polymer reports

Hydrogen bonding and crystallization behaviour of segmented polyurethaneurea: effects of hard segment concentration

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(Received 17 May 1991; revised 7 October 1991)

I.r. spectroscopy, d.s.c., WAXD and optical microscopy were employed to investigate the differences between hydrogen bonding and crystallization behaviour depending on hard segment concentration in polyether- and polyester-based polyurethaneureas (PUUs). It has been found that the hard segment crystallization behaviour of polyether-based PUU is higher than polyester-based PUU for the same hard segment content. Hydrogen bonding in polyether-based PUU is formed mainly between hard segments, which promotes crystallization of hard segments. Hydrogen bonding in polyester-based PUU is formed mainly between soft and hard segments, which hinders the crystallization of hard segments.

(Keywords: polyurethaneurea; hard segment; hydrogen bonding; crystallization)

INTRODUCTION

Polyurethaneurea (PUU) block copolymers are made up of soft segments based on polyether or polyester and hard segments based on the reaction of diisocyanate and diamine extender. They can be divided into polyether- and polyester-based PUU depending on the soft segments used. The excellent characteristics of PUU elastomers have led to an extensive study during the past decade[1–8] of their synthesis, morphology and properties.

Sung *et al.*[2,5,9] have described the properties of segmented PUUs based on tolylene-2,4-diisocyanate (TDI), ethylenediamine (ED) and poly(tetramethylene oxide) (PTMO). A morphological investigation on these materials by SAXS has been carried out by Wilkes and Abouzahr[6]. Khransovskii[10] studied PUU composed of PTMO, TDI and 4,4-diaminodiphenyl methane (DAM). Ishihara *et al.*[11–13] reported the deformation mechanism of more crystallizable PUUs based on PTMO, 4,4-methylene bis(phenyl isocyanate) (MDI) and DAM. A symmetric MDI/DAM hard segment would have better packing efficiency than a non-symmetric TDI/DAM hard segment. As a result, the former exhibited a spherulitic texture. Wang and Cooper[7] studied the effect of urea linkage, hard segment content and block length on the extent of phase separation, domain structure and physical properties based on a polymer formed from MDI, ED and PTMO.

To date, studies of segmented PUU have been mostly limited to the crystallizable PTMO polyether as the soft segments, with the hard segment contents being mostly limited to <50 wt%. Consequently, it is of interest to synthesize a series of PUU to investigate how the crystallizability of the soft segment and the hard segment content affect hydrogen bonding and phase separation in these materials.

In this study, two series of PUU with crystallizable poly(butylene adipate) (PBA) polyester and non-crystallizable poly(propylene oxide) (PPO) polyether as the soft segments were synthesized. The hard segment contents of each series were 26–62 wt%.

EXPERIMENTAL

Synthesis

Segmented PUUs were formed from MDI, 3,5-diethyltoluene-2,4-diamine and 2,6-diamine (DETDA) and PPO-2000 (a linear PPO polyether with $M_n = 2000$) or PBA polyester ($M_n = 2000$) by a two-step solution polymerization method[14]. The solvent used was *N*,*N*-dimethyl formamide (DMF) which had been dried over molecular sieves and then vacuum distilled. MDI was also vacuum distilled.

The polymer was precipitated with water and dried in a vacuum oven at 70°C for 1 week. The molar ratio of PPO or PBA, DETDA and MDI was varied from 1:1:2 to 1:7:8 (*Table 1*).

Methods

I.r. studies. I.r. spectra were recorded on a PE580 i.r. spectrophotometer. A thin polymer film (-2 μm thick) was cast directly on a NaCl plate from DMF solution and dried in a vacuum oven.

Thermal analysis. D.s.c. was carried out on a Dupont 1090. The heating rate was 20°C min^{-1} and the weight of the sample was 10–20 mg.

WAXD studies. The WAXD intensity was recorded as a function of diffraction angle using a YS-I X-ray diffractometer with CuKα radiation.

0032-3861/92/061335-04

Table 1 Chemical composition and hard segment content for PPO-polyether-based and PBA-polyester-based PUUs

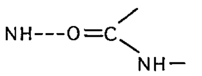
Sample	Chemical composition (molar ratio)	Hard segment content (wt%)
	PPO:DETDA:MDI	
ET-25-2000	1:1:2	25
ET-36-2000	1:2:3	36
ET-43-2000	1:3:4	43
ET-50-2000	1:4:5	50
ET-54-2000	1:5:6	54
ET-62-2000	1:7:8	62
	PBA:DETDA:MDI	
ES-25-2000	1:1:2	25
ES-36-2000	1:2:3	36
ES-43-2000	1:3:4	43
ES-50-2000	1:4:5	50
ES-54-2000	1:5:6	54
ES-62-2000	1:7:8	62

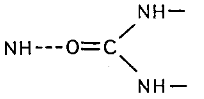
Optical microscopy. Polymer films were examined with a Zeiss polarizing microscope using a magnification of ×400.

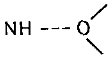
RESULTS AND DISCUSSION

Hydrogen bonding studies

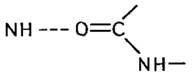
I.r. spectra of PUUs have been extensively studied[15–20]. In the polyether-based PUUs, the NH groups in the urea and urethane groups behave as proton donors, and the oxygens of the carbonyl groups in urea, urethane groups and in polyether behave as proton acceptors. Consequently hydrogen bonding occurs:

(I)

Urethane

(II)

Urea

(III)

Polyether

In the polyester-based PUUs hydrogen bonding also occurs:

(I)

Urethane

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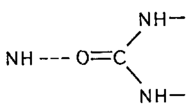
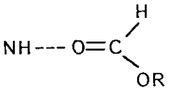

Urea

(III)

Polyester

Obviously, the formation of the inter-urethane and urea hydrogen bonds (I and II) are the strong driving force for hard segment domain cohesion. The hydrogen bonding (III) contributing to the hard segments is dissolved in the soft segment matrix.

Figure 1 shows the i.r. spectra of PPO-polyether-based PUU and PBA-polyester-based PUU. Two main regions are of interest in this study, i.e. the NH and carbonyl absorption regions.

In *Figure 1a*, the major NH absorption appears at 3260 cm^{-1}, typical of hydrogen-bonded NH groups (B_{NH}), a small shoulder on the higher-frequency side of this band at ~3460 cm^{-1} is characteristic of the free N groups (f_{NH}). In the carbonyl region between 1620 cm and 1750 cm^{-1}, the peak at 1731–1734 cm^{-1} is assign to free urethane carbonyl ($f_{CO,ut}$), the peak at 1715–17 cm^{-1} is assigned to the hydrogen-bonded uretha carbonyl ($B_{CO,ut}$) and the band at 1665–1675 cm^{-1} assigned to the hydrogen-bonded urea carbonyl ($B_{CO,u}$ A free urea carbonyl peak at 1695 cm^{-1} was not detecte

In *Figure 1b*, the absorption peaks at ~3390 a 3460 cm^{-1} show hydrogen-bonded NH groups (B_{N} and free NH groups (f_{NH}), respectively. In the carbon region, the urethane and ester carbonyl absorptions we overlapped at 1720 cm^{-1}, and free peaks were n observed. A hydrogen-bonded urea carbonyl peak occu at 1658 cm^{-1}. *Figure 2* shows the i.r. spectra of t NH and carbonyl absorption regions for the PP polyether-based and PBA-polyester-based PUUs wi different hard segment contents. It is clearly seen th the absorption intensities of the hydrogen-bonded N (B_{NH}) and carbonyl peaks ($B_{CO,ut}$ and $B_{CO,ua}$) increa and the free NH (f_{NH}) and carbonyl peaks ($f_{CO,}$ decrease as the hard segment content is increased.

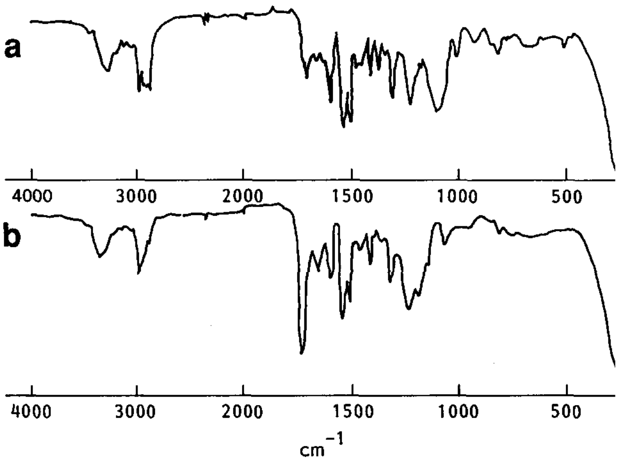


Figure 1 I.r. spectra of (a) ET-50-2000 and (b) ES-50-2000

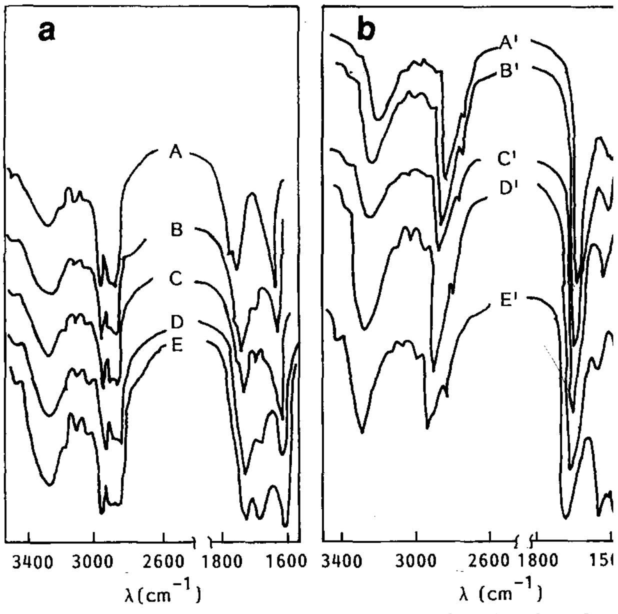


Figure 2 I.r. spectra showing the NH and carbonyl regions for PPO-polyether-based and (b) PBA-polyester-based PUUs: ET-36-2000; (B) ET-43-2000; (C) ET-50-2000; (D) ET-54-2000; ET-62-2000; (A') ES-36-2000; (B') ES-43-2000; (C') ES-50-2000; (ES-54-2000; (E') ES-62-2000

Table 2 Distribution of hydrogen bonds in PPO-polyether-based and PBA-polyester-based PUUs

Sample	$(X_b)_{CO,ut}$	$(X_b)_{NH}$	C_h
ET-25-2000	0.40	0.84	—
ET-36-2000	0.50	0.84	0.24
ET-43-2000	0.55	0.85	0.71
ET-50-2000	0.56	0.84	—
ET-54-2000	0.71	0.85	0.88
ET-62-2000	0.74	0.81	0.98
ES-25-2000	—	0.79	0.57
ES-36-2000	—	0.80	0.71
ES-43-2000	—	0.82	0.72
ES-50-2000	—	0.82	0.83
ES-54-2000	—	0.85	1.17
ES-62-2000	—	0.84	1.10

Table 2 summarizes the distribution of hydrogen-bonded NH and carbonyl groups for these samples with different hard segment contents. The fraction of hydrogen bonding is given by[21,22]:

$$(X_b)_{CO} = \frac{1}{1 + 1.2(A_f)_{CO}/(A_b)_{CO}}$$

$$(X_b)_{NH} = \frac{1}{1 + 3.46(A_f)_{NH}/(A_b)_{NH}}$$

where (A_b) and (A_f) are, respectively, the absorbance of bonded and free carbonyl(CO) or NH groups. The cohesive force index of the hard segments is given by[23]:

$$C_h = A_{ua}/A_{1600}$$

where A_{ua} and A_{1600} are, respectively, the absorbance of bonded urea carbonyl and the peak at 1600 cm^{-1}.

The results indicate that the values of C_h for both PPO-polyether-based and PBA-polyester-based PUUs increase with increasing hard segment contents. The $(X_b)_{NH}$ for the PPO-polyether-based PUUs remains at ~0.84 whilst the $(X_b)_{NH}$ for the PBA-polyester-based PUUs increases.

The inter-urethane and urea hydrogen-bonded hard segments (I and II) are generally regarded as residing in the interior of the hard domains, while the hard segments possessing free carbonyl groups are present in the mixed soft phase or at the interface[24]. It is clearly seen that the more cohesive hard segments of PPO-polyether-based PUUs impart higher values for $(X_b)_{CO}$ and C_h as the hard segment contents are increased and this results in a higher degree of order in the hard domains. In addition, the hydrogen bonding of the NH-ether is much weaker than others leading to a lower degree of mixture of hard segment in soft matrix. This implies that better phase separation for higher hard segment contents will take place for PPO-polyether-based PUUs.

The hard–soft segment hydrogen bond (NH-ester) in the PBA-polyester-based PUUs is stronger than that in PPO-polyether-based PUUs, and makes a larger contribution to $(X_b)_{NH}$ when the hard segment contents are low. As the hard segment contents are increased (i.e. urea groups are increased), the cohesion of hard segments is strengthened and the extent of inter-urethane and urea hydrogen bonding is increased resulting in the hard–soft segment hydrogen bonding becoming less.

It can be seen that most hydrogen bonding is formed in the inter-urethane and urea of hard segments with increasing hard segment contents, leading to a higher degree of order in the hard domains and better phase separation for the higher hard segment contents for PPO-polyether-based and PBA-polyester-based PUUs.

Crystallization characteristics

Figure 3 shows the d.s.c. thermograms of PPO-polyether-based and PBA-polyester-based PUUs with different hard segment contents. It is evident that the heat of melting for hard segment crystallization for the PPO-polyether based PUUs increases as the hard segment content increases. This can be explained as the degree of order in the hard domain being increased owing to a higher degree of cohesiveness. The well-formed spherulites have been clearly observed by polarized light microscopy (PLM) when hard segment contents are high. The formation of spherulites is due to microphase separation of longer hard segments from the soft polyether matrix.

Results for the PBA-polyester-based PUUs series are significantly different from those for the PPO-polyether-based series. As shown in *Figure 3*, the melting endotherms of soft segment crystallization decrease sharply and even disappear when the hard segment content is increased from 26 to 50 wt%, and the melting peak of the hard segment crystallization is displayed clearly at ~240°C when the hard segment content is >50 wt%.

One possible explanation for this large difference is that PBA-polyester-based PUUs have stronger hydrogen bonds between hard and soft segments for phase mixing which causes an increased cohesion between the hard and soft segments with increasing hard segment contents, and higher hard–soft segment mixing present in these system may also prevent the crystallization of the soft segments. Similar behaviour has been reported elsewhere[7,9]. The hard segment content is then increased above 50 wt%. The higher degree of order of the hard segment led to a higher degree of hard segment crystalline organization and the cohesion between hard and soft segments is reduced. The hard segment crystallization promoted phase separation. This observation is consistent with the WAXD result.

Figure 4 represents WAXD curves of the PPO-polyether-based and PBA-polyester-based PUUs for samples with hard segment contents ranging from 25 to 54 wt%. The soft segment is amorphous for the PPO-polyether-based PUUs series since only a broad peak at 20° (2θ) is observed at low hard segment

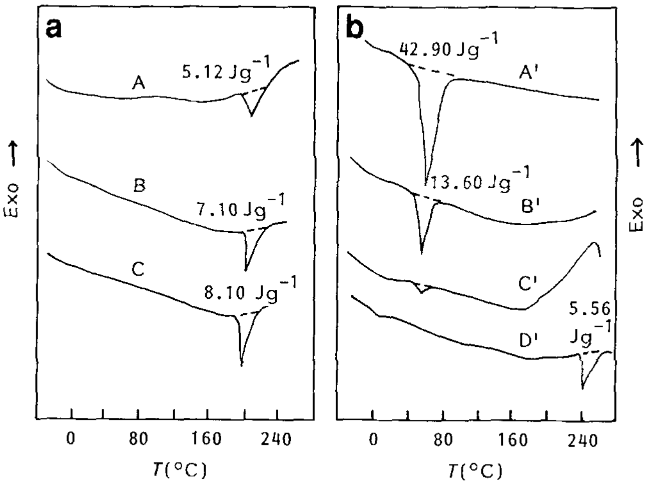


Figure 3 D.s.c. thermograms for (a) PPO-polyether-based and (b) PBA-polyester-based PUUs: (A) ET-25-2000; (B) ET-43-2000; (C) ET-50-2000; (A') ES-25-2000; (B') ES-43-2000; (C') ES-50-2000; (D') ES-62-2000

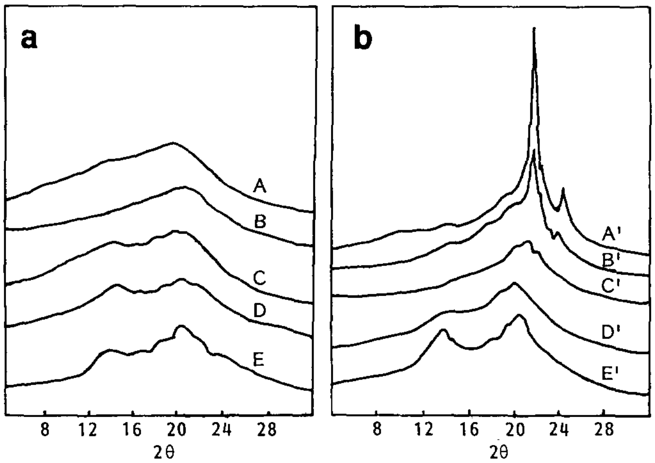


Figure 4 WAXD spectra for (a) PPO-polyether-based and (b) PBA-polyester-based PUUs: (A) ET-25-2000; (B) ET-36-2000; (C) ET-43-2000; (D) ET-50-2000; (E) ET-54-2000; (A') ES-25-2000; (B') ES-36-2000; (C') ES-43-2000; (D') ES-50-2000; (E') ES-54-2000

contents. The prominent crystallinity reflection of the hard segment is observed when the hard segment content is ~50 wt%, and the intensity of the reflections increases with increasing hard segment content.

For PBA-polyester-based PUUs series, at low hard segment contents, prominent crystallinity reflection of the polyester soft segment is observed at 21.5° (2θ), which disappears if it is heated to 48°C (*Figure 5*). As the hard segment content increases, the intensity of the sharp reflections decreases until an amorphous-looking pattern is observed for a hard segment content of 50 wt%. When the hard segment contents are >50 wt%, the crystallinity reflection of the hard segment is observed at 13.90° (2θ).

CONCLUSIONS

Results obtained in this study by i.r., d.s.c., WAXD and PLM on two series of PPO-polyether-based and PBA-polyester-based PUUs provide more insight into the hydrogen bonding and crystallization behaviour of these phase-segregated systems with varied hard segment contents.

The PPO-polyether-based PUUs series exhibited a higher degree of hard segment crystallization than PBA-polyester-based PUUs series with the same hard segment contents, and this crystallization increased with increasing hard segment content. The hydrogen bonding of PPO-polyether-based PUUs is formed mainly within the hard segments, which promotes the crystallization of hard segments.

The PBA-polyester-based PUUs series are different from the PPO-polyether-based PUUs, since in the former there is a certain amount of crystalline soft segment and a stronger hydrogen bonding between the soft and hard segments, which hinders the crystallization of hard segments. As the hard segment contents are increased from 25 to 50 wt%, more hard segments are dissolved in the polyester soft segment matrix, resulting in higher hard–soft segment mixing which prevents the crystallization of the soft segments. When the hard segment contents are >50 wt% more cohesion in the hard segment domains led to a higher degree of hard segment crystalline organization. The crystallization of the hard segments finally promoted phase separation.

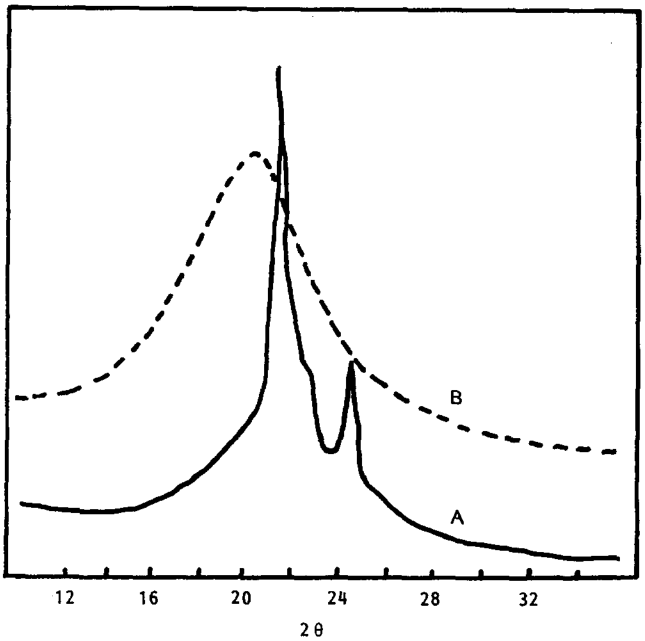


Figure 5 WAXD spectrum for ES-25-2000 at: (A) 25°C; (B) 48°C

ACKNOWLEDGEMENT

The authors wish to acknowledge financial support from the Natural Science Foundation of China.

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