Nuclear magnetic resonance studies of ionomers: 2. Proton transfer in polyurethane–poly(styrene-*co*-styrene sulphonic acid) mixtures in solution

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One- and two-dimensional proton nuclear magnetic resonance spectra of blends of a polyurethane (PU) and poly(styrene-*co*-styrene sulphonic acid) (poly(S-*co*-SSA)) are analysed to determine the mechanism of interaction between the two components of the blend. A sample of poly(S-*co*-SSA) containing 7.9 mol % SSA is used, and the blends contain 58 % poly(S-*co*-SSA). In dimethyl sulphoxide solution, the labile protons of the SSA groups are transferred to the tertiary nitrogen of the *N*-methyldiethanolamine (MDEA) chain extender of the hard segment of the PU and to the urethane, allophanate and other secondary structures. Model compound studies and a two-dimensional homonuclear correlated proton spectra pulse sequence are used to make the assignments in the spectra. The labile proton is transferred preferentially to the secondary structures, followed by the urethane nitrogen, and then by the tertiary nitrogen of the MDEA.

(Keywords: two-dimensional homonuclear correlated proton spectra; nuclear magnetic resonance; miscibility enhancement; proton transfer; Coulombic interactions; polyurethane blends)

INTRODUCTION

Miscibility of polyurethanes with poly(styrene-*co*-styrene sulphonic acid) (poly(S-*co*-SSA)) has been the subject of a series of recent investigations. Dynamic mechanical studies showed that a mixture of a segmented polyurethane (PU) containing a tertiary amine as chain extender with poly(S-*co*-SSA) behaved as a phase-separated material in which the poly(S-*co*-SSA) mixed with the hard segment of PU with the exclusion of the soft segment into another phase. Miscibility was confirmed by the one-phase behaviour of the mixture of poly(S-*co*-SSA) with a polyurethane containing only hard segments[1]. A mechanism of interaction between poly(S-*co*-SSA) and the hard segment of the polyurethane was postulated by analogy with other polymer mixtures employing similar miscibility enhancement techniques[2]. The labile proton from the SSA unit was transferred to the nitrogen of the tertiary amine, thus forming negative ions on poly(S-*co*-SSA) and positive ions on the PU chain. The Coulombic interactions between the two chains lead to an intimate mixing of the hard segment of the polyurethane with poly(S-*co*-SSA).

Further investigation into this type of system revealed that the proton of the SSA group can also be transferred to the urethane or urea nitrogen of the polyurethane[3]. Indeed, polyurethanes having different chain extenders formed phase-separated blends with poly(S-*co*-SSA), the poly(S-*co*-SSA) being again intimately mixed into the hard segment. Model studies confirmed the presence of salt-like interactions between the two components.

An extensive *FT*i.r. study was performed in order to elucidate the proton transfer mechanism[4]. The *FT*i.r. spectra of the blends presented a new absorption at 3428 cm^{-} due to the stretching vibration of the N^{+}–H bond. The 1012 cm^{-1} band of the SO$_3$H group shifted to lower frequency, indicating a decrease in the degree of protonation. The symmetric stretching vibration of the SO$_3^-$ group also shifted to lower frequency, suggesting a lower polarization of the S–O dipole due to the removal of H$^+$. Semiquantitative studies on the deprotonation of the SO$_3$H group in a stoichiometric mixture indicated that $\sim$90% of the protons have been transferred.

This work is an n.m.r. spectroscopic study performed with the aim of examining in more detail the proton transfer mechanism. N.m.r. spectroscopy in solution is a powerful tool for investigating microstructural aspects of polymers. It can therefore be applied to study structural problems of ionomers. In the first paper of this series[5], it was demonstrated that proton transfer from an SSA group to a pyridine ring can be seen easily and that it takes place very quickly in a mixture of poly(S-*co*-SSA) and poly(methylmethacrylate-*co*-4-vinylpyridine) in dimethylsulphoxide (DMSO) solution. However, the newly formed N$^+$–H proton generates a weak and broad signal in the spectrum of the blend, and it can interchange with the protons of the traces of water present in the solvent. Usually, such a signal cannot be observed in the spectrum. This study therefore analyses indirect effects of the protonation of the nitrogen present in the polyurethane.

In order to obtain maximum information from the spectra, normal spectra and decoupling procedures are used together with two-dimensional techniques. Two-dimensional spectra are a relative recent development of

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n.m.r. spectroscopy[6]. Homonuclear correlated proton spectra (COSY) provide information on direct scalar coupling between protons, allowing easier assignments in complicated spectra.

EXPERIMENTAL

The polyurethane used in this study was prepared by a two-step polycondensation reaction[1] from poly(caprolactone) diol (PCLD) (average $MW = 830$, Aldrich), 4,4′-methylenebis(phenyl isocyanate) (MDI) (Eastman Kodak) and *N*-methyldiethanolamine (MDEA) (Aldrich) in anhydrous *N,N*′-dimethylformamide (DMF).

The prepolymer was prepared as follows: MDI was dissolved in DMF at a concentration of about 40% by weight. This solution was added to a solution of DMF, PCLD (40% by weight) and stannous octoate (0.1% by weight). The synthesis of the urethane prepolymer was carried out at 65°C for 2 h under vacuum, maintaining an NCO:OH molar ratio of 3:1. The chain extender, MDEA, in an appropriate quantity to maintain an NCO:OH ratio of 1:1 was added, and the reaction continued for an additional hour. Then the polyurethane was precipitated with warm water and was dried under vacuum at 80°C for two weeks.

The polystyrene ($MW = 125\,000$–$250\,000$, Polysciences) was sulphonated by the procedure developed by Makowski *et al.*[7] The sulphonation was carried out at 50°C in 1,2-dichloroethane solution, using a mixed anhydride of acetic acid and sulphuric acid as the sulphonating agent. Polymer containing 7.9 mol% SSA units was employed in this work.

The blends were prepared by dissolving PU in a tetrahydrofuran/dimethylsulphoxide (THF/DMSO) (90/10 (v/v)) mixture. Poly(S-*co*-SSA) was dissolved in THF and the solution was added dropwise to the vigorously stirred PU solution. The mixture was a gel-like precipitate. The blend, containing 58% poly(S-*co*-SSA), calculated to correspond to a stoichiometric amount of the newly formed ionic groups, was dried by evaporation of the solvent at progressively higher temperatures (up to 80°C). Finally, it was dried *in vacuo* for one week at 70°C.

Proton n.m.r. spectra were taken in DMSO-d_6 (100% deuterated, Aldrich) solutions at 85°C on Varian XL-200 and XL-300 spectrometers. The concentration of DMSO solution was approximately 5%. The flip angle was 40° and an acquisition time of ~4 s was used, long enough to ensure relaxation. No delay time between pulses was necessary.

Homonuclear correlated proton spectra were obtained using the DQF pulse sequence offered by Varian[8]. DQF provided suppression of intense signals on the diagonal. It consisted of a sequence of three 90° pulses, the first two being separated by an incremented delay (evolution period). The last two pulses had no delay interval between them and were followed by immediate detection. The preparation delay had to be at least three times the average proton relaxation time. The proton relaxation times were estimated by the well known inversion recovery method. To avoid the presence of quadrature image peaks that appear from the quadrature detection procedure, the spectral window was doubled, so as to cover the whole spectrum in its right half. Consequently, the two-dimensional spectrum covers only one-quarter of the frequency area swept by the instrument. This procedure was reported by other authors[9] and had as a side effect a certain loss of resolution. Some quadrature peaks were still present in the spectra (*vide infra*).

RESULTS AND DISCUSSION

The proton spectrum of PU in DMSO is rather complex, and its assignments can be made using the two-dimensional scalar coupling chart generated by the COSY pulse sequence. The two-dimensional spectrum is presented in *Figure 1* and the assignments in *Scheme 1*.

The aromatic protons of the MDI resonate at 7.31 ppm (a) and 7.08 ppm (b) and present an *ortho* coupling between them. The methylene bridge protons (e) resonate at 3.79 ppm and are not directly coupled to any other protons, as expected. Protons of the methylene groups (c) and (f) are directly coupled to each other and resonate at 4.13 and 2.68 ppm, respectively. The other group of

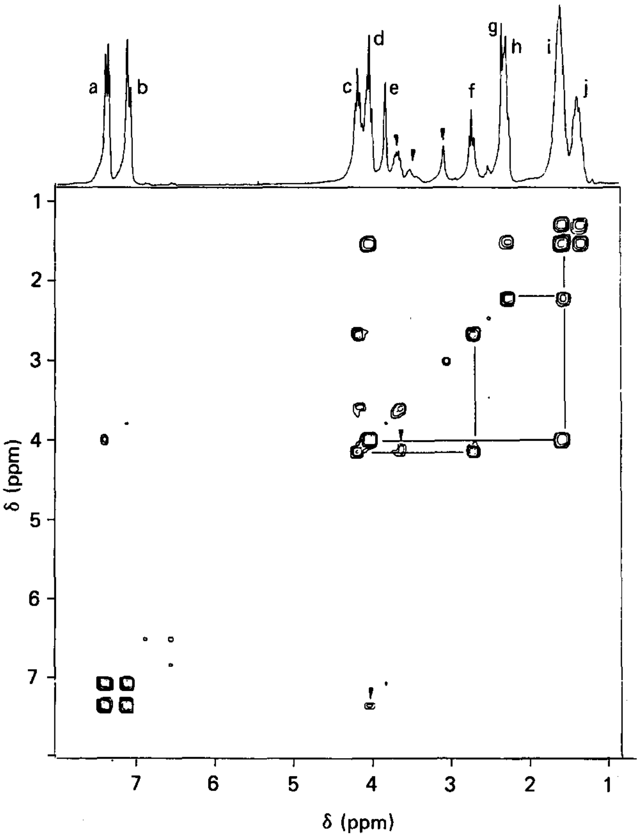
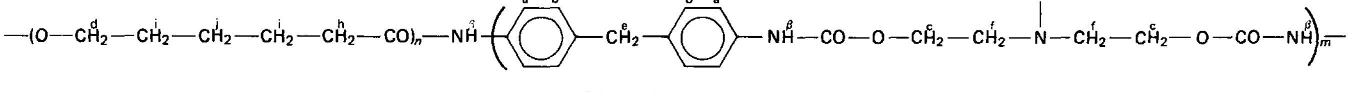


Figure 1 Two-dimensional COSY spectrum of PU in DMSO-d_6. The letters on the one-dimensional spectrum on top correspond to the formula in *Scheme 1*. The arrows belong to structural 'impurities'. The arrows in the two-dimensional spectrum are residual quadrature image peaks



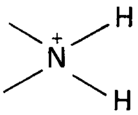
Scheme 1

MDEA, the methyl group, resonates as a singlet at 2.30 ppm and is not directly coupled. Protons of the soft segment, PCLD, resonate at 3.97 ppm (d), 2.29 ppm (h), 1.54 ppm (i) and 1.35 ppm (j). Only the CH_2 group (i) is directly coupled with all the other CH_2 groups. The signals noted with an arrow are 'impurities' for the proposed formula. The cross-peaks noted with an arrow are quadrature image peaks. They are easy to identify as such, because they do not appear on the same horizontal or vertical line with any diagonal peak.

Figure 2 presents together the spectra of PU and of the blend PU–P(S-*co*-SSA). There are a few spectral changes that occur:

(1) New signals at 1.4, 1.7, 6.5 and 7.5 ppm appear from the protons of P(S-*co*-SSA).

(2) The area between 8 and 10 ppm, where the labile proton resonances are found, has changed. Initially, there are four resonances in this area which can be assigned to the regular polyurethane NH at 9.20 ppm (β) and to allophanate and other secondary structures that appear from secondary reactions—*Scheme 2*. The assignment is made by comparison with model compounds found in the literature[10]. The blend PU–P(S-*co*-SSA) presents only the α and γ signals unchanged, together with a new, broad signal at 9.40 ppm. It is reasonable to assume that this new signal is due to newly formed



with the proton transferred from the SSA units. It appears that only labile protons belonging to β and δ structures participate in such a reaction.

(3) The protons belonging to MDEA change their resonance pattern. The methylene signal (c) seems to diminish and another signal appears at a slightly lower field (4.46 ppm). The methylene signal (f) seems also diminished, and part of it can be seen at 2.83 ppm. This change of the MDEA proton resonances is in accordance with the proposed mechanism of proton transfer from the SSA group of P(S-*co*-SSA) to the nitrogen of MDEA, inducing a positive charge on the nitrogen.

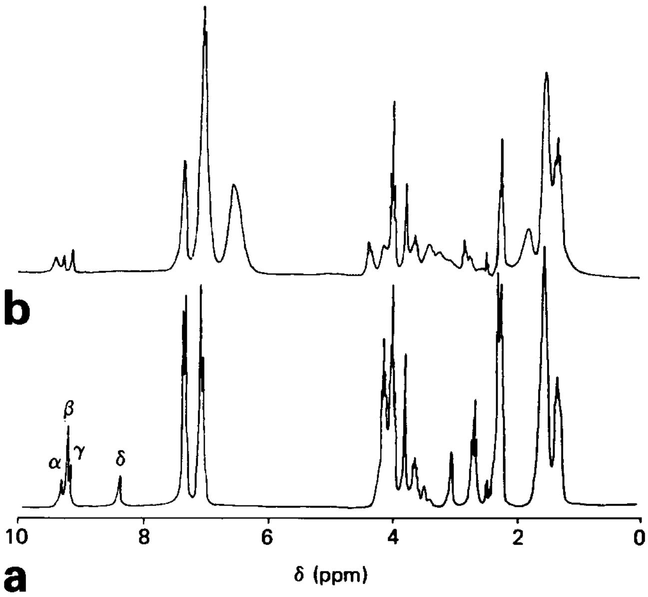
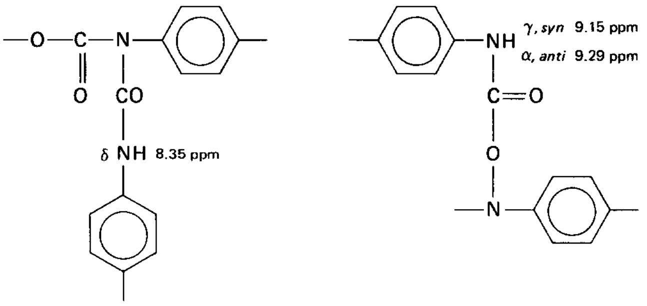


Figure 2 N.m.r. spectra of PU (a) and of its mixture with poly(S-*co*-SSA) (b) in DMSO-d_6. The Greek letters correspond to the formula in *Scheme 2*



Scheme 2

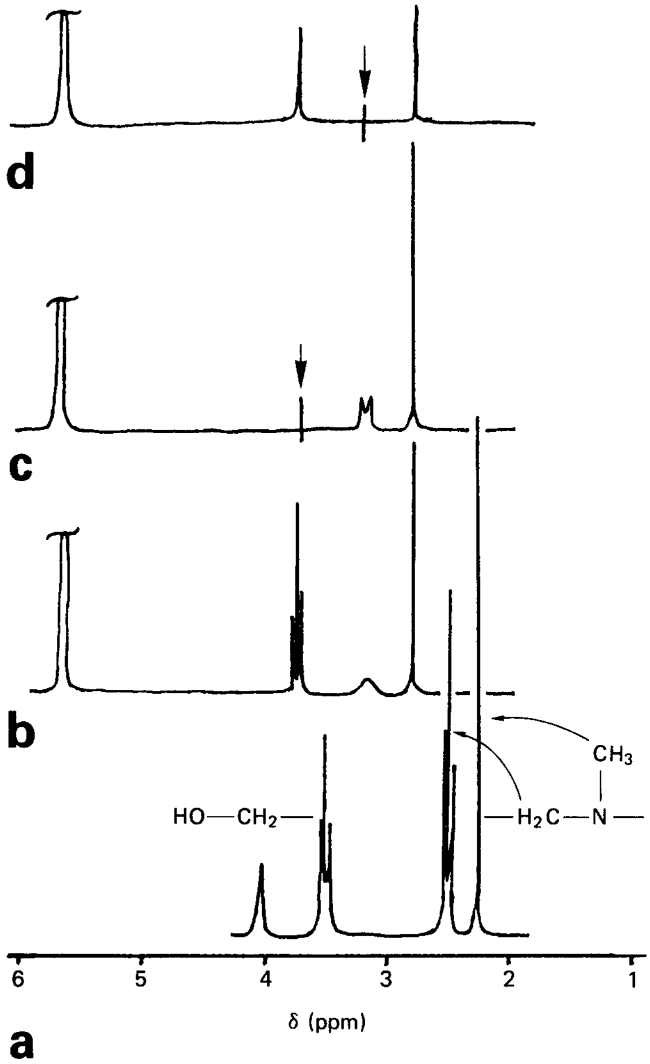


Figure 3 N.m.r. spectra of MDEA (a) and MDEA·HCl (b), (c) and (d) in DMSO-d_6. The arrows indicate the decoupling frequency

This behaviour can be verified using model compounds. *Figure 3* presents the spectra of *N*-methyldiethanolamine (MDEA) alone (*Figure 3a*), hydrochlorinated MDEA (*Figure 3b*), and two decoupled spectra of MDEA·HCl (*Figures 3c* and *3d*) for assignment purposes. The assignments in *Figure 3a* are straightforward and are presented in the figure. MDEA·HCl is dissociated in DMSO solution, and this dissociation produces important spectral changes. The methylenes neighbouring the OH shift downfield from

3.45 to 3.68 ppm. The methylenes neighbouring the nitrogen are dramatically changed. Their downfield shift is higher (from 2.45 to 3.14 ppm) and their signal broadens almost to the point of disappearance. The methyl protons also shift downfield (from 2.22 to 2.74 ppm), but otherwise the signal remains the same. To confirm that the broad signal at 3.14 ppm can indeed be assigned to the CH_2 groups bonded to the positive nitrogen, decoupling experiments were performed. Irradiation at 3.68 ppm (*Figure 3c*) produces a slight enhancement of the signal at 3.14 ppm, as expected, and the coupling between the CH_2 and the ^+NH can be observed. Irradiation at 3.14 ppm (*Figure 3d*) produces total decoupling of the methylene signal at 3.68 ppm. These irradiation experiments confirm the assignments presented before.

The conclusion that can be drawn from model studies is that the MDEA component in PU should present spectral changes when the nitrogen is quaternized by a proton. These spectral changes are visible in *Figure 2*, mainly in the area 4–4.5 ppm. The signal of the methylenes (c), which appeared as a triplet at 4.13 ppm in the PU spectrum, is split into two parts, at 4.13 and 4.46 ppm, both with triplet appearances. Therefore, it seems that roughly half of the methylene protons experience proton transfer to the nitrogen of MDEA and shift to 4.46 ppm, whereas the other methylene protons do not change and resonate at 4.13 ppm.

To verify this hypothesis, *Figure 4* presents the two-dimensional COSY spectrum of the blend in the region 3.1–4.6 ppm. There are three non-diagonal peaks, two of them being quadrature image peaks. The third, the real one, reflects the *ortho* coupling of the methylene at 4.46 ppm to the broad signal at ~3.5 ppm. This is in agreement with the behaviour of MDEA in the ionized state (*Figure 3*).

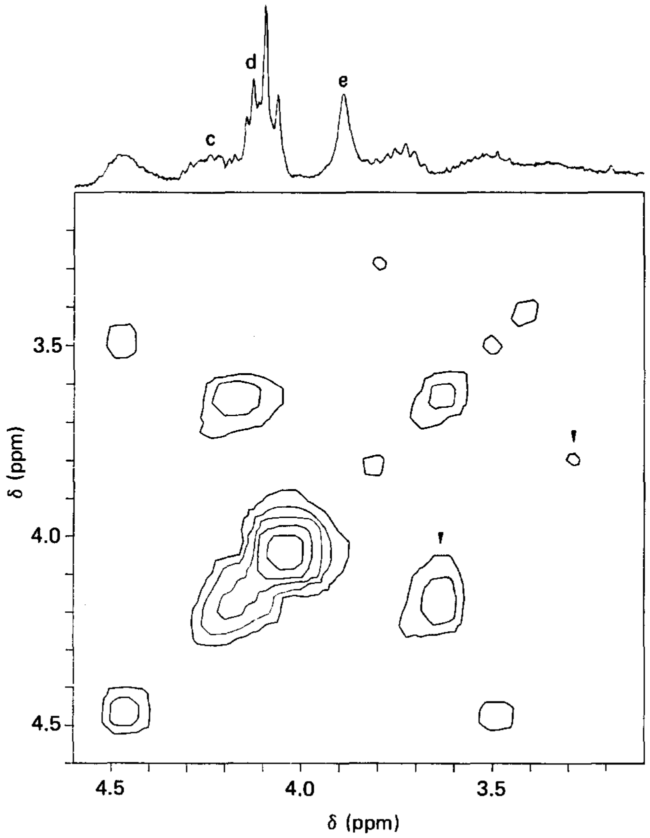


Figure 4 Two-dimensional COSY spectrum of the mixture PU–poly(S-*co*-SSA) in DMSO-d_6. The arrows indicate residual quatrature image peaks

Consequently, it is clear that the proton is transferred from the SSA units to the polyurethane. *FT*i.r. studies demonstrate that the sulphonic group becomes ionic to an extent of ~90%. There are several ways for the proton to react with the polyurethane chain. The n.m.r. spectra reveal that it reacts with the nitrogen of the MDEA segment, with the nitrogen in the urethane groups and with the nitrogen in the allophanate and secondary structures. It seems that the secondary structures are the most likely to receive the proton. In a blend of P(S-*co*-SSA) with a hard-segment-only polyurethane, no proton is transferred to the MDEA part. This can be seen from the unchanged signals of the MDEA residue in the spectrum of the blend. Dynamic mechanical measurements[1], *FT*i.r.[4] data and the 8–10 ppm region of the n.m.r. spectra, however, demonstrate that proton transfer takes place in this kind of blend. The hard-segment-only polyurethane has a relatively high concentration of secondary structures that appear because the reaction mixture was calculated to contain 'free' isocyanate groups. Therefore, it appears that the proton transferred from the SSA group has a preference to react with the secondary and urethane structure before reacting with the tertiary nitrogen of MDEA.

CONCLUSIONS

Normal and decoupled proton n.m.r. spectra of blends of PU with poly(S-*co*-SSA) and of model compounds in DMSO solution, together with two-dimensional COSY spectra, demonstrate that the labile protons of the SSA groups are transferred to the PU to form an intimate mixture between the styrene polymer and the hard segment of the PU. The protons are transferred to the secondary structures, to the urethane nitrogens and to the tertiary nitrogens of the MDEA chain extender, in this order.

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