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Amide II and Amide III Bands in Polyurethane Model Soft and Hard Segments

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Summary

Amide II and III bands in polyurethane (PU) have been often taken as two of the characteristic bands indicating the formation of urethane structure. Since these bands, however, are very complicated, further studies, especially the effect of H-bonds on amide II and III bands in PU, were seldom reported. In the present work, we report a new finding on the correlation of amide II and amide III bands with different H-bonding interactions in PU model soft and hard segments. The PU model soft segment (PUMSS) is based on poly(tetrahydrofuran) (PTHF) and diphenylmethane-4,4'-diisocyanate (MDI) whereas the PU model hard segment (PUMHS) is based on MDI and n-butanol (BO). FTIR results show that the H-bond is formed by NH…carbonyl (C=O) (Type I) in PUMHS while the H-bond is mainly formed by NH…ether(O) (Type II) in PUMSS; the amide II band, however, is more related to the Type II H-bonding interaction while amide III band is more dependent upon the Type I H-bonding interaction.

Introduction

Segmented polyurethanes (PU) are a type of polymers which consist of alternating soft and hard segment units. It has been accepted that many of the unusual properties of these materials are primarily due to the two phase structure which is closely related to the relating H-bond [1-2]. H-bond has been an active topic of research for many decades due to its widespread occurrence and importance, and has been investigated by different methods including FTIR [3–9], and simulation calculations [10–13].

It is well accepted that νNH and νC=O bands in FTIR are the two typical bands used to judge if the H-bonds have been formed in PU. Their frequencies are usually used to analyze the H-bond strength. Both νNH and νC=O bands will shift to lower frequency when H-bond (NH…O=C) is formed. νC=O band from urethane is also sometimes called amide I band, which usually appears at 1700-1740 cm^{-1} for diol extended PU. There are actually five amide bands including amide I, II, III, IV and V. Furer [14-17] has well studied the spectroscopic vibrational characteristics, including amide bands, for model PUs using both FTIR and simulation methods. The results show that amide bands are sensitive to states and conformations. They are composed of different vibrational modes and have complicated structures. Therefore, other four except amide I band have seldom been deeply studied on the relation with H-bonds. In some times, amide II and III bands at about 1530-1540 cm^{-1} and 1220-1230 cm^{-1} are used to make additional proof for the formation of urethane structure and H-bond in PU. They were often mentioned as δ(N-H) + ν(C-N) [6,18-19], which shift to higher frequency, and are usually used only to confirm the urethane structure and the H-bond strength associated with amide I band. The differences of amide II and III bands relating to different H-bonds, however, have usually been ignored, possibly because their difference is not as big as in our model soft and hard segments.

In the present work, we report a new finding that amide II and III in PU are closely related to different H-bonding interactions in model PUs. These results are expected to be helpful in further understanding the effect of H-bonds on amide II and III bands. They can also be used, as one of the additional data, to further analyze the H-bonds in PU. The PU model soft segment (PUMSS) in this work is based on poly(tetrahydrofuran) (PTHF) and diphenylmethane-4,4'-diisocyanate (MDI) whereas the PU model hard segment (PUMHS) is based on MDI and n-butanol (BO). FTIR was used as the main tool to study the correlation between amide II or III bands with the H-bonds in PUMSS and PUMHS.

Experimental

2.1 Materials

Isocyanate used in the present work is MDI, purity >99.6 %, freezing point >38.1°C, Yantai Synthetic Leather General Factory; BO used is reagent from Shanghai, which was stored over well-dried molecular sieve (4Å) for a week before use. PTHF (Mn = 1000g/mol) was purchased from Germany, which was vacuumed to remove possible moisture before use.

2.2 Polymerization

Both PUMSS and PUMHS were prepared in three-neck round bottom flasks fitted with an overhead stirrer, a thermometer and under a constant dry nitrogen blanket. The molar ratio of MDI and PTHF was 1:1.05 while that of MDI and BO is 1:2.1. Of them, PUMHS was prepared in solution with dimethyl sulfoxide (DMSO) as solvent. The reaction temperature in both model soft and hard segments was kept by not higher than 90^{o}C. The prepared PUMHS was precipitated, washed, and dried firstly at room temperature and then in a vacuum oven at 60^{o}C for a week.

2.3 FTIR

The infrared spectra were obtained using a SHIMADZU FTIR-8700 Spectrophotometer. The frequency range covered was from 4000 to 400 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}. PUMSS sample was directly sprayed onto KBr window pellet while PUMHS was prepared as KBr pellet.

Results and discussion

The present paper will mainly report the effect of H-bonding types on amide II and III bands. Before discussing that, however, we will briefly present the different H-bonding interactions in both PUMHS and PUMSS.

Different H-bonding interactions in PUMHS and PUMSS

Fig. 1 shows the scheme structures representing PUMSS and PUMHS, respectively. As is shown in the top of Fig. 1, there are one strong H-bond donor NH and one H-bond acceptor C=O in PUMHS. Therefore, the band at 3332 cm^{-1} shown in Fig.2 should be the H-bonded νNH band when NH forms the H-bond NH…C=O (Type I) whereas the band at 1705cm^{-1} is its relative H-bonded νC=O band. Such assignments have also been confirmed by some other researchers using similar PU model molecules [4, 20].

Different from PUMHS, there is still one strong H-bond donor NH but two strong possible acceptors C=O and ether O in PUMSS (bottom of Fig.1). Fig. 2 shows their obvious differences in FTIR spectra in both νNH and νC=O bands. First, the peak of νNH at 3298 cm^{-1} is much lower than that in PUMHS, suggesting the H-bond in PUMSS based on NH as donor is stronger than that in PUMHS. Since there is obvious free νC=O band at 1732 cm^{-1}, the H-bond in PUMSS should be NH…ether O (Type II). This is consistent with the fact that ether O in PUMSS is the main H-bond acceptor although the shoulder band at 1713 cm^{-1} shows a part of Type I H-bond still

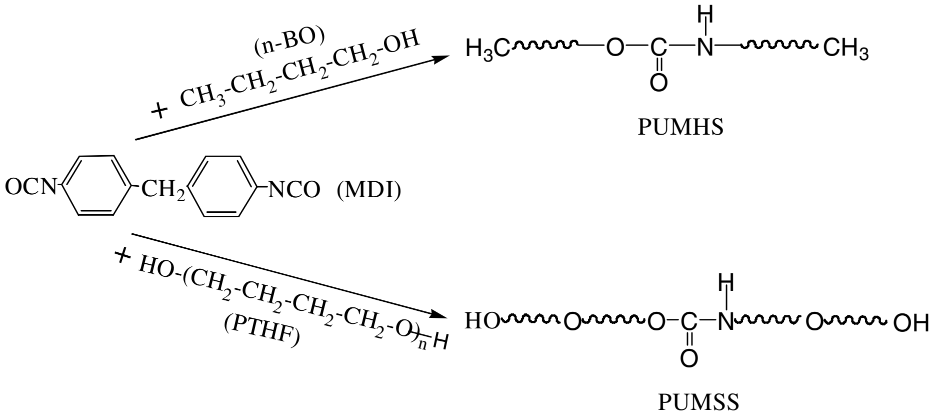


Fig. 1 Preparation and structure schemes of PUMHS and PUMSS

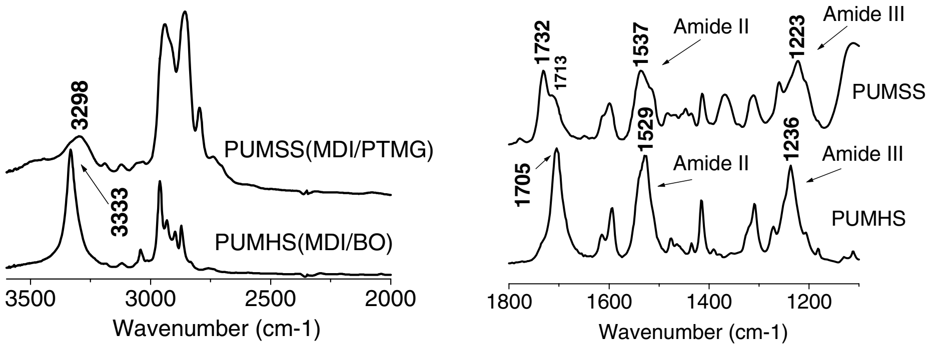


Fig. 2 FTIR spectra of model hard and soft segments

exists. The fact that the H-bond NH…ether (O) is stronger than the H-bond NH…O=C has also been reported by other researchers [1, 21].

It can be concluded from above results that Type I H-bond only exists in PUMHS while Type II H-bond is the main H-bond in PUMSS. It can also be no doubt concluded from the present work that Type II H-bond is in the lower wavenumber than that in Type I. Another result which is worth noting is that these two types of H-bonds seem to have different effects on amide II and III bands. The possible relation between these H-bonds and amide II/III bands in FTIR seem more obvious in PUMHS and PUMSS.

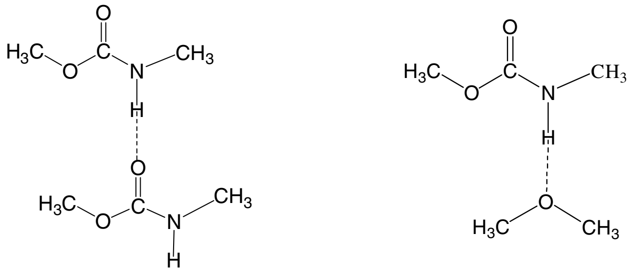
Effect of H-bonding type in PUMSS and PUMHS on amide II and III bands

As are shown in Fig. 2 and Table 1, amide II and III bands are obviously different in PUMSS and PUMHS. The amide II band is at 1537cm^{-1} in PUMSS while at 1529cm^{-1} in PUMHS; the amide III band is at 1223 cm^{-1} in PUMSS while at 1236 cm^{-1} in PUMHS. The frequency of amide II in PUMSS is higher than that in PUMHS while that of amide III in PUMSS is lower than that in PUMHS. When correlating them with νNH bands in the two model molecules, it can be easily seen that amide II is more related to Type II H-bond while amide III is closer to the Type I. Namely when NH mainly forms the H-bond with ether O, the amide II will have more shifting towards higher frequency while when NH forms the H-bond with C=O, amide III will have larger change along with it.

Since amide II and III bands have complicated vibration modes, and are also sensitive to different factors, we cannot simply conclude they must have a defined relation with Type I and Tape II H-bonds. They can be explained, however, to be closely related to the H-bonding types as well as the H-bonding configurations (i.e. the H-bonds based on the donor and acceptor with different conformers) in PUMHS and PUMSS,

Table 1 Comparative main FTIR bands in PUMSS and PUMHS

Band type	νNH	νC=O	Amide II	Amide III
Shift in PUMSS (cm^{-1})	3298	1732	1537	1223
Shift in PUMHS (cm^{-1})	3333	1705	1529	1236



a. One H-bond configuration in PUMHS b. One H-bond configuration in PUMSS

Fig. 3 H-bonds in PU model soft and hard segments

respectively. In spite of it, above results in the relatively simply model PUs will help further study and understand the H-bonding interactions in PU. Since the only difference between the two types of H-bonds is their different acceptors (Fig.3), the reason leading to above results is worth to be further explored. And further researches are being under investigation.

Conclusion

PU Model soft segment (PUMSS) based on PTHF and MDI as well as PU model hard segment (PUMHS) based on MDI and BO were respectively synthesized. FTIR was used to study the H-bonds in the simplest model PUs representing soft and hard segments. It was found that the H-bond is formed by NH…O=C (Type I) in PUMHS while the H-bond is mainly formed by NH…ether (O) (Type II) in PUMSS. The results not only prove again that the Type II H-bond is indeed in lower frequency than that of Type I, but also show some correlations between amide II or III band and above two types of H-bonding interactions, namely the amide II band is more related to the H-bonding interactions based on NH…ether (O) while amide III band is more dependent upon the H-bonding interactions based on NH…carbonyl (C=O).

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