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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Chen, W. C. , Chen, Y. S. , Yu, T. L. and Tseng, Y. H.(1997) 'Effect of Polyester Side Chain on the Physical Properties of Polyurethane', Journal of Macromolecular Science, Part A, 34: 8, 1369 – 1380

**To link to this Article:** DOI: 10.1080/10601329708011050

**URL:** <http://dx.doi.org/10.1080/10601329708011050>

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## **EFFECT OF POLYESTER SIDE CHAIN ON THE PHYSICAL PROPERTIES OF POLYURETHANE**

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Key Words: Polyurethane; DSC; TMA

### **ABSTRACT**

Polyester based polyurethanes were synthesized from 4,4'-Methylene bis(phenyl isocyanate) (MDI) with butanediol as a chain extender. The polyesters with various mole ratios of -CH<sub>3</sub> side chain were synthesized from adipic acid and glycols which were mixtures of various mole ratios of hexanediol and 1,2-propanediol. The effect of -CH<sub>3</sub> content of polyester on the crystallinity of hard segment and physical properties of polyurethanes was studied by DSC (differential scanning calorimetry) and TMA (thermal mechanical analysis).

### **INTRODUCTION**

The segmented polyester-based urethanes are thermoplastic elastomers with high elongation characteristics, along with typical properties of plastics, such as

modulus, strength, and processibility. It is generally agreed that the unique mechanical properties of polyurethanes, as compared to other types of elastomers, are predominantly the result of a two-phase morphology.<sup>1,2</sup> The polyester based urethanes consist of an aromatic diisocyanate with a glycol chain extender as the hard segment and a low molecular weight polyesters as the soft segment. They are considered to be linear segmented block copolymer, made up of alternating hard and soft block segments. Compositional variables and processing conditions are known to affect the degree of phase segregation, phase mixing, hard segment domain organization, and subsequent polyurethane properties.<sup>2-4</sup> Depending on the relative incompatibility of hard and soft segments, phase segregation will occur during processing and post-cure annealing. The effects of polyurethane composition and structure on the resultant properties has been investigated by several researchers.<sup>5-31</sup> These studies have been concentrated on the model compounds based on aromatic diisocyanates, such as toluene diisocyanate (TDI)<sup>5,6</sup> or diphenyl methane diisocyanate (MDI).<sup>5-8</sup> The phase segregation of hard and soft segment domains have been demonstrated by: small and wide angle X-ray scatterings,<sup>9-20</sup> differential scanning calorimetry,<sup>9-18,21-24</sup> infrared spectroscopy,<sup>24,29</sup> and microscopy<sup>16,30,31</sup> small angle laser light scattering (SALS),<sup>16</sup> and dynamic mechanical thermal analysis (DMTA).<sup>18</sup>

In this work, the soft segment polyester-diols were synthesized from adipic acid and glycols which were mixture of various mole ratios of 1,2-propanediol and hexanediol. 1,2-propanediol provided  $-\text{CH}_3$  side chain in polyester soft segment. The effect of the concentration of polyester  $-\text{CH}_3$  side chain on the hard and soft segment segregation and the thermal mechanical properties of polyurethanes was studied by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA). Attempt has been made to correlate the thermal mechanical behavior and the morphology change introduced upon the change of polyester  $-\text{CH}_3$  side chain concentration.

## EXPERIMENTAL

### (a) Polyester-Diol

Polyester was synthesized using a conventional method from 1,2-propanediol, hexanediol, and adipic acid (Riedel-de Haen Co.) with an OH/COOH mole ratio of 1.18/1 under nitrogen atmosphere. The chemical compositions of five

TABLE I. Chemical Composition and Molecular Weight of Polyester

Sample	1	2	3	4	5
adipic acid/mole	1.000	1.000	1.000	1.000	1.000
1,2-propanediol/ mole	-----	0.452	0.590	0.728	1.180
hexanediol/ mole	1.180	0.728	0.590	0.452	-----
acid value/ mg KOH g <sup>-1</sup>	3.60	3.81	3.22	4.10	3.20
M <sub>n</sub>	2155	2075	2500	2075	2500
M <sub>w</sub> / M <sub>n</sub>	1.82	1.76	1.80	1.80	1.96

polyesters are listed in Table I. 1,2-propanediol was first reacted with adipic acid, the reaction temperature was increased by stepwise control as following: 140°C/1 hour, 150°C/1 hour, 160°C/1 hour, and 170°C /1 hour. The reaction mixture was then cooled down to 90°C and mixed with hexanediol. The reaction temperature was then increased to 150°C and increased by stepwise control as following: 150°C/1 hour, 160°C/2 hours, 180°C/2 hours, and 200°C/4 hours. The acid values of the final polyesters are listed in Table I. Thus, primary -OH terminal ends were obtained for all of the polyesters except polyester-5. The molecular weight distributions were determined by GPC (Waters model 746 with  $\mu$ -styragel columns of pore sizes of 500 Å, 10<sup>3</sup> Å, and 10<sup>4</sup> Å, and a RI detector) at 25 °C. Tetrahydrofuran (THF, Merck Co.) was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co.) were used in a linear calibration. The M<sub>n</sub> and M<sub>w</sub> of these polyesters are also listed in Table I.

### (b) Polyurethane

The polyester-diols synthesized from experimental procedure (a) were used to synthesize polyurethanes with MDI (Tokyo Kasei Kogyo Co) and 1,4-butanediol (Riedel-de Haen Co.) as a chain extender by prepolymerization method. The chemical composition of these polyurethanes are shown in Table II. Thus these polyurethanes consisted of polyester soft segments with various concentrations of CH<sub>3</sub> side chain. Polyester-diol was first reacted with diisocyanate at 90-100°C for 1 hour in N,N-dimethyl formamide (DMF, Merck Co.). The prepolymer was then reacted with butanediol at 90-100°C for another one hour in DMF. The final polymer was then precipitated from methanol and the residual solvent was removed under vacuum at 60°C for 24 hours. The polymer was then compression molded on a press at 175°C for 10 min. followed by cooling at an ambient temperature and

TABLE II. Chemical Compositions of Polyurethanes

Polyurethane*	Polyester (mole)	MDI (mole)	Butanediol (mole)	Soft segment content (wt%)
PU-1	0.326	2.1	1.673	51.0
PU-2	0.339	2.1	1.661	51.0
PU-3	0.283	2.1	1.716	51.0
PU-4	0.339	2.1	1.661	51.0
PU-5	0.283	2.1	1.716	51.0

\* The polyurethanes were synthesized from the polyesters which has the same designated numbers as shown in Table I.

environment. The samples were then kept at room temperature for at least one week before DSC and TMA measurements. Before polymerization, polyester was distilled at 90°C under vacuum for 2 hours to remove moisture and butanediol and DMF were treated with molecular sieve (Merck, pore size 0.4 mm drying agent. MDI was used as it received without further purification. The final polyurethane contained 51.0 wt % of polyester.

#### (c) Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a Du Pont 910 DSC. The heating rate was 10°C/min for the temperature range of 100-240°C. The samples sizes were around 10 mg for all measurements. Temperature calibration was done with a multiple indium-lead-nickel standard, an indium standard was used for heat flow calibration.

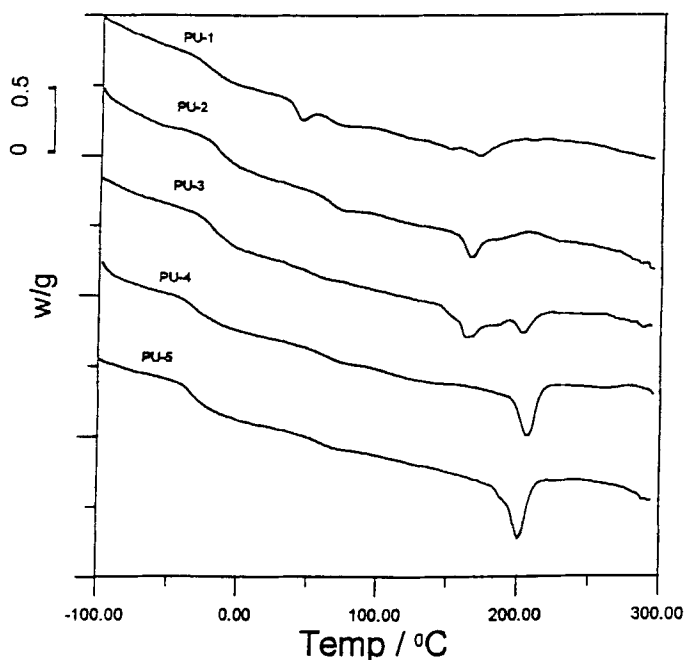
#### (d) Thermal Mechanical Analysis (TMA)

Penetration mode TMA measurements were carried out on a DuPont TMA (Model 943). The heating rate was 10°C/min for the temperature range of 20-220°C. The sample size was 3x4x0.7 mm. The reported transition temperatures were calibrated to the softening temperature of indium.

## RESULTS AND DISCUSSION

#### (a) DSC Study

DSC curves of these five polyurethanes are shown in Figure 1. The positions of the DSC endotherm peaks and thermal transitions are listed in Table III.



**Figure 1.** DSC curves of polyurethanes.

The uncertainty associated with each temperature is approximately  $\pm 2^\circ\text{C}$ . DSC thermal behavior is apparent in five temperature ranges.

The soft segment glass transition temperature ( $T_{g1}$ ), a second order transition, appears as a base line shift in the region of  $-40 \sim -18^\circ\text{C}$ .  $T_{g1}$  values can be used as an indication of relative purity of the soft segment regions. The more soft segment domains are contaminated with the dissolved high glass transition temperature hard segments, the higher will be the soft domain  $T_{g1}$ . The extent of hard segment/soft segment mixing will depend on the overall hard segment content, both segment lengths, and the affinity of one segment for the other. The soft segment  $T_g$  is influenced by the restricted movement imposed at the hard segment junction and at phase boundaries where the hard domain acts as a filler particle. The  $T_g$  of polyesterdiol also depends on the molar ratio of 1,2-propanediol/ hexanediol. The polyester with a higher content of 1,2-propanediol has a lower soft segment  $T_g$ .

The second region of interest is that corresponding to crystalline melting of soft segment ( $T_{m1}$ , between  $40\text{--}50^\circ\text{C}$ ). The degree of polyester soft segment crystallinity decreases as the concentration of polyester  $-\text{CH}_3$  side chain (i.e. the molar ratio of 1,2-propanediol/ hexanediol) increases.

Table III. DSC Data of Polyurethane

Polyurethane	PU-1	PU-2	PU-3	PU-4	PU-5
$T_{g1}/^{\circ}\text{C}$	-23.4	-18.3	-21.5	-29.7	-28.1
$T_{m1}(\text{peak})/^{\circ}\text{C}$	42.9	-----	-----	-----	-----
$\Delta H_1/\text{J g}^{-1}$	1.94	-----	-----	-----	-----
$T_{m2}(\text{I-peak})/^{\circ}\text{C}$	70.1	71.5	-----	-----	-----
$\Delta H_2(\text{I})/\text{J g}^{-1}$	1.52	1.82	-----	-----	-----
$T_{g2}/^{\circ}\text{C}$	----	-----	59.4	71.3	67.6
$T_{m2}(\text{II-a-peak})/^{\circ}\text{C}$	170.2	165.4	161.0	-----	-----
$\Delta H_2(\text{II-a})/\text{J g}^{-1}$	8.63	10.40	8.38	-----	-----
$T_{m2}(\text{II-b-peak})/^{\circ}\text{C}$	-----	-----	201.8	204.7	200.6
$\Delta H_2(\text{II-b})/\text{J g}^{-1}$	-----	-----	2.22	13.01	16.96

\*The subscripts 1 and 2 correspond to soft and hard segments respectively.

The remaining regions of DSC thermal behavior result from transition and endotherms associated with hard segment domains. The transition or endotherm of region-I around 55-75°C ( $T_{g2}$  or  $T_{m2}(\text{I})$ , denoted region-I) results from the breakup of short range order of hard segment induced by room temperature annealing.<sup>9</sup> The endotherm around 155-220°C corresponds to microcrystalline hard segment melting ( $T_{m2}(\text{II})$ , denoted Region II).

As indicated in Figure I and Table III, the soft segment glass transition temperature ( $T_{g1}$ ) decreased with the molar ratio of 1,2-propanediol/ hexanediol. Thus, PU-4 and PU-5 had the lowest  $T_{g1}$  indicated highest degree of the soft segment and hard segment phase segregation.<sup>32</sup> When there are hard segments dispersed in the soft domains, the  $T_{g1}$  is raised.  $T_{m1}$  and  $\Delta H_1$  of soft segments are indicators of soft segments crystallization.<sup>32</sup> The experimental results revealed that only PU-1 had soft segment crystallization, suggesting that the presence of polyester- $\text{CH}_3$  side chain led to a reduction of the degree of soft segment crystallinity, i.e. less ordering of soft segments.

The transition ( $T_{g2}$ ) and endotherm ( $T_{m2}(\text{I})$ ) around 55-75°C are indicative of dispersion of discrete hard segment within the soft segment phase and the short range continuous ordering of hard segment domain induced by annealing at room temperature respectively.<sup>32</sup> Comparing the DSC data of PU-1 - PU-5, we

found that PU-1 and PU-2 had melting endotherms around 55-75°C and PU-3 - PU-5 had hard segment glass transitions ( $T_{g2}$ ) around 55-75°C. Similar results were also observed in TMA data and will be discussed later. The experimental results revealed that the introducing of -CH<sub>3</sub> side chain in polyester resulted in a reduction of the dispersion of short range ordering hard segment domain in soft segment and no melting endotherms  $T_{m2}(I)$  were found for PU-3, PU-4, and PU-5. The increase in  $T_{g2}$  in order from PU-3 to PU-5 indicated less discrete hard segment was dispersed into polyester soft segment with increasing polyester -CH<sub>3</sub> side chain.

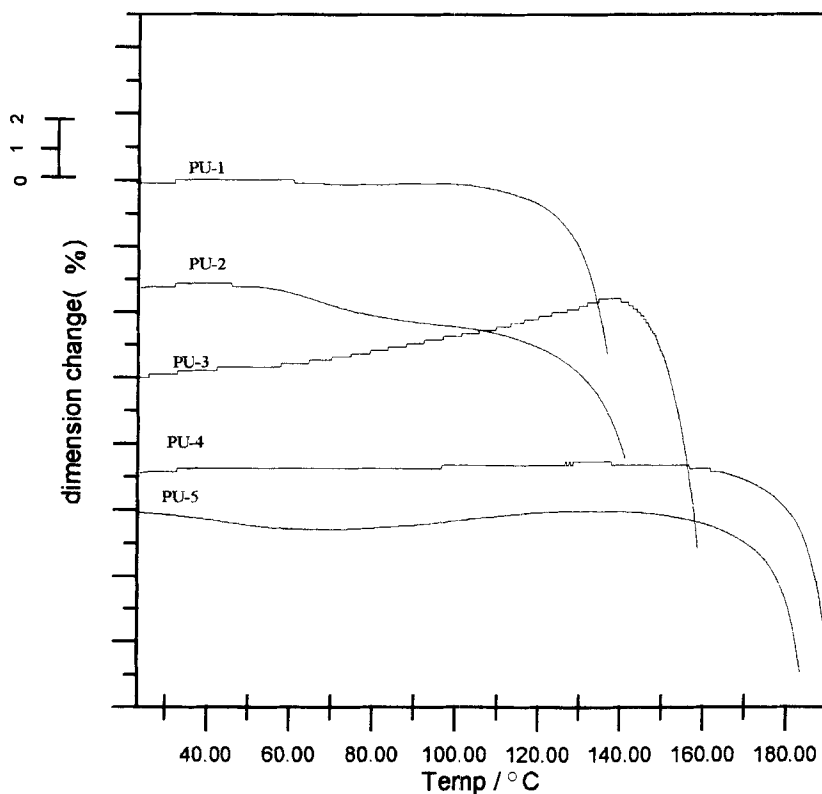
However, melting endotherm  $\Delta H_2(II)$  of microcrystalline hard segment increased with the content of polyester -CH<sub>3</sub>. As shown in Figure 1, the peak of hard segment endotherm II was sharp and  $T_{m2}(II)$  was higher for PU-4 and PU-5, while the peak of hard segment endotherm II was broader and  $T_{m2}(II)$  was lower for PU-1 and PU-2. The glycol of polyester has a 1/1 mole ratio of hexanediol and 1,2-propanediol for PU-3). The DSC result of PU-3) showed two  $T_{m2}(II)$  endotherms.  $T_{m2}(II-a)$  corresponds to hexanediol-based polyester PU, while the  $T_{m2}(II-b)$  corresponds to the 1,2propanediol-based polyester PU. These results suggested that the presence of polyester -CH<sub>3</sub> side chain improved the ordering of hard segment domain.

### (b) TMA Study

Typical TMA scans of these five polyurethanes are shown in Figure 2. The TMA data revealed the temperature dependence of polyurethane dimension change. For all these specimens two transition points are noted in the region between room temperature and 240°C: a change of slope in the probe position vs. temperature scan between 60 and 80°C and complete penetration of the probe as the specimens soften at temperatures higher than 120°C. The lower temperature transition with positive slope was due to the glass transition of hard segment and that with negative slope was due to melting of short range ordering hard segment. Koberstein, et al. found similar penetration behavior for polyurethane block copolymers. Similar results of isoprenebutadiene block copolymer were also reported by Cohen et al.<sup>33</sup>

Koberstein, et al.<sup>12</sup> observed a distinct transition in penetration probe behavior as the hard segment microdomain structure changed from discrete to continuous with increasing polyurethane hard segment content. From their results, we concluded that the slope of the penetration probe position vs. temperature plot around 55-75°C depends on the size and the quantity of hard segment dispersed in the soft domain. A positive slope was due to the discrete hard segment dispersed in the soft





**Figure 2.** TMA curves of polyurethanes.

segment domain whilst the negative slope due to the short range continuous hard segment microphase dispersed in the soft segment domain. The value of positive slope is proportional to the quantity of discrete hard segments dispersed in the soft segment domain.

Due to the crystallization of soft segment for PU-1 and the short range continuous ordering of hard segment microphase for PU-1 and PU-2, negative slope of dimension change vs temperature was observed around 60–80 °C due to the melting of soft segment crystalline and short range continuous hard segment microphase. However, due to the dispersion of discrete hard segment microphase in the soft segment domain, positive TMA slopes were observed around 50–80 °C for PU-3 - PU-5. Comparing the DSC and TMA scans of PU-3, PU-4, and PU-5, the  $T_{g2}$  of hard segment increased and the slope of TMA dimension change vs. temperature decreased with increasing content of polyester  $-CH_3$  side chain. These

TABLE IV. TMA Data of Polyurethane Linear Expansion Coefficient

Polyurethane	Inflection $-1 / ^\circ\text{C}$	At Inflection $-1 / \%^\circ\text{C}^{-1}$	Inflection $-2 / ^\circ\text{C}$
PU-1	65.4	$-0.97 \times 10^{-2}$	133.3
PU-2	53.6	$-3.82 \times 10^{-2}$	136.6
PU-3	63.6	$2.24 \times 10^{-2}$	150.1
PU-4	96.8	$0.35 \times 10^{-2}$	180.2
PU-5	82.5	$1.29 \times 10^{-2}$	186.6

results suggested that PU3 had the highest degree of discrete hard segment microphase dispersed in the soft domain. An increasing amount of discrete hard segment joined the microcrystalline domain (region-II) and the degree of discrete hard segment dispersion within the soft domain decreased with increasing polyester  $-\text{CH}_3$  side chain as shown in PU-4 and PU-5.

The inflection points at higher temperature ( $\geq 120^\circ\text{C}$ ) of complete penetration of the probe as the specimens soften are shown in Table IV. The softening point of TMA is coincident with the onset of DSC hard segment endotherms, supporting the evidence from the TMA experiment that these hard segments maintain mechanical integrity up to temperatures corresponding to the disruption of the hard segment. The TMA results showed that the plateau temperature range was broader for PU with higher  $T_{m2}(\text{II})$ , suggesting higher thermomechanical stability for PU with higher polyester  $-\text{CH}_3$  side chain content.

### (c) Discussion

In this study, both DSC and TMA results showed that  $T_{g2}$  and  $T_{m2}(\text{II})$  of PU-5 were slightly lower than those of PU-4. This phenomena could be due to the presence of secondary  $-\text{OH}$  of polyester (composition 5) which led to less ordering of hard segment and more discrete dispersion of microphase hard segment in the soft segment domain. The experimental results also revealed that for polyurethane annealed at room temperature, the  $T_{m2}$  and  $AH_2(\text{II})$  of microcrystalline hard segment domain increased and the dispersion of hard segment in the soft domain decreased with increasing polyester  $-\text{CH}_3$  side chain. These results suggested that the mobility of hard segments in the soft segment domain had a strong influence on the morphology of polyurethanes. The polyurethanes with a higher polyester  $-\text{CH}_3$  side chain content caused a lower viscosity of soft segment and a higher mobility of hard segment molecules within the soft domain. Increasing the mobility of hard

segment molecules within the soft domain resulted in an increase in the aggregation of hard segments and an increase in soft- and hard-segment segregation during annealing.

## CONCLUSION

The DSC and TMA data revealed that the hard segment micro-crystalline domain and the degree of soft- and hard- segment segregation of polyurethane increased with the polyester -CH<sub>3</sub> side chain content. These results suggested that the morphology of polyurethane annealed at room temperature strongly depended on the mobility of hard segment within the soft domain. The DSC study of the structural changes of segmental polyurethane during annealing was reported by Camberlin, et al.<sup>34</sup> The results Camberlin, et al. indicated that the logarithm of the equilibration time was a linear function of the viscosity of the pure soft phase. Their results were consistent with the results of the present study.

## ACKNOWLEDGEMENT

The authors would like to thank for the financial support by Far Eastern Textile Co. Ltd. through grant CFF 84002.

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Received November 10, 1996

Revision Received February 5, 1997