

FTIR STUDIES ON THE MODEL POLYURETHANE HARD SEGMENTS BASED ON A NEW WATERBORNE CHAIN EXTENDER DIMETHYLOL BUTANOIC ACID (DMBA)*

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Abstract Three model polyurethane hard segments based on dimethylol butanoic acid (DMBA) and 1,6-hexane diisocyanate (HDI), toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI) were prepared by the solution method. Fourier Infrared (FTIR) spectroscopy was employed to study the H-bonds in these model polyurethanes. The model polyurethane hard segment prepared from HDI and 1,4-butanediol (BDO) was used for comparison. It was found that the incorporation of the pendent carboxyl through DMBA into the model hard segments weakens the original $\text{NH}\cdots\text{O}=\text{C}$ H-bond but gives more H-bond patterns based on the two H-bond donors, urethane NH and carboxylic OH. The carboxylic dimer is one of the main H-bond types and is stronger than another main H-bond type $\text{NH}\cdots\text{O}=\text{C}$. In addition, the H-bond in aromatic model hard segments is stronger than that of aliphatic hard segments. The appearance of the free $\text{C}=\text{O}$ and the fact that almost all $\text{N}-\text{H}$ is H-bonded suggest that there possibly exist either the third H-bond acceptor or the H-bond formed by one acceptor with two donors.

Key words Model hard segment, H-bond, Polyurethane with carboxyl, FTIR spectroscopy

INTRODUCTION

Segmented polyurethanes are one of the most widely investigated types of copolymers composed of alternating soft and hard segments. The hard segments, which are based on diisocyanates and low molecular weight chain extenders, act as the physical crosslinking points and play the key role in determining the mechanical properties, toughness, elasticity and hardness in the segmented polyurethane copolymers.

Like diisocyanates, types of chain extender also determine the hard segment structure and affect the final polyurethane properties. In addition, incorporation of a special chain extender into polyurethanes is one of the important ways to make polyurethanes functionalized^[1]. DMBA, a newly commercialized trifunctional chain extender with a tertiary carboxyl and two reactive hydroxyls, can be used to prepare the functional polyurethanes. It was reported that DMBA has 10 times the solubility in acetone and can offer better properties with faster reaction rate than dimethylol propionic acid (DMPA), and can find many potential applications such as waterborne polyurethanes and waterborne polyesters^[2] etc.

Typical polyurethanes are extensively H-bonded^[3]. 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 relevant H-bond^[3–7]. In addition, a recent study has shown that the H-bond may control the crystallization process in some polyurethanes^[8]. Polymers containing carboxyl are also a potential component to prepare self-assembly

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nanoparticles through H-bonding^[9–12]. Therefore, polyurethanes containing carboxyl are an important intermediate for further preparing water-borne polyurethanes and self-assembly nanoparticles. It is important to study the H-bond in these polyurethanes and it is also necessary to investigate, as the first step, the model polyurethane hard segment containing carboxyl in order to understand the structure and interactions in the segmented polyurethanes with the same hard segment. There is no report, however, on the deep H-bond investigations based on the polyurethanes with carboxyl although there have been many investigations concerning the typical polyurethanes, including the model hard segments prepared by diisocyanates and the extender diol^[13–15].

Incorporation of DMBA into the polyurethane chain is expected to make the H-bond behavior more complicated as it will lead to an increase of one more H-bond donor and one acceptor derived from carboxylic OH and carboxylic C=O, respectively, compared with the typical polyurethane hard segments in which there is actually only one type of H-bond $N-H\cdots C=O$, although there are three potential H-bond acceptors^[16, 17].

In the present work, we prepared three new model hard segments containing carboxyl groups by using DMBA and the three most commonly used diisocyanates, TDI, MDI and HDI, to investigate their H-bonds by FTIR spectroscopy. The results were compared with the model hard segment without the carboxyl groups and the possible H-bond patterns were also considered.

EXPERIMENTAL

Materials and Synthesis of the Model Hard Segments

The raw materials used in the present work included dimethylol butanoic acid (DMBA), 1,6-hexane diisocyanate (HDI) toluene diisocyanate (TDI) with 2,4/2,6-isomer = 80/20, 4,4'-diphenylmethane diisocyanate (MDI); 1,4-butanediol (BDO) (AR) and acetone (AR) were available commercially.

The polyurethane model hard segments were synthesized by the solution method. Diisocyanate and DMBA were stoichiometrically added into a three-necked flask equipped with a reflux condenser. A portion of acetone was added to the mixture and heated to its refluxing temperature under stirring and kept for 2 h. Another portion of acetone was added during the preparation to keep the reaction going smoothly until the final polyurethane concentration was about 20%.

Characterization

FTIR, NMR, and DSC were used to characterize the three model hard segments. FTIR spectra were recorded on a Shimadzu FTIR-8700 spectrometer from 4000 to 400 cm^{-1} averaging 45 scans at a resolution of 4 cm^{-1} . The solution samples were directly coated onto a piece of KBr plate and measured after the acetone was completely removed. ^1H -NMR spectra were recorded at 300 MHz in deuterated DMSO with a Bruker Avance 300 instrument. DSC experiments were carried out on a Swiss DSC 822e analyzer (Mettler Toledo) with both heating and cooling at a rate of 20 K/min in a nitrogen atmosphere.

FTIR (Fig. 1) spectra show that there is no band at about 2230 cm^{-1} , suggesting NCO has completely reacted while there are obvious amide I (1700–1730 cm^{-1}), amide II (1500–1540 cm^{-1}) and amide III (1200–1300 cm^{-1}) bands beside the ν_{NH} band, showing the expected urethane group was formed. In addition, there is a broad band at 2300–3000 cm^{-1} , suggesting the existence of carboxyl. ^1H -NMR spectra also verify the expected structure. The signals at $\delta = 12.7$ –12.8 indicate the presence of carboxyl. The other signals at lower field correspond to the OCONH bonded to the hydroxyl of DMBA, among which the signal resonating at $\delta = 9.6$ is associated with MDI based OCONH, the multiplets (due to 2,4- and 2,6-TDI isomer) in the range $\delta = 8$ –9.6 come from TDI while another singlet at $\delta = 7.1$ (shifting to higher field since there is no phenyl ring) is relating to HDI. The multiplets at $\delta = 7$ –7.5 in MDI and TDI based hard segments correspond to the protons of phenyls in the two aromatic diisocyanates but there is no such signal in the HDI based model hard segment since there is no phenyl ring in it. In addition, signals are also found at about $\delta = 0.8$ for the CH_3 in DMBA, the signals at $\delta = 1.5$ for the CH_2 attached to CH_3 , the signal at about $\delta = 2.0$ for CH_3 attached to TDI as well as the signals at $\delta = 2$ –4.5 for CH_2 in $\text{HO}-\text{CH}_2-$ and $-\text{CH}_2-\text{OCO}$.

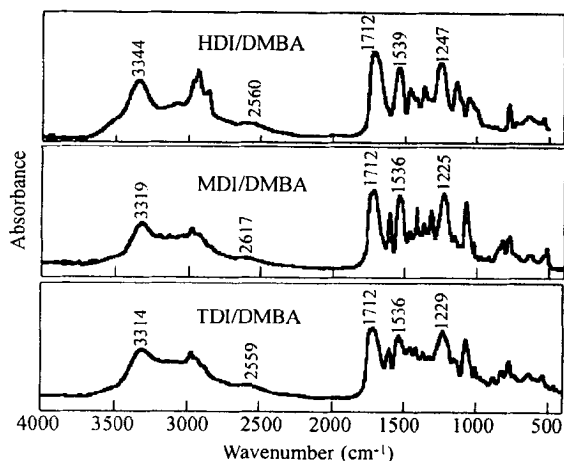


Fig. 1 $\nu_{\text{C-H}}$ bands in the FTIR spectra of three model hard segments

DSC results show that there are multiple melting peaks in all three model hard segments (as received), among which HDI/DMBA is at 120–190°C, MDI/DMBA is at 120–200°C, TDI/DMBA is at 120–170°C. There are no melting or crystallization peaks, however, in the cooling or second heating scan from room temperature to 200°C; instead, the obvious T_g appears at 71.32°C for HDI/DMBA, 161.41°C for MDI/DMBA and 149.91°C for TDI/DMBA in the second heating scan, respectively, suggesting that the model polyurethane hard segment with carboxyl can crystallize but cannot crystallize in a relatively short time. However, the model hard segment (BDO/HDI) without carboxyl still has the obvious melting point at 174.13°C even in the second heating scan, showing its strong crystallization behavior.

Results and Discussions

Figure 2 is the FTIR spectra of different model hard segments, including the BDO/HDI hard segment without carboxyl. It can be seen that the N—H Stretching Vibration band ($\nu_{\text{N-H}}$) appears prominently at 3314–3344 cm^{-1} for all the four types of model hard segments, showing the N—H group is almost all H-bonded for each model hard segment. Meanwhile, the difference in the N—H bands between the model hard segments with and without carboxyl is quite obvious. For HDI/BDO, there are no additional bands at 2500–3000 cm^{-1} whereas for all the other three model hard segments with carboxyl, there is an obvious shoulder band at 2500–2600 cm^{-1} , which is similar to the band in ethylene-methacrylic acid copolymers^[18] and can be assigned to the H-bonded ν_{OH} from carboxylic acid. In addition, the broad band at 2500–3000 cm^{-1} for each model hard segment with carboxyl, which is very common in pure carboxylic acids, is another characteristic of carboxylic acids, implying the existence of carboxylic acid dimer^[19].

As mentioned above, the presence of more than one H-bond donor and one acceptor would expect to lead to more H-bonds, which should make the H-bond behavior more complicated. In the common polyurethanes extended by diol, urethane N—H is the only H-bond donor, while in these new model hard segments both N—H and O—H (from carboxylic acid) are the H-bond donors. Luckily, $\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$ do not overlap, thus they provide the convenience to investigate the two types of H-bonds and to study the effect of pendent carboxyl on the H-bond resulting from NH and other H-bond acceptors.

It can also be seen from Fig. 2 that the ν_{NH} band is at different frequencies for different hard segments. As far as the two HDI based hard segments are concerned, incorporation of the pendent carboxyl weakens the original H-bond as the ν_{NH} band in the HDI/DMBA hard segment shifts from 3322 to 3340 cm^{-1} . This is reasonable because the pendent carboxyl is expected to increase the volume hindrance between the N—H and C=O (urethane) groups, resulting in increasing of distance and weakening of the original H-bond intensity. The broadness of the ν_{NH} band itself in the three DMBA based hard segments indicates that N—H may have very

different H-bonded states due to either the different distances among the same type of H-bond or the different H-bonds between N—H and other acceptors. It can also be seen that the ν_{NH} band for TDI/DMBA appears at the lowest frequency whereas that for HDI/DMBA hard segment is at the highest frequency, suggesting the H-bond strength of NH in HDI/DMBA is the weakest.

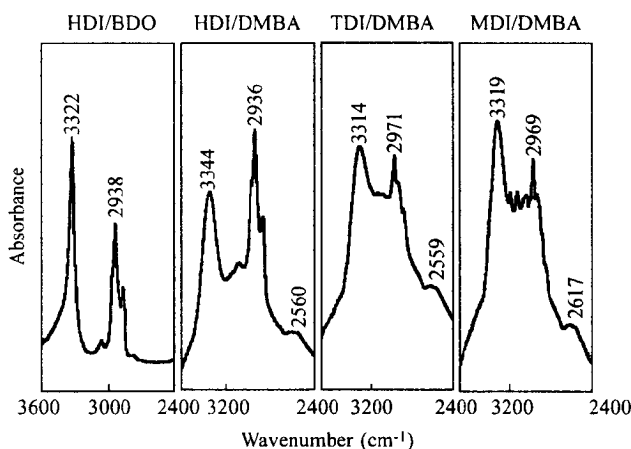


Fig. 2 $\nu_{\text{N-H}}$ bands in the FTIR spectra of the different model hard segments

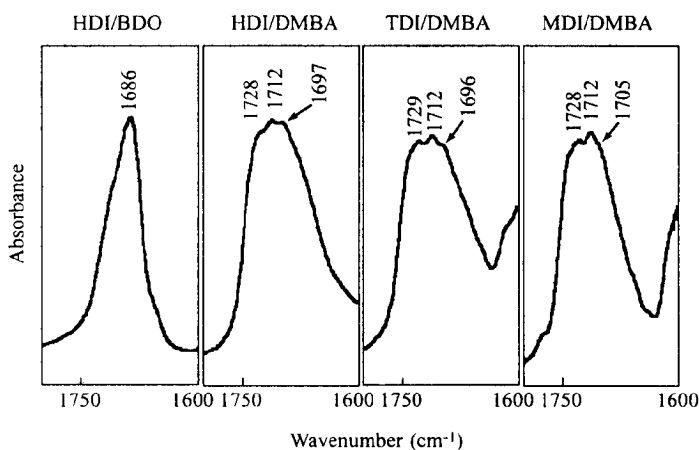


Fig. 3 $\nu_{\text{C=O}}$ bands in the FTIR spectra of the different model hard segments

It can be seen from Fig. 3 that the $\nu_{\text{C=O}}$ bands of the model hard segments with carboxyls and that without carboxyl are different; however, it is similar for the three model hard segments with carboxyl themselves. The $\nu_{\text{C=O}}$ band in these three hard segments is broader and is composed of three not clearly distinguishable peaks. One is at 1728–1729 cm^{-1} , which may be assigned to the free C=O H-bond; whereas considering the frequency of the characteristic bands of the common carboxylic acid^[19], the H-bond in ethylene-methacrylic acid copolymer^[18], we can safely assign the band around 1700 cm^{-1} (1696–1705 cm^{-1}) to the carboxylic acid dimer; then the one at 1712 cm^{-1} must be the H-bonded urethane C=O. It is worth noting that the frequency of the carboxylic acid dimer stretching band is lower than that of H-bond $\text{NH}\cdots\text{C=O}$, suggesting the H-bonded dimer is stronger than the H-bond $\text{NH}\cdots\text{C=O}$.

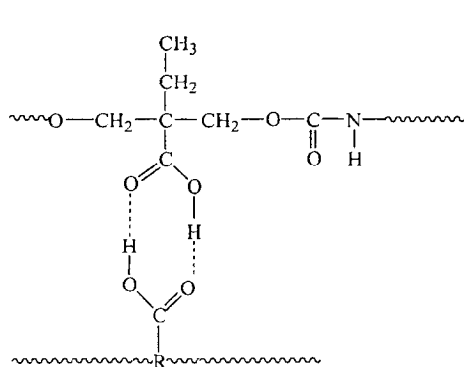
The appearance of the three $\nu_{\text{C=O}}$ bands in the spectra of model hard segments with carboxyl results obviously from the incorporation of carboxyl into the hard segment. Compared with HDI/BDO, which has only one H-bonded C=O band at 1688 cm^{-1} , the same H-bonded C=O band in HDI/DMBA shifts to 1712 cm^{-1} , suggesting the strength of H-bonded $\text{NH}\cdots\text{C=O}$ becomes weaker after the incorporation of carboxyl in this

aliphatic polyurethane. In Table 1, aromatic polyurethanes show the same results. For MDI based aromatic model hard segment, the H-bonded $\nu_{\text{C=O}}$ shifts from 1703 to 1712 cm^{-1} while for TDI based aromatic model hard segment, the H-bonded $\nu_{\text{C=O}}$ shifts from 1706 (in 2,6-TDI) or 1708 (in 2,4-TDI) to 1712 cm^{-1} . These results are consistent with the weaker H-bonded NH in the model hard segment HDI/DMBA with carboxyl as mentioned above. The bigger difference in $\nu_{\text{C=O}}$ frequency difference between the HDI based hard segments with and without carboxyl is expected to result from their large difference in crystallization.

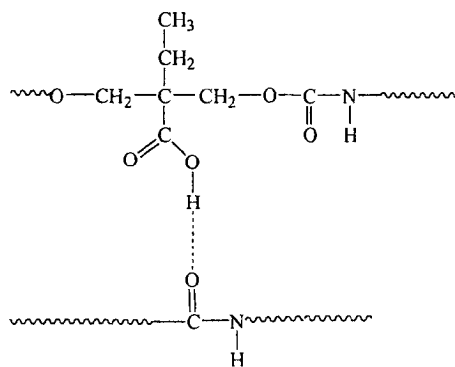
Table 1. Comparison of the H-bonded urethane C=O frequencies of the model hard segments with and without carboxyl*

Hard segment	HDI/BDO	TDI/BDO	MDI/BDO	HDI/DMBA	TDI/DMBA	MDI/DMBA
$\nu_{\text{N-H}}$ (cm^{-1})	3322	3300/3310	3330	3344	3314	3319
$\nu_{\text{C=O}}$ (cm^{-1})	1686	1706/1708	1703	1712	1712	1712

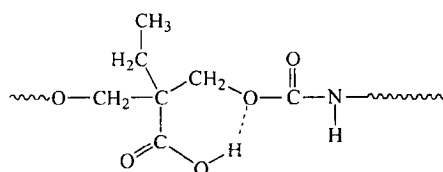
* The absorption frequency data related to H-bonded $\nu_{\text{C=O}}$ of TDI/BDO and MDI/BDO are cited from Ref. [13].



(a) Carboxylic dimer (carboxylic OH versus carboxylic C=O)

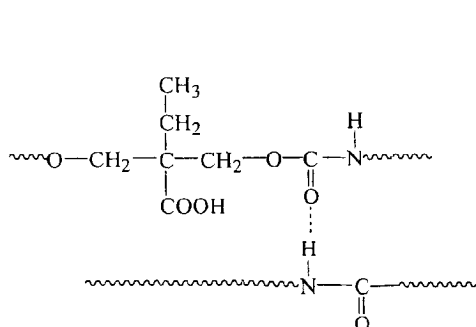


(b) OH versus urethane C=O

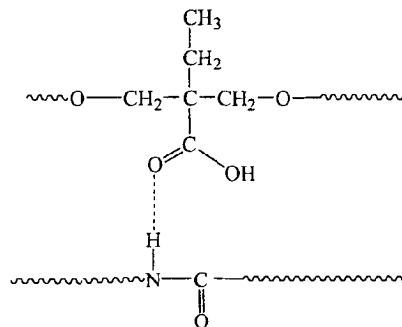


(c) Intramolecular H-bond OH versus alkoxy oxygen

Scheme 1 The possible H-bond patterns formed by carboxylic OH with other acceptors



(a) N-H versus urethane C=O



(b) N-H versus carboxylic C=O

Scheme 2 The possible H-bond patterns formed by urethane NH with other acceptors

If the two H-bond donors (NH from urethane and OH from carboxylic acid) form H-bonds with the two acceptors (urethane C=O and carboxylic C=O), respectively, and suppose that one H-bond acceptor can only form a H-bond with one donor, there will be no free C=O since there is no obvious free NH. We think, however, that there are two possible reasons for the existence of obvious free C=O. One reason is that there must be a third H-bond acceptor besides the carboxylic C=O and the urethane C=O. Suppose one acceptor can form the H-bond with only one donor, the two donors (N—H and O—H) will face three acceptors, and leave one acceptor in the free state. Another possible reason is that one acceptor forms two H-bonds with two donors at the same time between the two donors and two acceptors. It is also possible to leave one acceptor (C=O) free in the second case. We need to further verify this speculation in our future work. The most likely single H-bond types are shown in Schemes 1, 2, yet we have not shown the possible combination scheme for the H-bond between one acceptor with two donors, up to now.

CONCLUSION

Incorporation of carboxyl into the polyurethane model hard segments gives a variety of possible H-bond patterns based on the two H-bond donors, urethane NH and carboxylic OH. Among them, all the model hard segments with the pendent carboxyl have the H-bonded carboxylic dimer besides the H-bonded NH $\cdots$ O=C. Besides, since almost all the N—H in model hard segments is H-bonded while part of C=O is obviously free, there must exist either the third H-bond acceptor besides the urethane C=O and carboxylic C=O or the special H-bonds in which two H-bond donors, OH and NH, form the H-bond with one acceptor C=O at the same time. Among the different H-bond patterns, the H-bonded carboxylic dimer is stronger than that in other H-bond patterns whereas the H-bond in aromatic diisocyanate based model hard segments is stronger than that in aliphatic ones. Both structure and crystallization differences between the two types of model hard segments (with and without carboxyl) may lead to the different H-bond states especially in the aliphatic model hard segments.

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