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Hydrogen-Bonding Properties of Segmented Polyether Poly(urethane urea) Copolymer

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ABSTRACT: FTIR was used to investigate the effects of thermal annealing on the hydrogen-bonding properties of a poly(urethane urea) copolymer. The copolymer was based on ethylene oxide-capped poly(propylene oxide) diol, 4,4′-diphenylmethane diisocyanate (MDI), and 3,5-diethyltoluenediamine (DETDA). The result showed that thermal annealing caused the rise of the number of free urethane groups and the ordering of urea groups. The ordered urea hydrogen bonds were not destroyed below the melting point of the DETDA−MDI hard domain.

Introduction

Segmented polyether poly(urethane urea) (SPUU) copolymer is a kind of block copolymer of the type $(AB)_n$ composed of alternating soft and hard segments along the molecular chains. The hard segments are based on diisocyanate and diamine, while the soft segments are typically polyether blocks. Due to the thermodynamic incompatibility between these two kinds of structural units, microphase separation occurs and results in hard segment-rich hard domains and in a soft segment-rich soft matrix. Even though the morphological feature of the copolymer can be affected by many factors such as chemical composition, sequence length of the hard segment, and hydrogen bonding, it is generally accepted that hydrogen bonding between functional groups is very closely related to the phase separation.[1−4]

There are basically three factors that make the hydrogen bonding in the SPUU copolymer very complex.[4−8] Firstly, multiple hydrogen bonds may be formed between two kinds of proton donators (urethane N−H and urea N−H groups) and three kinds of proton acceptors (urethane C═O, urea C═O, and C−O−C groups) in the copolymer. Secondly, the strength of the hydrogen bonds between urea groups is stronger than that between urethane groups because the polarity of urea groups is stronger than that of urethane groups. Some FTIR spectra showed that hydrogen bonding resulted in a shift of the absorption band of the stretching vibration mode from a higher frequency value to a lower one (see Table 1).[3−10] Lastly, the hydrogen-bond geometry of the urea groups may be substantially different from that of urethane groups. One urea group is constructed of one carbonyl group and two N−H groups. One urethane group, however, only contains one N−H group. The three-dimensional structure of hydrogen-bonded urea groups was studied in some previous reports,[3,9−11] but the concrete structure of the 3-D hydrogen bonds was not clearly described. A hexagon structure could be formed by the hydrogen bonding between two urea groups. This structure was used to explain the crystalline structure of polyurea by some investigators.[7,8,12,13] Born labeled this hexagon structure as a planar bifurcated structure and calculated the length of the urea hydrogen bond.[13] His calculation showed that this length (4.63 Å) was shorter than that between two urethane groups (5.10 Å), so the strength of urea hydrogen bonding should be stronger than that of urethane.

A spectral technique, mainly Fourier transform infrared (FTIR) thermal analysis, was commonly used to study the hydrogen-bonding properties of polyurethane[2,13−18] and SPUU copolymers.[1,3−7,9−11] Thermal annealing of polyurethane or SPUU copolymers could lead to the rearrangement of hydrogen bonds.[1,3,5] Several studies suggested that the microphase mixing of hard and soft segments was improved in polyether polyurethane copolymers if the annealing temperature increased. Lee[2] quenched a polyurethane melt from 110 °C to liquid nitrogen temperature at a rapid speed to fix the morphology of the melt state, i.e., the microphase-mixing state. When the temperature was raised again, the hydrogen bonds between the urethane groups formed and microphase separation occurred. Above 75 °C, however, the hydrogen bonds weakened. The spectroscopic changes in both the N−H and C═O stretching regions were clearly observed, which verified the rearrangement of hydrogen bonds. The rearrangement was that the hard segment−soft segment hydrogen bonding (N−H···O−) in the phase-mixing state changed into the hard segment−hard segment hydrogen bonding (N−H···O═C) in hard domains. Ishihara[5] studied the IR spectra of an SPUU copolymer based on MDI, propylenediamine (PDA), and poly(tetramethylene glycol) (PTMG) from room temperature to 250 °C; he observed a stronger absorbance band at 1640 cm^{-1}, attributed to the associated urea C═O stretching vibration mode and rapid orientation of hard segments above 100 °C. At about 150 °C, scission of the interurea hydrogen bonds between hard segments was observed, as was proved by the decreasing intensity of the 1640 cm^{-1} band. He pointed out that the sample did not melt at 150 °C but at about 271 °C. Zhao[3] studied an SPUU based on MDI, PTMG, and ethylenediamine. He indicated that hydrogen bonds in the copolymer were very sensitive to temperature. The urea hydrogen bonds were dissociated at 140 °C. Miller[1] reported by using near-infrared spectroscopic analysis, that the annealing at 100 °C enhanced microphase separation of the SPUU copolymer based on MDI, PDA, and PTMG. An increase in the number of free urethane groups and a decrease in the number of free urea and urethane carbonyl groups were observed in his study. Although he suggested several possible mechanisms to explain the changes, more information was necessary to identify the exact structural changes that occurred by annealing.

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In the present work, FTIR and differential scanning calorimetry (DSC) experiments were used to study the effects of thermal annealing on hydrogen-bonding properties of an SPUU copolymer in a broad range of annealing temperatures. The SPUU copolymer was based on 4,4′-diphenylmethane diisocyanate (MDI), ethylene oxide-capped poly(propylene oxide) diol (PPO), and diethyltoluenediamine (DETDA). The liquid aromatic diamine, DETDA, was a typical chain extender used in reaction injection molding (RIM). It was confirmed that such an SPUU copolymer could form crystallites in its hard segment domains.[8]

Experimental Section

1. Raw Materials and Synthesis of the SPUU Copolymer. Raw materials used in the present work included 4,4′-diphenylmethane diisocyanate (MDI, purity >99.6%, freezing point >38.1 °C, Yantai Synthetic Leather General Factory), 3,5-diethyltoluenediamine (DETDA, 2,4-/2,6-isomer = 80/20, Ethyl Chemical Co.), ethylene oxide-capped poly(propylene oxide) diol (PPO, ZS-2185, content of ethylene oxide = 15%, $\bar{M}_n$ = 2000, Jinling Petrochemical Industry Corp.), and *N*,*N*-dimethylformamide (DMF) as the polymerization medium.

Polyether diol was dried at 40 °C under vacuum for more than 24 h. MDI was heated at 60 °C for 2 h and then filtered through a heated filter. The surveyed NCO content of the purified MDI was 33.18%.

In a stirring vessel, MDI (1.084 g) was dissolved in 15 mL of DMF and the temperature was controlled at 60 °C. Stoichiometrical DETDA and PPO were mixed in 15 mL of DMF. The concentration of catalyst DBTDL was at a level of 1.0×10^{-3} g/g of PPO. This mixture was injected into the MDI/DMF solution by a surgical syringe. After reacting for 20 min, an additional 10 mL of DMF was added to the reaction system, and the reaction continued for 4 h more. The hard-segment content of the resultant SPUU was 30%.

2. FTIR Study. FTIR spectra were recorded with a Nicolet 5DXC Fourier transform infrared spectrometer. Two hundred scans at 4 cm^{-1} resolution were signal averaged and stored as data files for further analysis. The 5% SPUU copolymer solution in DMF was directly coated onto a piece of KBr plate. A thin film of the SPUU sample formed on the KBr plate after rapid evaporation of the DMF under vacuum; then the SPUU film specimen was maintained in a vacuum oven at 60 °C for 1 week to remove the trace of DMF. Survey spectra did not show any existence of residual solvent (see Figure 2).

The dried SPUU film sample was held between two pieces of KBr plate and placed into a temperature-variable unit connected to the numerical temperature controller (Model WMNK 402, available from Shanghai Medical Instrument Factory) with an accuracy of ±2 deg. The temperature of the SPUU sample was monitored by a copper−constantan thermocouple held directly on the sample between the two salt plates. The temperature was held constant for 20 min before one spectrum was recorded. In the infrared analyses, the integrated intensities of absorption bands were corrected for the differences of sample thickness by using the CH_3 stretching band at nearly 2980 cm^{-1} as a normalizing factor. A curve-resolving technique of nonlinear least-squares optimization, based on a combination of Lorentzian and Gaussian curve shapes, was used to fit the band outlines in the carbonyl region.

3. DSC Experiment. The DSC experiments were conducted in a nitrogen atmosphere by using a DuPont 1090A calorimeter. The sample size was approximately 10 mg. DSC scans were carried out at a heating rate of 20 °C/min by starting from −80 °C.

Results and Discussion

Spectral Feature and Band Assignment. The unit structures of the SPUU copolymer are shown schematically in Figure 1. As shown in Figure 1, urea groups only exist in the interior of hard segments and they were formed by reacting DETDA with MDI. Urethane groups, however, exist mainly on the boundaries between hard and soft segments. The urea hydrogen bonds were, therefore, sensitive to the morphological changes in hard segment domains, while the urethane hydrogen bonds were more sensitive to those on the phase boundaries.

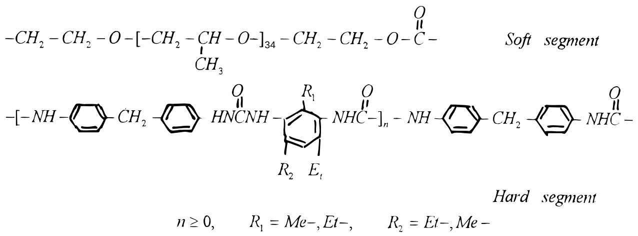


Figure 1. Scheme of unit structures in the SPUU copolymer based on MDI, DETDA, and PPO.

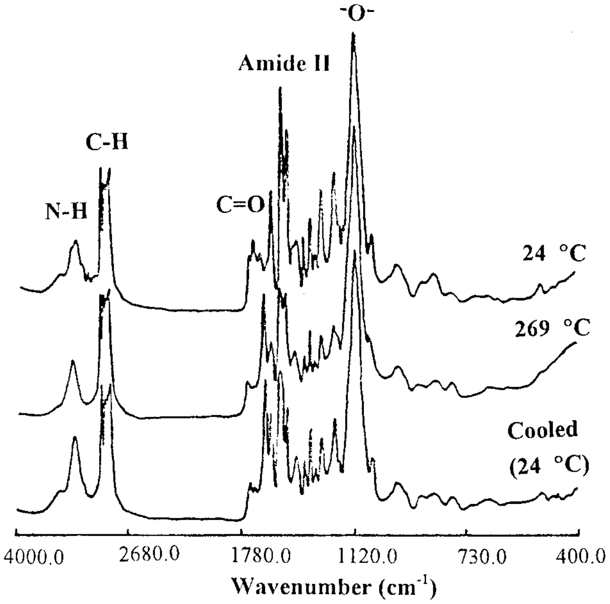


Figure 2. FTIR spectra of the SPUU copolymer at different temperatures.

Figure 2 shows the FTIR spectra of the SPUU sample recorded at different temperatures. From Figure 2, spectral changes of the SPUU copolymer can be seen obviously in the regions at 3500−3200 cm^{-1} (N−H stretching mode), 1780−1600 cm^{-1} (C=O stretching mode), and 1560−1300 cm^{-1} (amide II and III regions). The changes were all related to the hydrogen bonding of urethane or urea groups. Multiple absorption bands are observed in the C=O regions, which should reflect the complex properties of hydrogen bonding in the SPUU copolymer. Band assignments of characteristic groups in the SPUU copolymer are listed in Table 1. The carbonyl region in the FTIR spectra is most applicable to the analysis of the hydrogen-bonding properties.[4,7,15−18] The ordered urea hydrogen bonding (1637 cm^{-1}) in Table 1 is related to the crystallites in hard domains, which reflects the long range ordering of urea hydrogen bonding. We suggested that the ordered urea hydrogen bonds were of the planar bifurcated form in the crystallite structure of the MDI−DETDA hard segments.[8] The disordered urea hydrogen

Table 1. Assignments of the Absorption Bands in FTIR Spectra of the SPUU Copolymer

frequency (cm^{-1})	assignment	frequency (cm^{-1})	assignment
3480	ν(NH), free	1691	ν(C=O) free urea carbonyl
3289, 3270	ν(NH), hydrogen-bonded	1666	ν(C=O), hydrogen-bonded, disordered urea carbonyl
3191	ν(NH), cis–trans isomers, bonded	1643–1628	ν(CO), hydrogen-bonded, ordered urea carbonyl
2980	$\nu(CH_3)$	1600	ν(C=C), benzene ring
2270	ν(NCO)	1540	δ(N–H) + ν(C–N), amide II
1729–1739	ν(C=O), free urethane carbonyl	1240	δ(N–H) + ν(C–N), amide III
1706–1713	ν(C=O), hydrogen-bonded urethane carbonyl	1110	ν(C–O–C), ether group

bonding (1666 cm^{-1}) could be observed in the infrared spectra of solid SPUU samples.[3–6,9,10] We showed previously that the disordered band could also be observed clearly in the infrared spectra of a liquid urea compound based on polyether diamine and phenyl isocyanate.[4] This result revealed that the disordered urea hydrogen bonds (1666 cm^{-1}) had the property of short range ordering. The disordered band did not associate with crystallites in the hard domain at all. The annealing-induced morphological changes could be shown in the the range of C=O absorption bands related to urethane and urea hydrogen bonding.

The CH_3 absorption band at 2980 cm^{-1} and the C–O–C band at 1110 cm^{-1} are relatively unaffected by thermal annealing, as shown in Figure 2. The NCO absorption at 2270 cm^{-1} is not detected in the spectrum recorded at 269 °C (Figure 2c). The FTIR results in Figure 2 indicate that the SPUU sample did not undergo any chemical reactions and only rearrangement of hydrogen bonds was observed during the temperature-variable FTIR experiment.

Hydrogen Bonding of Urethane C=O Groups. The stretching vibration mode of the urethane carbonyl group in the SPUU copolymer should be observed from 1780 to 1700 cm^{-1}. Figure 3 shows the C=O regions in the FTIR spectra of the SPUU copolymer recorded as a function of increasing temperature. The distribution of carbonyl groups and the frequency shift of "free" urethane carbonyl groups at different temperatures are listed in Table 2.

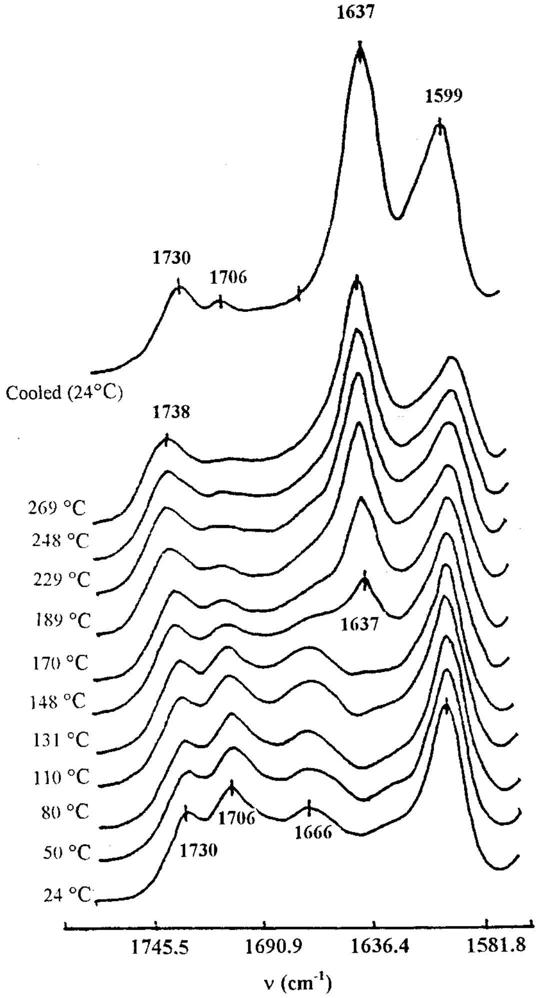
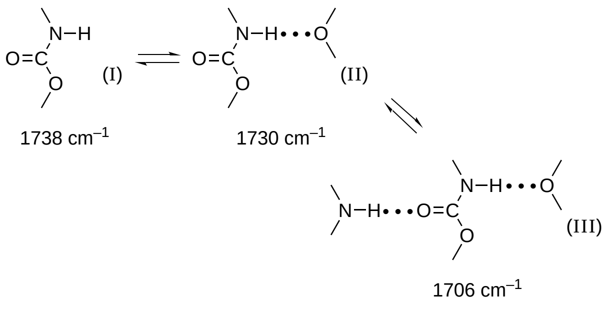


Figure 3. Carbonyl absorption in the FTIR spectra of an SPUU sample recorded as the function of increasing temperature.

Figure 3 and Table 2 indicate that the peak intensity of the absorption band at 1706 cm^{-1} decreased with increasing temperature from 24 to 269 °C and is finally regained after slowly cooling the sample to room temperature. During the thermal annealing process, the intensity of the 1730 cm^{-1} band increased with the rising temperature, and the band position shifted gradually from 1730 to 1738 cm^{-1}. After the sample was cooled to room temperature, the peak position changed from 1738 to 1730 cm^{-1}. Coleman[16] showed that the free urethane carbonyl in an amorphous polyurethane (APU), synthesized from butanediol and a mixture of the 2,4- and 2,6-isomers of toluene diisocyanate, was located at 1737 cm^{-1}. The free urethane carbonyl band was shifted to 1733 cm^{-1} when the APU was mixed with a poly(ethylene oxide-*co*-propylene oxide) copolymer. Coleman's result revealed that the free urethane carbonyl (1733 cm^{-1}) was actually in the form of the urethane group associated with the ether group. Strikovsky[18] studied the equilibrium association of urethane groups in poly(ether urethane). He indicated that free urethane groups without any hydrogen bonds were absorbed at 1738 cm^{-1} and appeared distinctly only at a temperature as high as 40 °C. The absorption band at 1729 cm^{-1} was attributed to the urethane end group associated with an ether group. According to these results,[16,18] the frequency shift from 1730 to 1738 cm^{-1} in the present work should be the result of the rearrangement of the urethane hydrogen bonds in the SPUU copolymer:



(1)

This simplified hydrogen bonding equilibrium (eq 1) could be used to explain the intensity changes in the

Table 2. Distribution of Hydrogen Bonds and the Shift of the "1730 cm^{-1} Band" at Different Temperatures

		integrated intensity (%)				
T (°C)	shift of "1730" cm^{-1}	"1730" cm^{-1}	1709 cm^{-1}	1691 cm^{-1}	1666 cm^{-1}	1637 cm^{-1}
24	1729.3	54.55	45.55	29.08	64.67	6.25
50	1730.9	42.01	57.99	23.96	47.12	28.92
80	1729.9	44.40	55.60	26.32	46.20	27.48
110	1730.3	47.15	52.85	21.67	47.60	26.39
131	1731.3	47.13	52.87	21.43	47.34	31.24
148	1732.9	53.37	46.63	17.36	32.37	50.27
170	1733.5	57.50	42.50	10.88	24.16	64.96
189	1735.4	58.78	41.22	8.78	20.60	70.62
208	1735.9	61.16	38.84	8.80	19.73	71.46
229	1736.3	63.54	36.46	7.89	18.89	73.23
248	1736.8	62.51	37.49	7.39	18.13	74.48
269	1738.1	63.39	36.61	7.10	18.18	74.72
cooled[a]	1729.4	52.36	47.64	7.46	11.65	80.90

[a] Slowly cooling from 269 to 24 °C and then recording the spectrum.

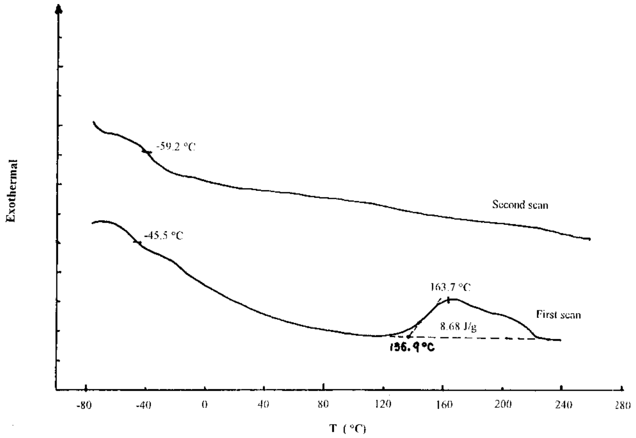


Figure 4. DSC spectra of the first and second scans for the SPUU copolymer.

urethane C=O region of the infrared spectra (Figure 3) during thermal annealing.

Hydrogen Bonding of Urea C=O Groups. The stretching vibration region of urea carbonyl groups was from 1700 to about 1620 cm^{-1}. Figure 3 and Table 2 indicate invariable intensity of the absorption for urea carbonyl groups at temperatures below 130 °C. However, disordered urea carbonyl (1666 cm^{-1}) disappeared gradually above 130 °C, while the ordered urea hydrogen bond (1637 cm^{-1}) became more intensive at elevated temperature. The absorption band of free urea carbonyl (1691 cm^{-1}) was not observable directly in Figure 2, but it could be resolved by least-squares curve-fitting (see Table 2). The number of free urea carbonyls decreased at elevated temperature. The sharp changes of urea hydrogen bonding took place in the temperature range of about 130–230 °C.

Formation of ordered urea hydrogen bonds should be an exothermic process. The exothermic process was observed clearly in the temperature range of 130–220 °C in the DSC spectrum (see Figure 4a). The exothermic range was in good agreement with that of the rapid formation of ordered urea hydrogen bonds shown in FTIR analysis (see Table 2). The exothermic process disappeared in the DSC trace when the specimen underwent the second scan (Figure 4b). The result was reasonable because the ordered urea hydrogen bonds had been formed during the first scan process. The urea hydrogen bonds were strong enough and did not dissasociate during the thermal treatment under the melting point of the MDI–DETDA hard segment. The DSC result showed that thermal annealing was advantageous to the formation of the ordered urea hydrogen bonds of the SPUU sample.

Relationship of Morphological Changes and Hydrogen Bonding. Five processes, which might take place during the thermal annealing of the SPUU copolymer, were as follows: (1) rearrangements of urethane and urea hydrogen bonds; (2) vitrification of hard segments; (3) reconstruction of hard domains (for glassy hard segments, only microphase separation would be reconstructed; for crystalline hard segments, both microphase separation and crystallization of hard segments would proceed); (4) mixing of soft and hard segments resulting in a phase-mixed state; (5) thermal degradation of the SPUU copolymers.

The melting point of DETDA–MDI hard segments is about 347 °C.[4,8] Thermal degradation of the hard segments begins at above 360 °C.[4,8] Ryan and Stanford et al.[19,20] reported that the glass transition temperature of DETDA–MDI hard segments, detected by dynamic mechanical thermal analysis, was about 190 °C. Willkomm,[21] however, indicated that DSC analysis found no evidence of hard segment vitrification of RIM polyurea, and the evidence from dynamic mechanical analysis was inconclusive. The glass transition temperature of the DETDA–MDI hard segment was not observed in DSC traces in our previous works,[4,8] which was in accordance with Willkomm's report.

We prepared the SPUU sample in the way of a fast evaporation of solvent at room temperature under vacuum. The purpose was to form a "quenched amorphous" sample because slow evaporation would benefit the ordering arrangement of urea groups. Our purpose was achieved because no peak at 1637 cm^{-1} was observed directly in the infrared spectra below 131 °C. As a result, the sample with a "quenched amorphous" or a more disordered morphology was prepared before thermal annealing.

Miller and his co-workers have proved that thermal annealing increased the degree of microphase separation in SPUU copolymers.[1] After the second scan (Figure 4b), the SPUU sample showed a lower glass transition temperature of the soft segment (T_g^s) and a greater change of heat capacity at T_g^s in comparison with those shown in the first scan (Figure 4a). This result was in agreement with Miller's reports. The present work, however, emphasized that the increase of the degree of microphase separation should be accompanied by the ordering of urea hydrogen bonds during thermal annealing, and it should be considered that the reconstruction of hard domains was related closely to the rearrangement of hydrogen bonds, especially to that of urea hydrogen bonds.

It could be supposed that formation of crystallite or formation of long range ordered hard segments allowed the exclusion of soft segment "impurities" from hard domains and resulted in the formation of purified hard domains. The urethane groups were mainly situated on the boundaries between hard and soft segments and in the soft segment matrix. When the degree of phase separation was increased, the urethane groups as "impurities" in hard domains were forced into the soft phase matrix and phase boundaries, and the number of ordered urea hydrogen bonds in the hard domain might increase. This process would cause an increase of the number of free urethane carbonyl groups because hydrogen bond donors hardly existed in the soft phase matrix. This process would also decrease the formation probability of hydrogen bonding between urethane and urea groups, which was why the 1706 cm^{-1} band was regained partially after the SPUU sample cooled. Disassociation of the ordered urea hydrogen bonds was not observed in the present work. This was different from the results when aliphatic diamine was used as chain extender.[1,8] The difference could be attributed to the stiffness of the MDI−DETDA hard segment.

Conclusion

The hydrogen-bonding properties of an SPUU copolymer, based on DETDA, MDI, and polyether diol, were monitored during thermal annealing. The disordered urea hydrogen bonds were strong enough and did not disassociate below 130 °C. The ordered urea hydrogen bonds formed rapidly at 130−220 °C and then developed slowly at elevated temperature. The urethane hydrogen bonds disassociated during the thermal annealing process and were regained partly after the SPUU sample was cooled to room temperature again. The hydrogen-bonding properties could be closely correlated to morphological changes.

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