Amide I absorption band: description of the urethane group association scheme in polyether urethane elastomers

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On the strength of analysis of the amide I absorption band contour of the i.r. spectra of polyether urethane elastomers based on poly(tetramethylene oxide), poly(propylene oxide) and 4,4′-diphenylmethane diisocyanate, a scheme of association of urethane groups has been suggested. The amide I band has been shown to include five individual components at 1740, 1730, 1725, 1713 and 1702 cm^{-1}. The isolated bands are considered to be characteristic for urethane groups forming part of various associations.

(**Keywords: polyurethanes; i.r. spectroscopy; amide I band; deconvolution; association scheme**)

INTRODUCTION

The properties of polyether urethane elastomers (PUE) depend on their physical network. Although purely linear at relatively low molecular weights (25000–40000) they possess enhanced elasticity inherent in crosslinked polymers within a wide temperature range. At present the most widespread morphological conception of PUE is one of a microheterogeneous system[1,2]. The main emphasis is laid on studying the structure and behaviour of hard (diisocyanate) microphase[3,4] which may be considered as an element of the physical network of PUE. Since segregation of urethane segments as a separate phase is accompanied by the formation of diverse hydrogen bonds, the structure of such a physical network lends itself to quite effective control by the state of the hydrogen bonds.

Absorption bands related to NH-group vibrations cannot be used for quantitative assessment of the state of hydrogen-bonded urethane groups due to the bad resolution of its complex structure[5,6].

The band of amide I valency vibration (C=O) is most often used to study hydrogen bond structures. Two components of the amide I band have usually been considered as being related to urethane groups: hydrogen bonded with polyether (at 1732–1730 cm^{-1}) and to self-associated urethane groups (at 1710–1705 cm^{-1})[7–9].

However, recent research[6,10] has shown that the component of the amide I band responsible for self-association arises from band superposition at 1705–1703 cm^{-1} and 1715–1713 cm^{-1}. The first component has been associated with absorption of urethane groups included in the strongest hydrogen bonds of the system, and the second to absorption of urethane groups forming part of less strong and ordered structures.

However, a closer look at the process of association reveals that the number of amide I band components must be greater than three, because there is no room for urethane groups entirely free of hydrogen bonds within the identification of amide I bands in refs 6 and 10. At the same time some research[11,12] into the temperature dependence of the N–H stretching vibration band contour has observed the hydrogen-bond-free urethane group absorption band at higher temperatures. The corresponding amide I band may not have been isolated in ref. 13 because their proportion relative to the overall number of urethane groups is insignificant within a range close to room temperature.

For these reasons we have attempted to analyse in detail the contour of the amide I band in PUE using temperature measurements.

EXPERIMENTAL

The polymers we have studied were synthesized from 4,4′-diphenylmethane diisocyanate (MDI) and polyethers such as poly(propylene oxide) (PPO) and poly(tetramethylene oxide) (PTMO) of various molecular weights. Chemical formulae of the polymers are reported in *Figure 1*. The exclusion of commonly used low

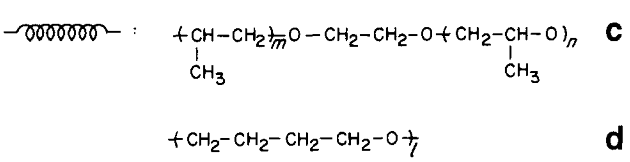

Figure 1 Schematic structure of model polyurethanes: (a) polymer; (b) hard segment; (c) soft segment PPO ($m + n = 3$–34); (d) soft segment PTMO ($l = 4$–7)

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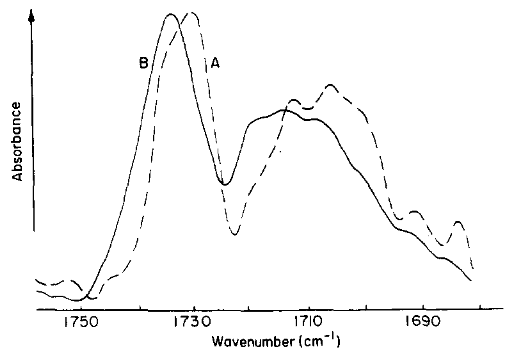


Figure 2 Results of contour deconvolution of amide I band in i.r. spectra of PTMO and MDI (44%) based PUE at 40°C (A) and 120°C (B)

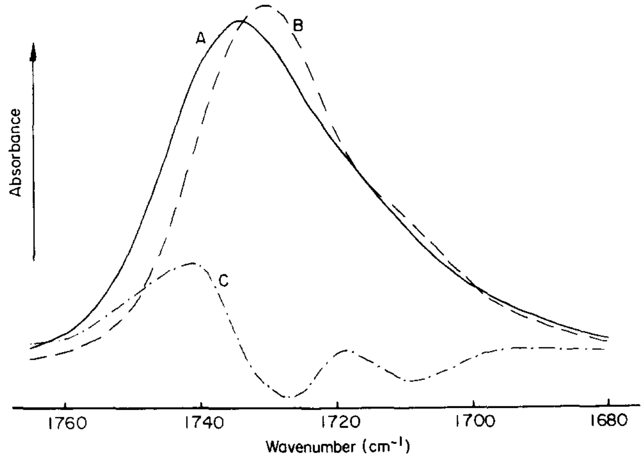


Figure 3 I.r. spectra of a PPO and MDI (11%) based PUE at 40°C (A) and 120°C (B); C, differential contour

molecular chain extenders is due to our attempt to avoid the influence of hard segment molecular weight distribution on hydrogen bond structure.

PUE samples in the main i.r. spectral region have been investigated as film specimens with thicknesses from 5 to 15 μm depending on the urethane group content. The films were cast from 5% solution of PUE in dimethylformamide on a CaF_2 window. The solvent was removed in an oven at 40–50°C and finally under vacuum. To study the spectra at elevated temperatures a thermostatic cell was designed and manufactured. It represented an air thermostat with forced air mixing. The cell temperature was controlled to within ± 0.5°C accuracy. Before measuring, specimens were exposed for 5 min at this temperature. To obtain i.r. spectra of *N*-phenyl butyl urethane in CCl_4, KBr cuvettes 0.2–0.02 mm thick, were employed. The spectra were recorded with a Bruker IFS-85 *FT*i.r. spectrophotometer.

To separate superimposed bands we resorted to the standard Fourier-deconvolution program forming part of the IFS-85 i.r. spectrophotometer software.

RESULTS AND DISCUSSION

The results of deconvolution of the amide I band contours of a PUE specimen at various temperatures are presented in *Figure 2*. The components at 1730, 1713 and 1702 cm^{-1}, already mentioned in refs 6 and 10, are quite obvious at 40°C. The 1740 cm^{-1} component is observed as a small boss leading to an asymmetric band at 1730 cm^{-1}. However, when the temperature increases up to 120°C the picture becomes more complicated; the above components are supplemented by a 1725 cm^{-1} band while the 1740 cm^{-1} band becomes dominant in the 1730–1740 cm^{-1} doublet. The components at 1740 and 1725 cm^{-1} may well be detected without deconvolution by subtracting the contours of the amide I band at various temperatures and compensating the absorption at 1730 and 1713 cm^{-1} during subtraction (*Figure 3*). It is worth noting that the position of the amide I band components of PPO-based PUE samples is slightly different from that for PTMO-based samples, with the band at 1740 cm^{-1} shifting to 1738 cm^{-1}, the band at 1730 cm^{-1} to 1729 cm^{-1}, the band at 1725 cm^{-1} to 1720 cm^{-1}, the band at 1713 cm^{-1} to 1711 cm^{-1} and the band at 1702 cm^{-1} to 1701 cm^{-1}. If the components at 1740 and 1730 cm^{-1} are compensated at subtracting contours of amide I bands for PUE specimens with various MDI contents (*Figure 4*), subsequent deconvolution clearly brings out components at 1725 and 1702 cm^{-1}. The component at 1713 cm^{-1} is manifested as a boss on the 1702 cm^{-1} band (*Figure 5*).

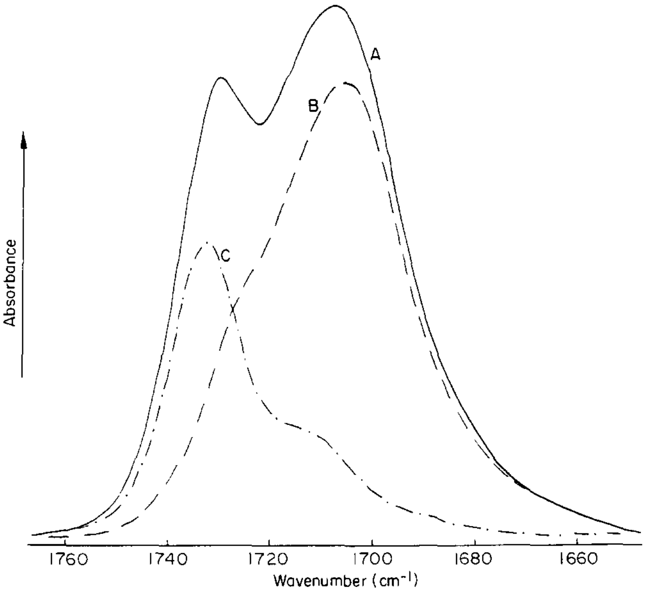
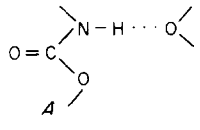


Figure 4 I.r. spectra of PTMO and MDI (50% and 12%) based PUE samples (A and C, respectively) ; B, differential contour

Thus, the amide I band is a combination of no less than five absorption bands with peaks at 1740, 1730, 1725, 1713 and 1702 cm^{-1}.

The identification of the 1740 cm^{-1} band is obvious, the position of this band having been determined[14] for dilute solutions of monomer urethanes in CCl_4. Therefore the band can doubtless be considered as inherent to urethane groups free from hydrogen bonds (both by N–H and C=O). The rest of the components are generally associated with urethane groups included in hydrogen bonds with various energies.

I



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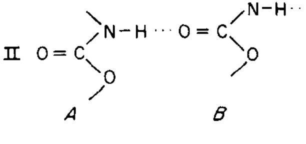

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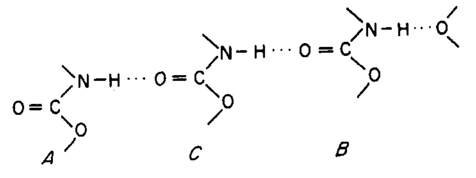

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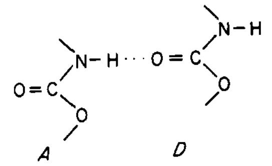

This association scheme fits X-ray diffraction data previously reported[15,16].

The 1730 cm^{-1} band has consistently been shown to be characteristic of urethane groups hydrogen bonded with polyether oxygen via NH group (C=O group remains free)[17]. It is obvious that in a more general case this band is inherent in the end group of any linear associate (*A*) having the C=O group free from hydrogen bonding.

The band at 1725 cm^{-1}, like the one at 1740 cm^{-1}, is typical of solutions of monomeric N-aryl urethanes in CCl_4 but only at higher concentrations. For instance, both 1740 cm^{-1} and 1725 cm^{-1} bands are expressly manifested during deconvolution of the amide I band contour of concentrated phenyl butyl urethane solution in CCl_4 (*Figure 6*). Thus the 1725 cm^{-1} band is characteristic of the association of urethane groups devoid of any proton acceptors except for oxygen of urethane groups proper.

Such associations are very few in PUE at 40°C because NH linkages of 'head' urethane groups of associate *B* are hydrogen bonded with polyether oxygen. Increases in temperature bring about polyether splitting away from the associate and the appearance of a band at 1725 cm^{-1} (the enthalpy of the urethane–polyether bond is appreciably higher than that of the urethane–urethane bond; this predetermines a higher temperature dependence of urethane–polyether association[18]). Therefore, the 1725 cm^{-1} band may be related to absorption of the 'head' urethane group of polyether excluding associate *D*.

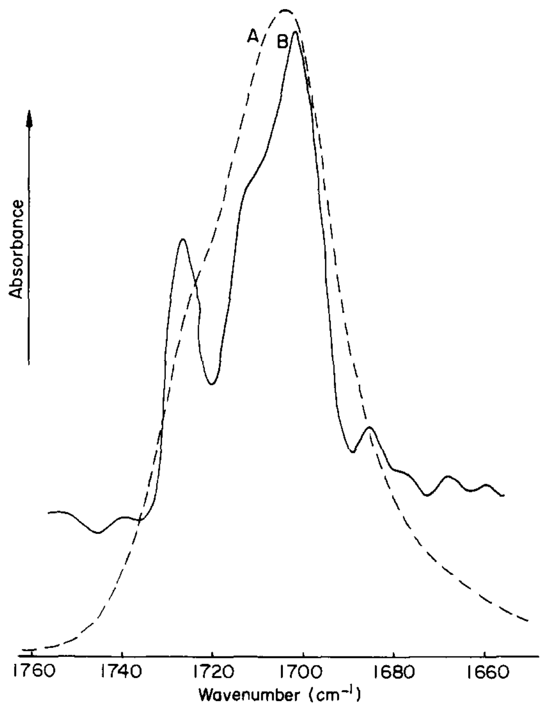

Figure 5 Differential i.r. spectrum of PUE samples based on PTMO and MDI (50% and 12%) (A); B, result of its deconvolution

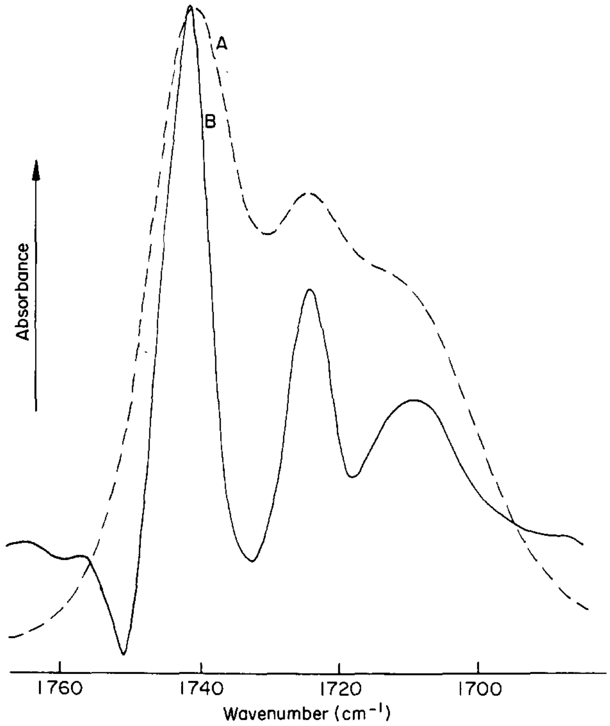

Figure 6 I.r. spectrum of phenyl butyl urethane solution in CCl_4 (0.56 mol l^{-1}) (A); B, deconvolution results

If we follow the chosen association scheme, the 1713 cm^{-1} band is related to the same 'head' group of the associate but is hydrogen bonded with polyether via the NH group (*B*). This leads to the frequency shift from 1725 to 1713 cm^{-1}.

It is common to associate the band at 1702 cm^{-1} with the absorption of urethane groups included in the most ordered hydrogen bond moieties, i.e. those situated 'inside' associate *C*.

CONCLUSIONS

The amide I band comprises five individual components at 1740, 1730, 1725, 1713 and 1702 cm^{-1}. The proportion of these within the complex band helps to easily control the content of urethane groups forming part of urethane association in one way or another. Another consequence is the possibility to determine (following the above association scheme) the content of urethane associates of various lengths, which is important for further calculations of association thermodynamic parameters.

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