

Effect of Polymerization Procedure on Thermal and Mechanical Properties of Polyether Based Thermoplastic Polyurethanes

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Abstract: Thermoplastic polyurethanes (TPUs) with different hard segment length has been prepared from a fixed molar ratio of poly(tetramethylene ether glycol), 4,4'-diphenylmethane diisocyanate, and 1,4-butanediol by different polymerization procedures. Results reveal that the on-set temperature of exotherms (T_{cc}) due to the crystallization of hard segments by cooling the TPUs from melt and the peak temperature of endotherms due to the melting of hard segments (T_{mh}) by heating the TPUs increased and levelled off with increasing the hard segment length of TPUs. It has also been observed that soft segment glass transition temperature (T_{gs}) of TPU decreased slightly with increasing the hard segment length, which explains less mixing of soft segments and hard segments. In tensile measurement of TPUs, strain hardening is observed with increasing the hard segment length, which is attributed to the strain induced crystallization of soft segments.

Keywords: polyurethane, crystallization, mechanical property, thermal property, hard segment length.

Introduction

Thermoplastic polyurethane (TPU) is one of the thermoplastic elastomers attracting attentions of researchers due to their various applications. TPU is a linear segmented block copolymer composed of soft segment and hard segment which undergo phase separation.¹⁻³ Properties of soft segment are determined by the type and molecular weights of polyols, while properties of hard segment are determined by the type of diisocyanate and chain extender. Thus, properties of TPU may be adjusted by the type of raw materials and the microphase separation of soft and hard segments.

TPUs in general show thermal transitions due to glass-rubbery transition of soft segments (T_{gs}) below room temperature and melting of crystalline hard segments (T_{mh}) above room temperature. T_{gs} of TPUs may be affected by the extent of phase separation of soft and hard segments as well as the types and the molecular weights of polyols.⁴ Multiple endotherms observed in the range of 140~230°C resulted from the different T_{mh} s due to variations of hard segment length.⁵ T_{mh} s are shifted to higher temperatures with thermal treatments, suggesting an increase in the average length of the hard segments involved.

Microphase separation and crystallization of hard segments

can be also controlled by polymerization methods. According to Wilkes⁶ and Cho,⁷ a broader distribution of hard segment lengths in TPUs prepared by one-shot method compared with that prepared by prepolymer method was observed. Martin and his coworkers⁸ observed an increase of T_{mh} with an increase in the hard segment length. Cooper⁹ and Koberstein¹⁰ suggested that there is most readily crystallizable hard segment lengths. There are many reports in literatures on the characteristics of crystalline hard segments.¹¹⁻¹⁶ However, there is few reports on the crystallization of hard segments of TPUs by cooling from melt or the relationships between the crystallization and the mechanical properties of TPUs with different hard segment length. We prepared TPUs by prepolymer method to change hard segment length systematically. Especially, polyether based TPUs with different hard segment length at fixed overall composition has been prepared by different polymerization procedures. Thermal and mechanical properties of the TPUs investigated are reported in this communication.

Experimental

TPU was prepared by a solution polymerization technique in *N,N*-dimethylformamide (DMF). Poly(tetramethylene ether glycol) (PTMEG: $M_n = 1,000$) was reacted with various amounts of 4,4'-diphenylmethane diisocyanate (MDI) at 60°C for 90 min to prepare prepolymer with terminal NCO

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Table I. Sample Code of the TPU Prepared by Different Polymerization Procedures

Sample Code	Type of Polyol	Prepolymer(1st Step)		Chain Extension(2nd Step)		Segment Structure*	
		Polyol(mole)	MDI(mole)	MDI(mole)	BD(mole)	Hard	Soft
PTM-1	PTMEG	1.0000	2.0000	-	1.0000	MBM	P
PTM-2	PTMEG	1.0000	1.5000	0.5000	1.0000	M(BM)BM	PMP
PTM-3	PTMEG	1.0000	1.2500	0.7500	1.0000	M(BM) ₃ BM	P(MP) ₂ MP
PTM-4	PTMEG	1.0000	1.1250	0.8750	1.0000	M(BM) ₇ BM	P(MP) ₆ MP
PTM-5	PTMEG	1.0000	1.0625	0.9375	1.0000	M(BM) ₁₅ BM	P(MP) ₁₄ MP

*M, B, and P in the description of segment structures denote MDI, BD, and PTMEG respectively.

groups. After the NCO content of the prepolymer was confirmed by a back titration method using *n*-dibutyl amine (ASTM D2572-80), the prepolymer was chain-extended in DMF by adding 1,4-butanediol (BD) and additional MDI at 60°C for 120 min. Both reactions were carried out under dry nitrogen atmosphere. Solid content of the final solution was 20 wt%. Table I gives sample codes and polymerization procedures to prepare TPUs with different segment structure. It is shown in Table I that TPUs with longer hard segment length have longer soft segments formed by linking PTMEG with MDI.

Samples for characterization were obtained by casting TPU solutions in silicone mold and drying them at 50°C. Molecular weights of the TPUs were measured by a gel permeation chromatography (GPC, Spectra-Physics SP8800). Thermal properties of the TPUs were studied by a differential scanning calorimeter (DSC) (DSC 910 from DuPont Instruments equipped with TA2000). In order to control the thermal history of the samples, all the samples were heated up to 230°C, maintained for 3 min, and then cooled down at -10°C/min in DSC. The samples were quenched to -120°C after exotherms due to crystallization of the TPUs were no more observed and reheated from -100 to 230°C with a heating rate of 10°C/min. Dynamic mechanical properties were measured by a dynamic mechanical analyzer (DMA, DMA 983 equipped with TA2000). Temperature sweeps for the samples were done by employing the DMA from -100°C at 1 Hz under nitrogen gas flow. Tensile properties were measured

by using a Universal Testing Machine at room temperature with a cross head speed of 500 mm/min.

Results and Discussion

The average molecular weights of TPUs prepared by different polymerization procedures are shown in Table II. They were not so much different. Thus, the difference in properties of TPUs investigated were not due to the difference in average molecular weights. The DSC cooling curves for TPUs are shown in Figure 1. Exothermic peaks due to the crystallization of hard segments were observed in TPUs. In Table III, on-set crystallization temperature (T_{cc}) and heat of crystallization (ΔH_c) are summarized. It is of interest to note that T_{cc} increased and became almost constant while ΔH_c decreased and levelled off with increasing the hard segment length of the TPUs. The increase of T_{cc} of TPU implies that the crystallization of hard segments results in a crystalline order that melts at higher temperatures. The decrease of ΔH_c

Table II. Molecular Weights of the TPU Prepared by Different Polymerization Procedures

Sample Code	Molecular Weights		Polydispersity Index
	M_n	M_w	
PTM-1	8,400	38,600	4.6
PTM-2	7,700	43,400	5.6
PTM-3	7,700	54,000	7.0
PTM-4	6,600	56,400	8.5
PTM-5	7,100	54,200	7.6

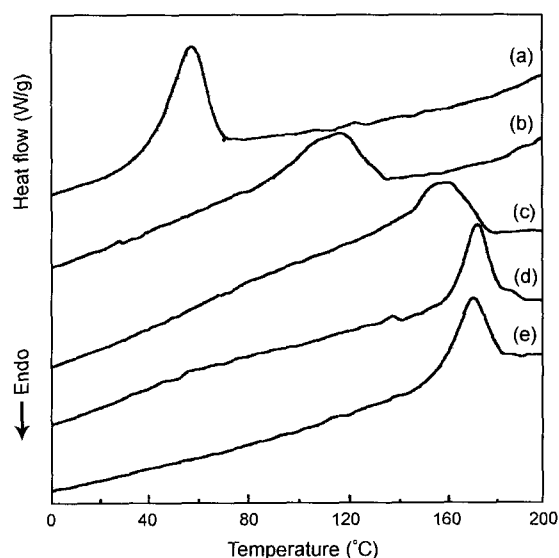


Figure 1. DSC thermograms of TPUs obtained by cooling with 10°C/min from 230°C: (a) PTM-1; (b) PTM-2; (c) PTM-3; (d) PTM-4; (e) PTM-5.

Table III. Cooling Crystallization Temperature (T_c) and Heat of Crystallization (ΔH_c) of the TPU Prepared by Different Polymerization Procedures

Sample Code	PTM-1	PTM-2	PTM-3	PTM-4	PTM-5
T_c (°C)	68.8	130.3	175.2	180.3	181.3
ΔH_c (J/g)	7.1	5.4	4.9	3.4	3.9

with increasing the hard segment length is attributable to the decrease of MDI portion in the hard segment even though the overall composition of TPUs is fixed as shown in Table I.

DSC thermograms obtained by heating the samples after crystallizations by cooling with 10°C/min are depicted in Figure 2. The T_{gs} s of TPUs decreased slightly and the T_{mh} s due to melting of the hard segment crystallites increased and became almost constant with an increase in the hard segment length. The slight decrease of T_{gs} owing to the lower degree of hard-soft segment mixing and the increase of T_{mh} resulted from the increase in the average length of hard segment involved. It can be seen that T_{mh} s of PTM-4 and 5 are similar. According to Koberstein,¹¹ there is a tendency in hard segments based on MDI and BD for intermediate length sequence to crystallize preferentially. It is speculated that increasing hard segment length of TPU resulted in both extended and folded hard segment conformations and the increase and the levelling off of T_{mh} were observed.

Figures 3 and 4 present the changes of storage moduli and loss moduli for TPUs investigated. The storage modulus of TPU showed a decrease on glass-rubbery transition of soft segments around -30°C and another decrease after rubbery plateau region due to melting of hard segment crystallites.

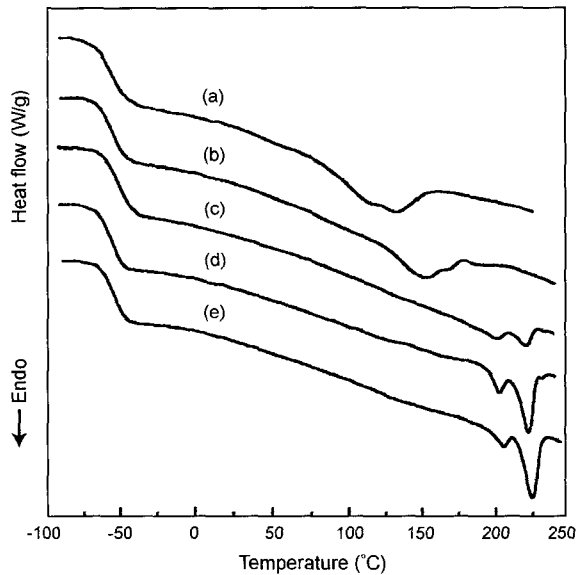


Figure 2. DSC thermograms of TPUs obtained by heating with 10°C/min after cooling : (a) PTM-1; (b) PTM-2; (c) PTM-3; (d) PTM-4; (e) PTM-5.

We observed that the rubbery plateau modulus increased with increasing the hard segment length. The increase of rubbery plateau moduli of TPUs indicates that the longer hard segments resulted in efficient physical crosslinking. It is of interest to note that the rubbery plateau region became broad with increasing the hard segment length due to the increase of T_{mh} s, as shown in Figure 2. The peak temperatures of loss moduli, which can be considered as T_{gs} s of soft

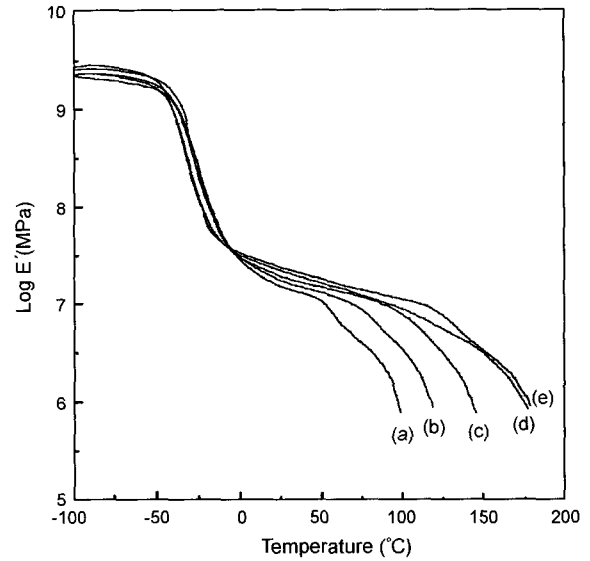


Figure 3. Temperature dependence of storage moduli (E') of different TPUs: (a) PTM-1; (b) PTM-2; (c) PTM-3; (d) PTM-4; (e) PTM-5.

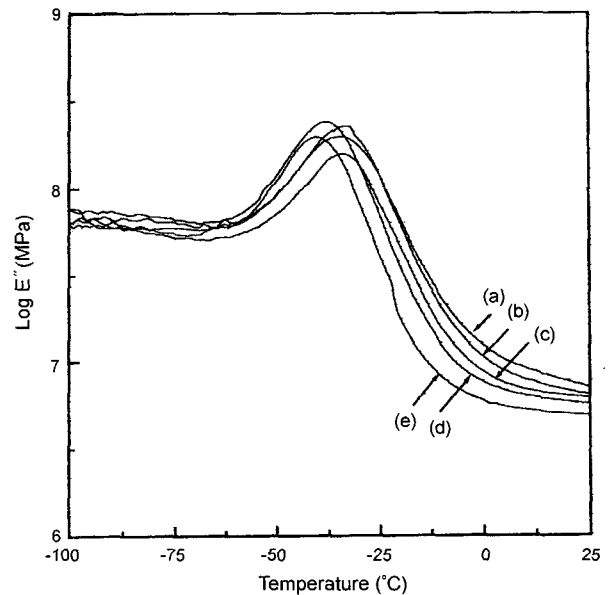


Figure 4. Temperature dependence of loss moduli (E'') of different TPUs: (a) PTM-1; (b) PTM-2; (c) PTM-3; (d) PTM-4; (e) PTM-5.

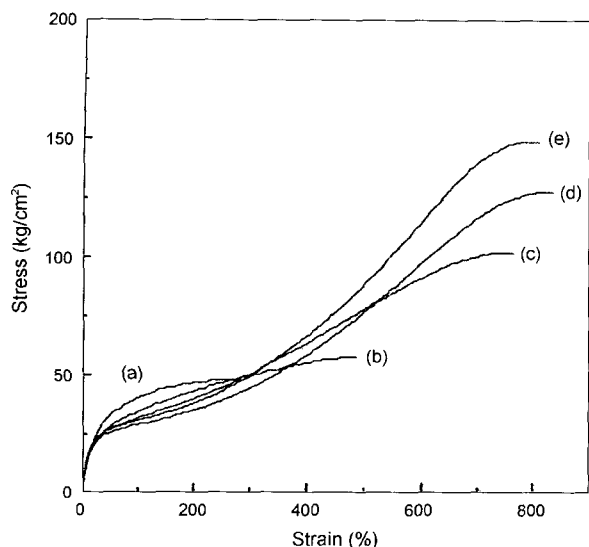


Figure 5. Stress-strain curves of different TPUs: (a) PTM-1; (b) PTM-2; (c) PTM-3; (d) PTM-4; (e) PTM-5.

segments, showed a little decrease with increasing the hard segment length. T_{gs} of TPU is generally affected by phase mixing of soft segments and hard segments, that is, dissolution of hard segments into soft segments results in the increase of T_{gs} . The decrease of T_{gs} explains that the soft segment domain contains less hard segments and has more phase separated morphology.

Stress-strain curves for TPUs are exhibited in Figure 5. A upturn in the stress-strain curves is obtained with increasing the hard segment length. Extension of elastomers frequently results in crystallization and strain hardening due to elevation of melting points. We could feel warming of the TPU specimens with extension to due to exotherms caused by crystallization of the TPUs. TPUs with longer hard segment length have longer soft segment as described in the segment structure of Table I. It indicates that the longer soft segment linked by urethane linkage enables stronger secondary bonding during extension, which is favorable for strain induced crystallizations. It is postulated that strain induced crystallizations of soft segments are responsible for the upturn in stress-strain curves with an increase in the hard segment length.

Conclusions

TPUs with different hard segment length at a fixed com-

position of PTMEG, MDI, and BD were prepared by pre-polymer methods. T_{cc} and T_{mh} increased and levelled off with increasing the hard segment length of TPU. We found that T_{gs} of TPU decreased slightly with increasing the hard segment length, which explains less mixing of soft segments and hard segments. In tensile test of TPUs, strain hardening was observed with increasing the hard segment length and such a phenomenon is attributed to strain induced crystallization of soft segments.

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References

- (1) C. Hepburn, *Polyurethane Elastomers*, 2nd Edition, Elsevier, London, 1991.
- (2) M. Szycher, *Handbook of Polyurethane*, CRC Press, London, 1999.
- (3) D. Dieterich and H. Hesse, in *Polyurethane Handbook*, 2nd Edition, G. Oertel, Ed., Hanser Publishers, Munich, 1993, Chapt. 2.
- (4) D. J. Martin, G. F. Meijs, P. A. Gunatillake, S. J. MaCarthy, and G. M. Renwick, *J. Appl. Polym. Sci.*, **63**, 803 (1997).
- (5) J. A. Miller, S. B. Lin, K. K. S. Hwang, K. S. Wu, P. E. Gibson, and S. L. Cooper, *Macromolecules*, **18**, 32 (1985).
- (6) S. Abouzahr and G. L. Wilkes, *J. Appl. Polym. Sci.*, **29**, 2695 (1984).
- (7) T. O. Ahn, S. C. Choi, H. M. Jeong, and K. Cho, *Polym. Int'l.*, **31**, 329 (1993).
- (8) D. J. Martin, G. F. Meijs, G. M. Renwick, S. J. MaCarthy, and P. A. Gunatillake, *J. Appl. Polym. Sci.*, **62**, 1377 (1996).
- (9) J. W. C. Van Bogart, P. E. Gibson, and S. L. Cooper, *J. Polym. Sci., Part A: Polym. Phys.*, **21**, 65 (1983).
- (10) J. T. Koberstein and R. S. Stein, *J. Polym. Sci., Part A: Polym. Phys.*, **21**, 1439 (1983).
- (11) L. M. Leung and J. T. Koberstein, *J. Polym. Sci., Part A: Polym. Phys.*, **23**, 1883 (1985).
- (12) J. W. C. Van Bogart, D. A. Bluemke, and S. L. Cooper, *Polymer*, **22**, 1428 (1981).
- (13) Y. C. L. Edmond, T. Quinn, and P. L. Valint, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 1767 (1995).
- (14) J. T. Koberstein and A. F. Galambos, *Macromolecules*, **25**, 5618 (1992).
- (15) C. D. Eisenbach, T. Heinemann, A. Ribbe, and E. Stadler, *Macromol. Symp.*, **77**, 125 (1994).
- (16) D. H. Choi, J. H. Kim, and K. J. Cho, *Korea Polym. J.*, **8**, 172 (2000).