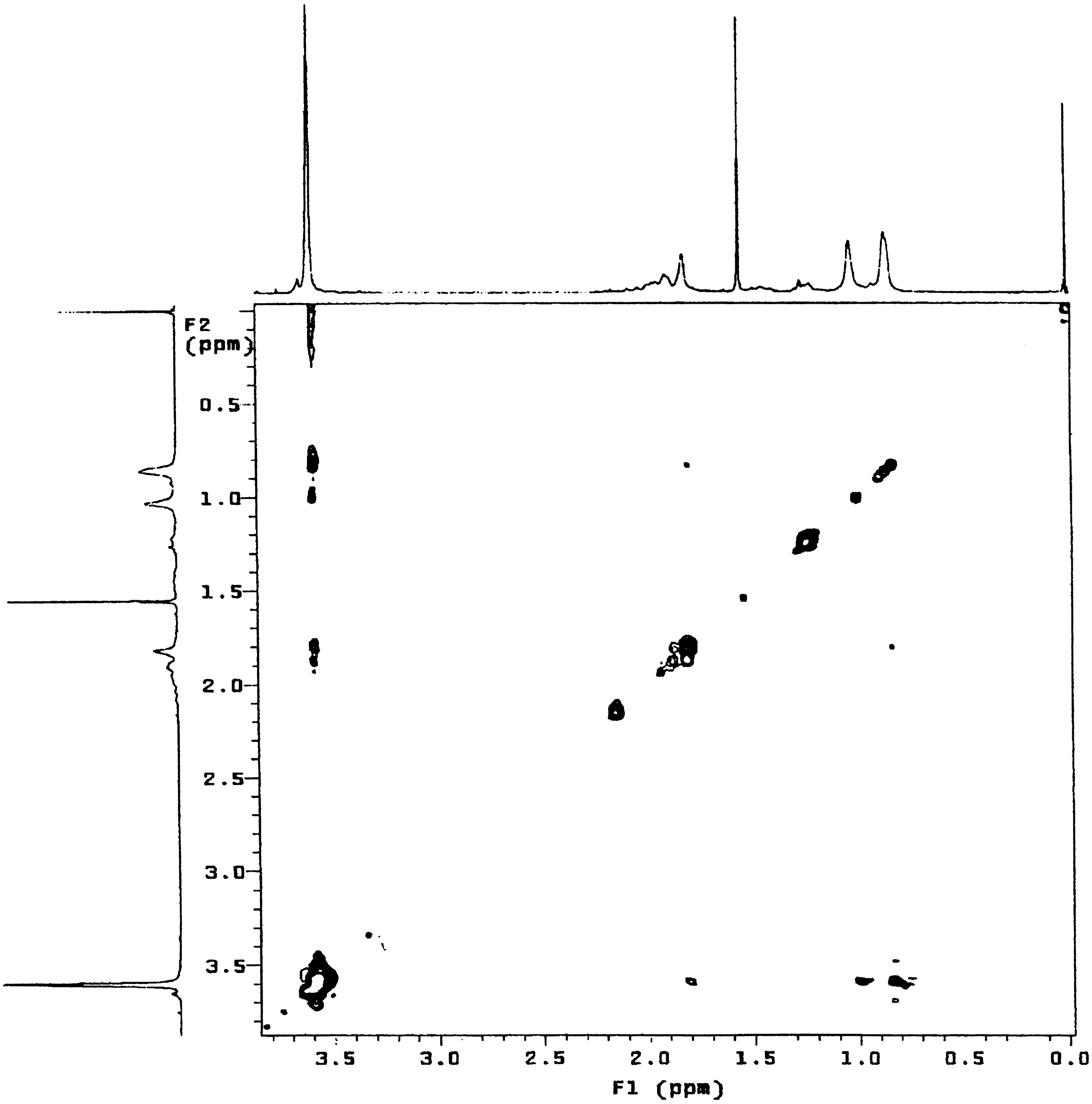
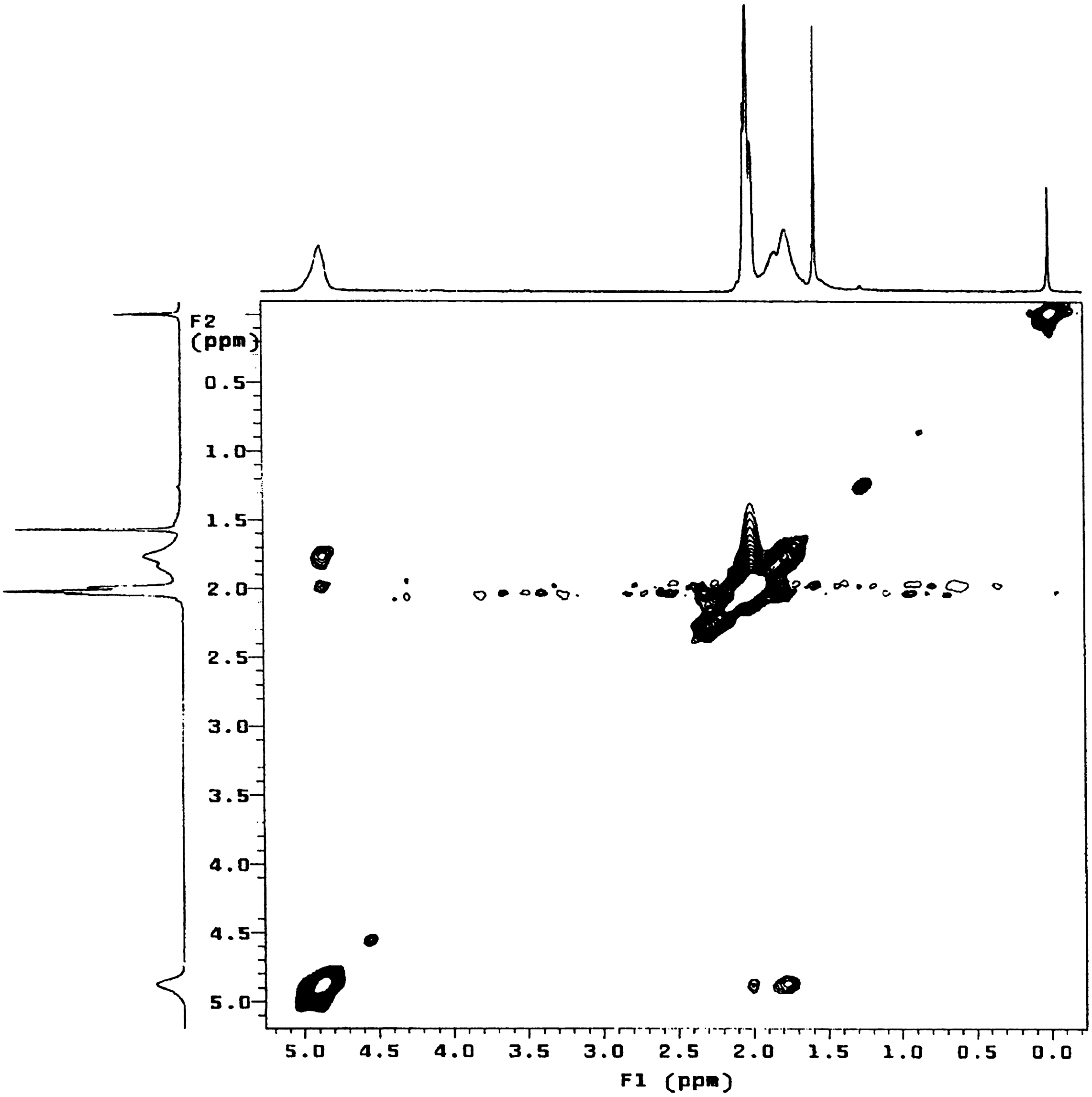
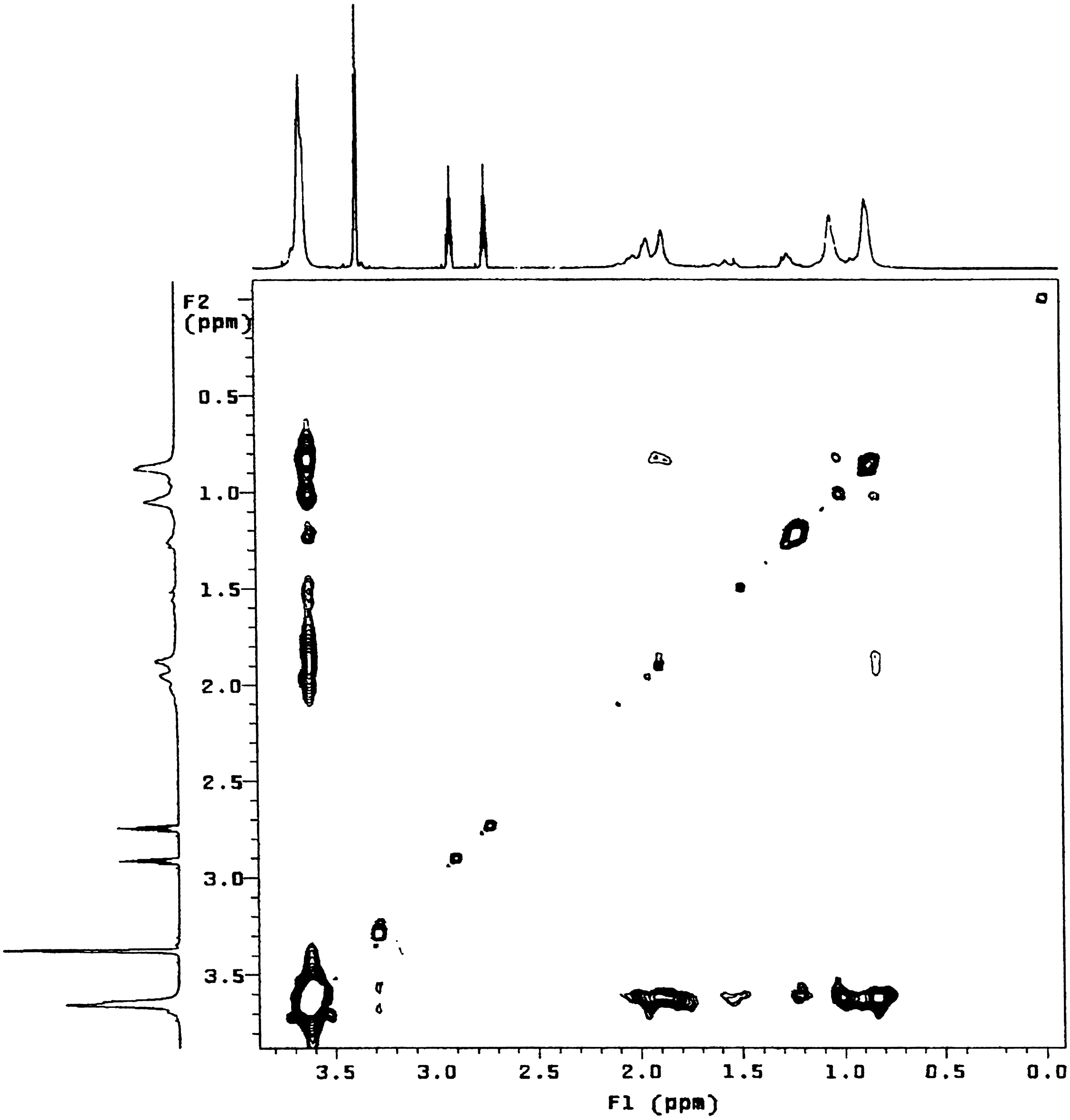
Appendix A



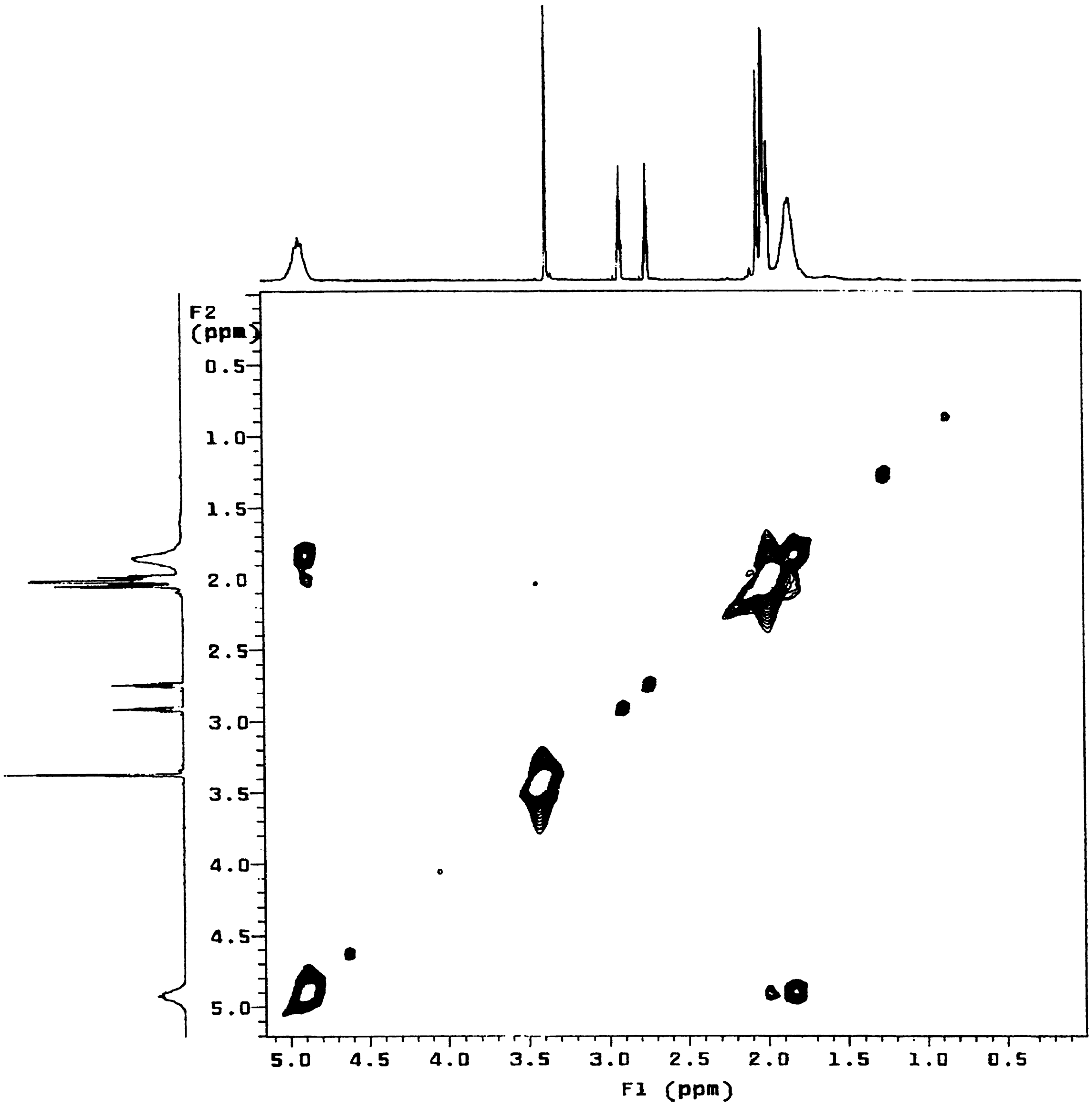
^{1}H NOESY spectrum of pure PMMA obtained in $CDCl_3$, (30% w/v) at 40 °C.



^{1}H NOESY spectrum of pure PVAc obtained in $CDCl_3$, (30% w/v) at 40 °C.



^{1}H NOESY spectrum of pure PMMA obtained in DMF-d_7 (30% w/v) at 40 °C.



^{1}H NOESY spectrum of pure PVAc obtained in DMF-d$_7$ (30% w/v) at 40 °C.

References

[1] Croasmun WR, Calson RMK. Two-dimensional NMR spectroscopy. New York: VCH, 1987.

[2] Pinciroli V, Rizzo V, Angelucci F, Tato M, Vigevani A. Magn Reson Chem 1997;35:2.

[3] Bovey FA, Mirau PA. NMR of polymers. New York: Academic Press, 1996.

[4] Natansohn A, Eisenberg A. Macromolecules 1987;20:323.

[5] Takegoshi K. Ann Rep NMR Spectrosc 1995;30:97.

[6] Crowther MW, Cabasso I, Levy GC. Macromolecules 1988;21:2924.

[7] Mirau PA, Bovey FA. Macromolecules 1990;23:4548.

[8] Mirau PA, Tanaka H, Bovey FA. Macromolecules 1988;21:2929.

[9] Takegoshi K, Ohya Y, Hikichi K. Polymer J 1993;25:59.

[10] Zhang X, Takegoshi K, Hikichi K. Macromolecules 1992;25:4871.

[11] Song M, Long F. Eur Polym J 1991;27:983.

[12] Crispim EG, Rubira AF, Muniz EC. Polymer 1999;40:5129.

[13] Sates DJ, Haberkorn RA, Ruben DJ. J Magn Res 1982;48:286.

[14] Bovey FA. Chem and Engng News 30 August 1965.

[15] Ramey KC, Field ND. Polym Lett 1965;3:69.

[16] Fugiwara Y, Fugiwara S, Fujii K. J Polym Sci 1966;4:257.

[17] Kumar A, Wagner G, Ernst RR, Wütrich K. J Am Chem Soc 1981;103:3654.

[18] Kalk A, Berendsen HJC. J Magn Res 1976;24:343.

[19] Gordon SL, Wütrich K. J Am Chem Soc 1978;100:7094.

[20] Schenk W, Reichert D, Schneider H. Polymer 1990;31:329.

[21] Corradini E, Rubira AF, Muniz EC. Eur Polym J 1997;33:1551.

[22] Sun Z, Wang W, Feng Z. Eur Polym J 1992;28:1259.