Solid State C-13 NMR Studies of a Potential Crosslinking Agent for Aliphatic Polyester–Urethane Block Copolymers

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Synopsis

Solid state C-13 NMR was used to characterize the complex of diphenylmethane 4,4'-diisocyanate (MDI) with acetone oxime as a potential crosslinking agent (PCA) for the aliphatic polyester–urethane block copolymers. The formation of MDI from the PCA was followed by heating the sample at 150°C. The active hydrogen atoms on the hard segments of the block copolymers can be made to react with the diisocyanate groups of the regenerated MDI from the PCA at the elevated temperature for the crosslinking. The regeneration of —N=C=O groups is also noted by the appearance of the 2270 cm^{-1} band in the FT-IR spectrum of the heat treated PCA.

INTRODUCTION

Elastomeric polyurethane fiber is made of aliphatic polyester–urethane block copolymer and can be prepared by spinning its concentrated solution into a water bath. Crosslinking modification has proved to be one of the most important means towards improving the mechanical properties of the elastomeric polyurethane fibers. Due to the presence of active hydrogen atoms on the hard segments of macromolecules, diphenylmethane diisocyanate (MDI) can be made to react with them, bringing about crosslinking.

Crosslinking may be scheduled either to follow fiber formation, i.e., crosslinking takes place in the fiber state by treating the fiber with a solution of MDI in an organic solvent (method I), or to precede it, i.e., a controlled crosslinking takes place in the spinning solution just before formation (method II).

Inert organic solvents must be used in method I. However, this shortcoming is compensated by better mechanical properties of the modified fiber. This is because the hard segments crytallize prior to crosslinking, with the result that the crosslinking takes place in the accessible regions of the hard segments. The links between polymer chains are further strengthened. In method II, the mechanical properties of the crosslinked fiber are not improved, although additional organic solvents may not be used here. This is because the crosslinking reaction takes place between polymer chains which are located in a disordered state. What is more, excessive crosslinking would make it impossible to carry out the spinning process owing to gelation.

If the isocyanate group of MDI can be blocked in advance, a stable derivative will be formed. On being mixed into the spinning solution, it will not react with the active hydrogen atoms of the hard segments; therefore, the gelation will not
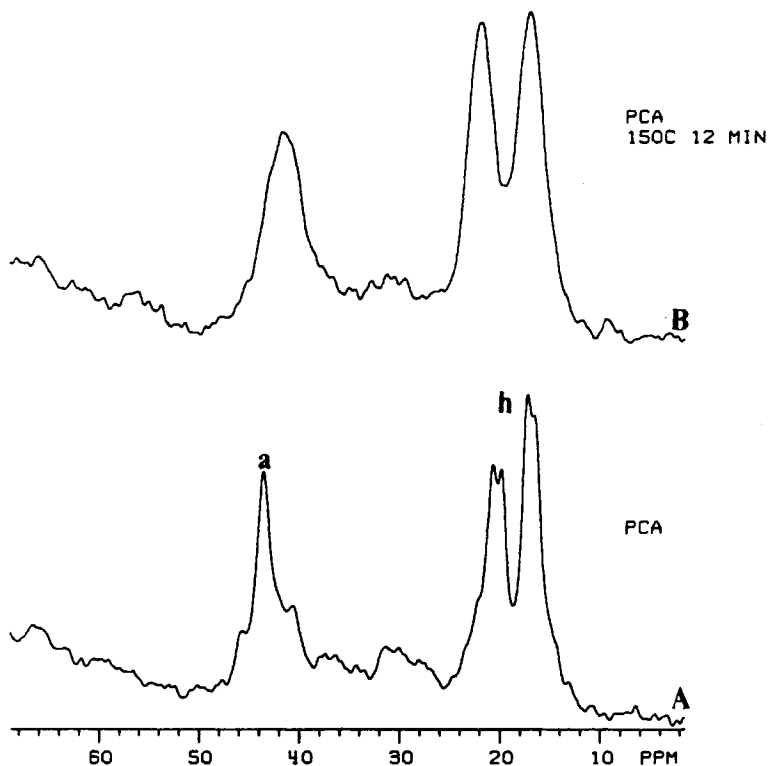
Fig. 1. CP/MAS C-13 NMR spectra (upfield region) of the potential crosslinking agent: (A) crystalline PCA, (B) PCA heated at 150°C for 12 min. Assignments of the resonances are indicated in the text. Both spectra were recorded at 37.7 MHz with a single contact time of 1.0 ms during CP and a recycle time of 2.0 s.

take place. When the fiber has been formed, the stable derivative must exist in the fiber, and crosslinking will not take place until the fiber is subjected to heat treatment. In order to realize this idea, a MDI–acetone oxime addition compound has been synthesized as a stable derivative with the mentioned requirements (it may be called the "potential crosslinking agent" or PCA), and it has also been observed by Sun and co-workers[1-3] that better mechanical properties are noted when the crosslinking takes place during fiber formation.

In this paper, we report the solid state C-13 NMR studies on the potential crosslinking agent (PCA) which can be used to improve the mechanical properties of elastomeric polyurethane fibers.

EXPERIMENTAL

The addition compound of MDI (diphenyl methane 4,4′-diisocyanate) and acetone oxime was used as a potential crosslinking agent. It was obtained by the method mentioned previously.[1-3] In this work the PCA was crystallized, with a melting temperature of 123°C.

The carbon-13 NMR spectra were recorded at 37.7 MHz with a Nicolet NT-150 Spectrometer equipped with a crosspolarization accessory. Radio frequency amplifiers delivering ca. 550 W at 150 MHz and ca. 1000 W at 37.7 MHz were adjusted to satisfy the Hartman–Hahn condition[4] at roughly 70 KHz. Cross-
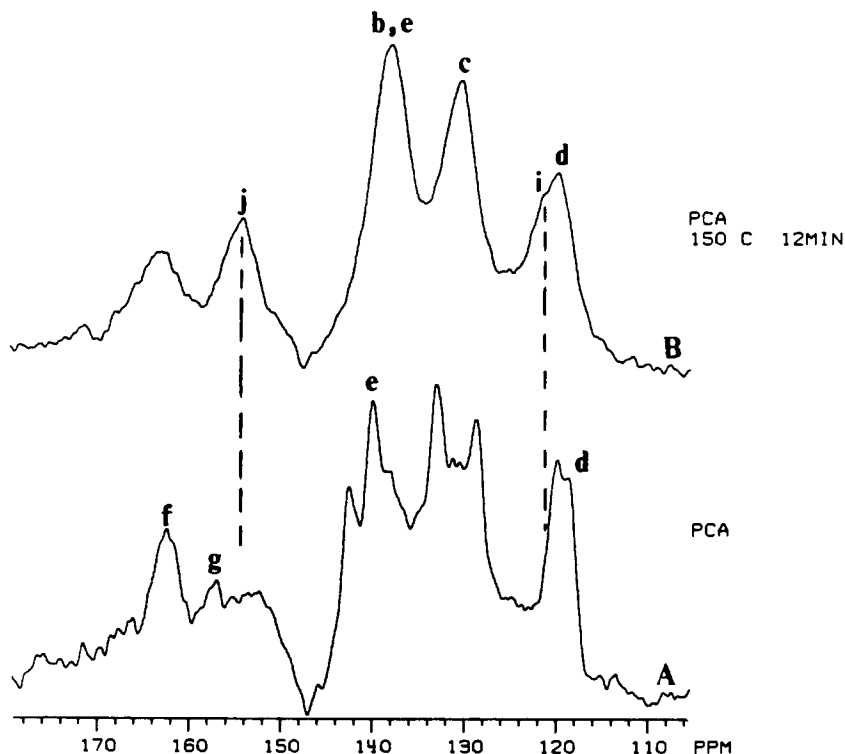
Fig. 2. Downfield region of the CP/MAS spectra of (A) crystalline PCA and (B) heated PCA.

polarization and magic-angle sample spinning (CP/MAS)[5–8] spectra were recorded with a single 1.0 ms contact time and a recycle time of 2.0 s. The magic angle of 54.7 was set by maximizing the intensity of the carbonyl resonance of the glycine. 10,000 transients were collected in the CP/MAS experiment. The resonance of the delrin rotor (89 ppm from tetramethylsilane) was used as a reference. Delrin spinners spun at about 3.5 KHz at the magic angle. Spin temperature alteration was used to eliminate the various artifacts.[9] The static field was not locked during accumulations.

RESULTS AND DISCUSSION

The C-13 CP/MAS spectrum of the crystalline potential crosslinking agent (PCA) is shown in Figures 1(A) and 2(A). The resonances at ca. 17.20 ppm are due to the methyl groups. The difference between the chemical shifts of the two methyl groups is primarily a steric shift.[10] The steric effect depends on the conformational isomerism. The intensity of these resonances indicates that the oxime substituents (methyl groups, h in the structure I) are not sterically identical. The methyl resonances appear as a doublet (0.8 ppm) in figure 1(A). The splitting may be due to the crystalline field. These splittings disappear for the sample heated at 150°C for 12 min in a vacuum. The C-13 resonance at 43.5 ppm is assigned to the methylene carbons between two phenyl groups (a). The assignments for the C-13 resonances of the aromatic carbons in the crystalline PCA (Fig. 2A) are complicated by the presence of the quadrupolar effect on the dipolar interactions and splittings due to the crystalline field. However, with the aid of solution NMR spectrum (15), it is possible to assign aromatic resonances in

Figure 2B. This quadrupolar effect results from the N14 quadrupolar moment interfering with the ability of magic-angle sample spinning to average out carbon–nitrogen interactions.[11,12] Naito et al.[11] have noticed ca. 45 Hz splitting for C carbons in L-alanine and L-serine amino acids. The magnitude of the splitting varies from one molecule to another, depending on the electric field gradient at the nitrogen in the molecule. This wide range of effects in the solid state C-13 NMR spectra may have some time difficulties of observation. The broad carbonyl resonance (f) may result from the above-mentioned effects.

The solid state C-13 NMR spectrum of heated PCA at 150°C for 12 min is also shown in Figures 1 and 2 (top). The crystalline order was destroyed, and the following reaction may take place:
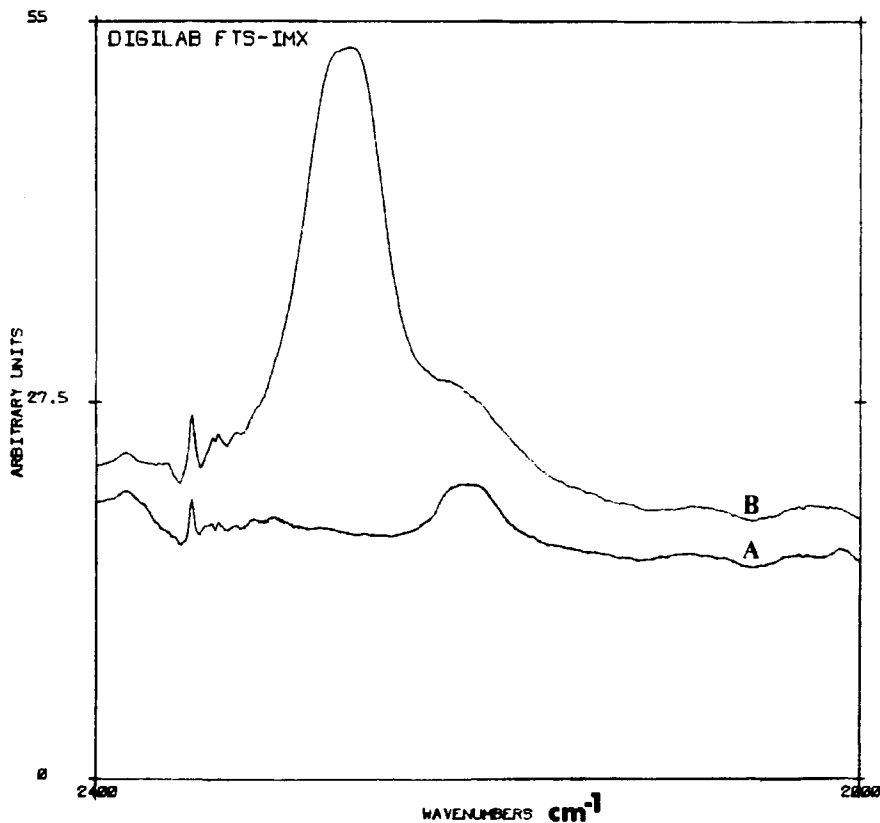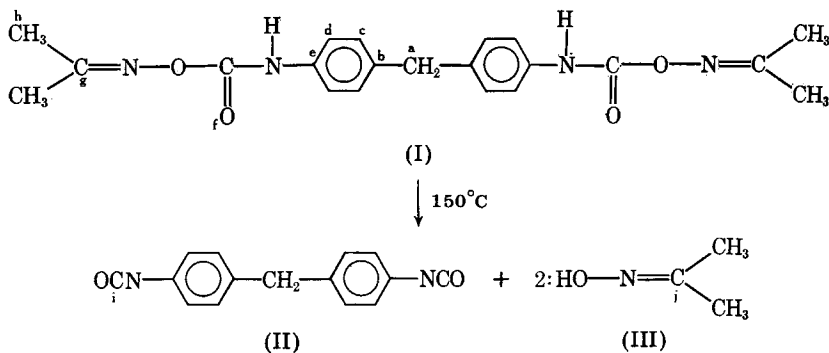

(I)

↓ 150°C

(II)   (III)

Fig. 3. The FT-IR spectra (2000–2400 cm⁻¹) of (A) PCA and (B) heated PCA. The 2270 cm⁻¹ peak is assigned to the stretching mode of the —N=C=O group.
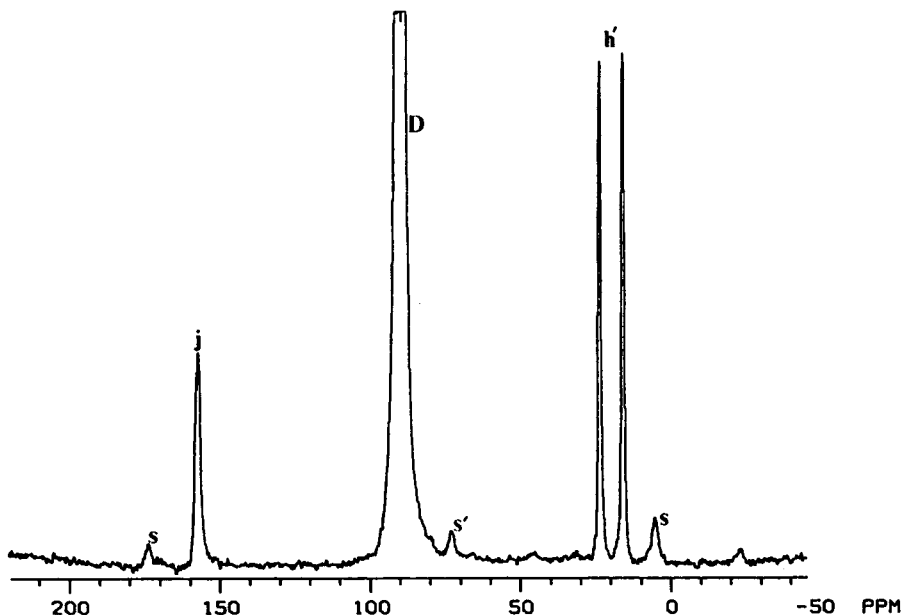
Fig. 4. CP/MAS spectrum NMR spectrum of acetone oxime. S,s' are the spinning side bands of the rotor (Delrin, D) and —C=N— carbon resonances, respectively.

The line widths of most of the C-13 resonances are increased as a result of heating the sample at an elevated temperature as compared to the crystalline PCA (Figs. 1 and 2). The chemical shift of the methylene carbons (a) is shifted from 43.5 ppm to 41.9 ppm. In the case of MDI and MDI dimethylurethane, the chemical shifts for these carbons are 40.7 and 41.9 ppm, respectively.[13] This result suggests that the main contribution to the methylene resonance in Figure 1(B) is from the MDI. The formation of —N=C=O groups can be seen from the appearance of a new resonance at 123.4 ppm [i.e., Fig. 2(B)]. This is also supported by our FT-IR studies.

The formation of MDI from the PCA is observed in the FT-IR spectrum of heated PCA. The 2000–2400-cm region of the FT-IR spectrum of PCA and heat-treated PCA are shown in Figure 3. The infrared spectra were recorded and then stored in memory by a Digilab Fourier Transform Spectrometer, FTS-20E. The coaddition of 300 scans per sample, 100 of which were of the reference chamber, resulted in a high signal-to-noise, and spectra were obtained with a resolution of 2 cm^{-1}. Samples were embedded in a KBr matrix. In the spectrum of PCA [Fig. 3(A)] —N=C=O stretching mode[14] frequency, the 2270 cm^{-1} band is absent, whereas, in the case of the heat-teated sample, the regeneration of the isocyanate group is clearly observed [Fig. 3(B)].

The decrease of the intensities of the carbons, type g(I) (158.0 ppm), and the increase of oxime carbons, j(III) (154 ppm), are seen in Figure 2. The CP/MAS spectrum of acetone oxime is shown in Figure 4 for comparison.

The solid state C-13 NMR and FT-IR studies clearly demonstrate the formation of MDI from the potential crosslinking agent after heating at a temperature of 150°C. This method allows us to identify the functional groups capable of crosslinking with the hard segments in the aliphatic–urethane block copolymers during fiber formation.

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