Synthesis and properties of thermoplastic polyurethane elastomers modified by poly(γ-methyl-L-glutamate) segment

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Thermoplastic polyurethane elastomers (TPUs) from diol-terminated poly(tetramethylene glycol) (PTMG), 1,4-butanediol (BD) and 4,4'-diphenylmethane diisocyanate (MDI) were modified by copolymerizing with diamine-terminated poly(γ-methyl-L-glutamate) oligomer (γ-PMG). In TPUs modified by the γ-PMG segment, the hard segment showed a decreased crystallinity and a melting point depression, as some of the hard segments were replaced by the γ-PMG segment. This behaviour is probably due to the strong interaction and phase mixing between γ-PMG and hard segments. The melting behaviour of the PTMG segment suggested a weaker interaction between γ-PMG and PTMG segments compared with that between hard segments and PTMG segments. When a small amount of hard segments was replaced by γ-PMG segments, the modulus increased and the elongation at break decreased.

(Keywords: polyurethane elastomer; poly(γ-methyl-L-glutamate); thermal properties)

Introduction

Thermoplastic polyurethane elastomers (TPUs) have interesting properties due to their unique phase-separated structure resulting from the thermodynamic incompatibility of the constituent segments[1,2]. Considerable effort has been devoted to understanding of the structure–property relationship of TPUs, because a wide variety of monomeric materials are now commercially available and tailor-made properties can be obtained by judicious choice of monomeric materials[3,4].

In our previous study[5], TPUs from diol-terminated poly(tetramethylene glycol) (PTMG), 1,4-butanediol (BD) and 4,4'-diphenylmethane diisocyanate (MDI) were modified by copolymerizing with diamine-terminated nylon-6/6,6 copolyamide oligomer (CPA), and their structure–property relationship was inferred from observed thermal and mechanical properties.

In this study, polyamide from α-amino acid, i.e. diamine-terminated poly(γ-methyl-L-glutamate) oligomer (γ-PMG), was used as a modifier instead of CPA. The thermal and mechanical properties of the modified TPUs were examined.

Experimental

Materials. Triphosgene (Aldrich) and formic acid (88%, Hanawa Co., Japan) were used as received. γ-Methyl-L-glutamate (Aldrich) was dried at room temperature in a vacuum oven for 10 h prior to reaction with triphosgene to prepare γ-methyl-L-glutamate-*N*-carboxyanhydride (NCA)[6]. PTMG (number-average molecular weight, $M_n = 2000$; Kyoken Chemical, Japan) was dried under vacuum at 85°C for >10 h. MDI (Tokyo Kasei, Japan) was melted at 45°C and MDI dimer precipitated in the melt was removed before use. BD (Tokyo Kasei, Japan) and *N,N'*-dimethylformamide (DMF, Duksan Chemicals, Korea) were used after dehydration by immersion of 4 Å molecular sieves for >1 week. 1,6-Hexanediamine (HA) was refluxed with CaH_2 followed by distillation at reduced pressure.

Synthesis of diamine-terminated poly(γ-methyl-L-glutamate). γ-PMG ($M_n = 1400$) was prepared as follows: NCA (50 g) was dissolved in DMF (150 ml) maintained at -20°C. HA (0.2842 g) was dissolved in DMF (45 ml) maintained at -20°C, and this solution was added to the solution of NCA. The reaction mixture was stirred for 30 min at -20°C, 1 h at 25°C and then 14 h at 45°C. After complete polymerization, the reaction mixture was poured into diethyl ether (1000 ml). The precipitated polymer was reprecipitated with DMF/diethyl ether three times and dried under vacuum at 40°C.

Synthesis of TPU. TPU was solution polymerized in DMF by the prepolymer method[7]. In brief, PTMG ($M_n = 2000$) was reacted with MDI for 30 min at room temperature and then for 90–120 min at 60°C to prepare a prepolymer with terminal NCO groups. The prepolymer was subsequently chain extended with BD for 30 min at room temperature and then for 3–6 h at 60°C. Then, a 20 wt% solution of γ-PMG in DMF was added dropwise into the reactor at 40°C and the reaction mixture was further reacted at 45°C for 8 h. Formic acid (0.1–0.3 wt% on a solid basis) was used to inhibit gelation. DMF was occasionally added to the reactor when the viscosity of the reaction mixture was too high. The residual isocyanate groups after polymerization were removed with methanol (~ 1 wt% on a solid basis). The final polymer concentration was ~ 25 wt%. Details of the TPUs prepared with

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sample designation codes are given in *Table 1*. The sample designation code indicates the weight percentages of the constituent segments. For example, 40N8 indicates a TPU synthesized with 40 wt% of PTMG, 8 wt% of γ-PMG and 52 wt% of hard segment (MDI + BD). The mole ratio of MDI/(BD + PTMG + γ-PMG) was kept at 1.01/1.00 to obtain linear polymers.

Measurements. The inherent viscosity of TPU was measured in a DMF (0.5 g dl^{-1}) solution at 25°C.

The ^{1}H n.m.r. spectrum of γ-PMG was measured in dimethyl-d_6 sulfoxide (Aldrich) to estimate the molecular weight of γ-PMG, using a Varian EM360L n.m.r. spectrometer (60 MHz).

Samples for thermal property measurements were prepared by casting a TPU solution on glass slides and then drying them in a convection oven at 60°C for 12 h. They were further dried at 50°C under vacuum for 10 h before measurement. Thermal properties were measured by d.s.c. (Du Pont DSC-910). Sample weights were 15.0±0.5 g. After melting at 225°C for 2 min in a differential scanning calorimeter, samples were cooled down to −120°C at a cooling rate of 20°C min^{-1}. D.s.c. thermograms were obtained in the next heating cycle to 250°C at a heating rate of 20°C min^{-1}.

Samples for mechanical testing were prepared by the same method as those for thermal property measurements. The thickness of the film was ~0.15 mm. The test specimens were 10 mm wide and the gauge length was 50 mm. Tensile properties were measured using a Tensilon (RTM-1T, Orientec) instrument at room temperature with a crosshead speed of 200 mm min^{-1}.

Results and discussion

Figure 1 shows the ^{1}H n.m.r. spectrum of γ-PMG. From the intensity ratio of the methylene proton (c) of the iminohexamethyleneimino unit and the methyl proton (d) in the amino acid repeating unit, M_n of γ-PMG was determined to be 1400.

The melting temperature (T_m) and heat of fusion (ΔH_f) of the hard segments in the TPUs are given in *Table 2*. As some of the hard segments are replaced by γ-PMG

Table 1 Characteristics of the TPUs prepared

Sample designation code	Composition (wt%)			Inherent viscosity (dl g^{-1})
	PTMG	γ-PMG	Hard segment (MDI + BD)	
40N0	40.0	0.0	60.0	0.541
40N8	40.0	8.0	52.0	1.036
40N11.5	40.0	11.5	48.5	0.847
40N15	40.0	15.0	45.0	1.003
40N22	40.0	22.0	38.0	0.436
50N0	50.0	0.0	50.0	0.595
50N8	50.0	8.0	42.0	0.860
50N11.5	50.0	11.5	38.5	0.770
50N15	50.0	15.0	35.0	0.627
50N22	50.0	22.0	28.0	0.471
60N0	60.0	0.0	40.0	0.976
60N8	60.0	8.0	32.0	1.024
60N11.5	60.0	11.5	28.5	0.697
60N15	60.0	15.0	25.0	0.757
60N22	60.0	22.0	18.0	0.429

Table 2 Melting behaviour of the hard segments

Sample designation code	T_m^{a} (°C)	ΔH_f (J g^{-1})
40N0	223	81
40N8	183	77
40N11.5	177	66
40N15	172	52
40N22	170	53
50N0	187	65
50N8	177	62
50N11.5	170	59
50N15	164	47
50N22	144	40
60N0	185	49
60N8	164	34
60N11.5	Broad	29
60N15	Broad	29
60N22	Broad	27

^{a} Largest peak temperature of a multiple endothermic peak

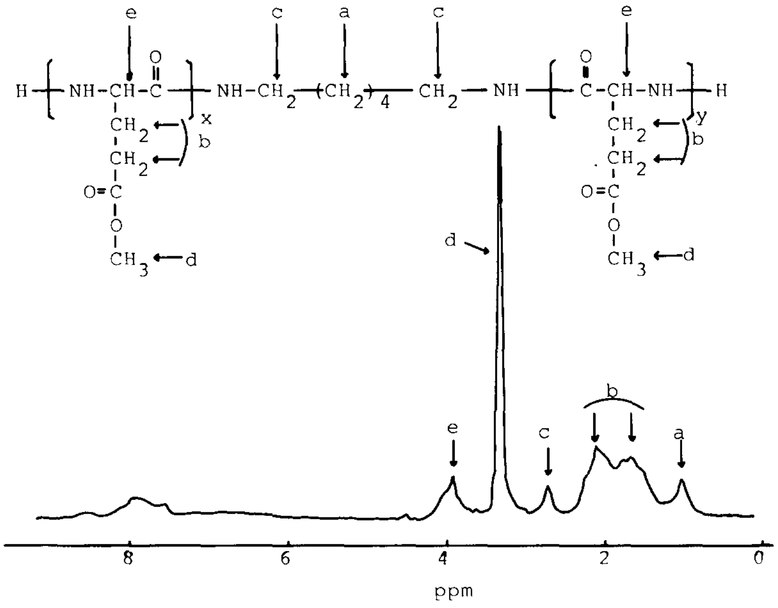

Figure 1 ^{1}H n.m.r. spectrum of diamine-terminated poly(γ-methyl-L-glutamate)

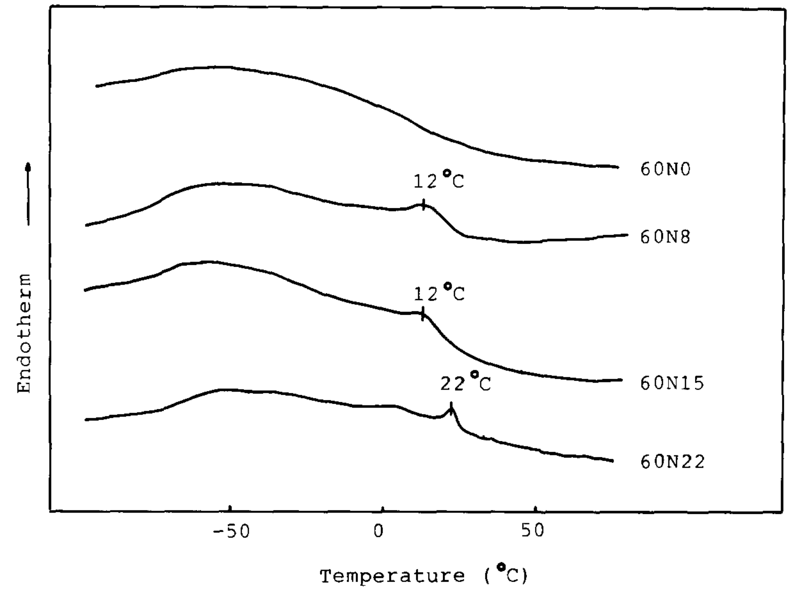

Figure 2 D.s.c. thermograms of the TPUs indicated

Table 3 Tensile properties of the TPUs

Sample designation code	Secant modulus (MPa)		Elongation at break (%)
	3% modulus	200% modulus	
40N0	304	13	480
40N8	415	20	480
40N11.5	321	14	390
40N15	231	12	340
40N22	293	2	190
50N0	95	8	470
50N8	325	11	380
50N11.5	139	9	540
50N15	104	7	510
50N22	79	5	440
60N0	42	6	540
60N8	279	10	490
60N11.5	284	12	420
60N15	36	4	620
60N22	36	2	550

segments at a fixed PTMG segment content, the T_m and ΔH_f generally decrease (*Table 2*). These results suggest that there exist interactions and phase mixing between the hard and γ-PMG segments to cause hindered crystallization of the hard segment in the presence of the γ-PMG segment[8]. The same trends were observed in our previous study[5], where the CPA segment, which is an aliphatic polyamide, was used as a modifier. As some of the hard segments are replaced by γ-PMG segments, the average length of the hard segment decreases. This might also be the reason for the T_m depression, because T_m increases with hard segment length[9].

The d.s.c. thermogram of 60N0 (*Figure 2*) does not show an obvious endothermic melting peak of the PTMG segment. As some of the hard segments are replaced by γ-PMG segments, the endothermic melting peak of the PTMG segment becomes evident and its peak temperature moves to higher temperature. This result suggests a weaker interaction between γ-PMG and PTMG segments compared with that between hard and PTMG segments, because a higher T_m implies a reduced amount of γ-PMG or hard segment dissolved in the PTMG segment domain, i.e. reduced phase mixing[2,10]. When an aliphatic polyamide, the CPA segment, was used as a modifier instead of the γ-PMG segment in our previous study[5], similar results were observed.

The tensile properties of TPUs are shown in *Table 3*. As some of the hard segments are replaced by γ-PMG segments at a fixed PTMG content, the moduli generally decrease after an initial increase, showing a maximum. The TPUs with maximum moduli have reduced values of elongation at break compared with unmodified TPUs. These results show that the role of the hard segment domain as a thermally reversible physical crosslinker and a reinforcing filler for the rubbery soft segment domain is promoted with a small amount of γ-PMG segment.

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References

1 Wang, C. B. and Cooper, S. L. *Macromolecules* 1983, **16**, 775
2 Paik Sung, C. S., Hu, C. B. and Wu, C. S. *Macromolecules* 1980, **13**, 111
3 Gogolewski, S. *Colloid Polym. Sci.* 1989, **267**, 757
4 Petrović, Z. S. and Ferguson, J. *Progr. Polym. Sci.* 1991, **16**, 695
5 Ahn, T. O., Choi, I. S., Lee, S. W. and Jeong, H. M. *Makromol. Chem.* in press
6 Daly, W. H. and Poché, D. *Tetrahedron Lett.* 1988, **29**, 5859
7 Abouzahr, S. and Wilkes, G. L. *J. Appl. Polym. Sci.* 1984, **29**, 2695
8 Wang, C. B. and Cooper, S. L. *Macromolecules* 1983, **16**, 775
9 Harrell Jr, L. L. *Macromolecules* 1969, **2**, 607
10 McLennaghan, A. W. and Pethrick, R. A. *Eur. Polym. J.* 1988, **24**, 1063