

PEO와 PTMO를 가지고 있는 양친화성 폴리우레탄의 미세상분리 거동

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Microphase Separation Behavior of Amphiphilic Polyurethanes Involving Poly(ethylene oxide) and Poly(tetramethylene oxide)

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Introduction

Microphase separation arising from the thermodynamic immiscibility between hard and soft segments of polyurethanes (PUs) has attracted extensive interest due to their possible applications for binder resins, coatings, fibers and particularly biomaterials.^{1,2} The hard segment usually consists of an aromatic diisocyanate such as 4,4'-methylene bis(diphenyl diisocyanate) (MDI) extended by either a low molecular weight diol such as 1,4-butanediol (BD) or a low molecular weight diamine. The soft segment is usually either polyether or polyester macroglycols with molecular weight ranging between 600 and 3,000. MST or ODT (order-disorder transition) has commonly been investigated in diblock and triblock copolymers by X-ray scattering^{3,4}, calorimeter⁵, and rheological measurements.^{6,7} The microphase separation in segmented PU, however, typically lacks the high order peaks in scattering experiments due to the polydispersity in sequence distribution.⁸

For biomedical applications such as artificial organs, typical segmented PUs with MDI/BD hard segments are not relevant due to the lack of hydrophilicity. Thus, poly(ethylene oxide) (PEO) as a hydrophilic segment has generally been introduced to decrease the interfacial energy with biological fluids. PEO segments can also enhance the hydrophilicity of segmented PUs through the migration of the hydrophilic PEO moieties to the surfaces and improve the resistance to protein adsorption and cellular adhesion.⁹ Compared with conventional segmented PU with MDI/BD hard segments, the structural change with temperature and the microphase separation behavior in amphiphilic polyurethanes have not been fully studied. In present study, we synthesized two amphiphilic polyurethanes composed of poly(ethylene oxide) (PEO) as a hydrophilic block and poly(tetramethylene oxide) (PTMO) as a hydrophobic block: multiblock polyurethanes (MPU) and triblock polyurethane (TPU). The crystalline nature and microphase separation behavior of the block PUs were investigated by differential scanning calorimeter (DSC), wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS),

rheological measurements and FT-IR. The effect of sequence regularity and hydrogen bonding density of PUs on the structural change is also examined.

Experimental

Multiblock and triblock polyurethane was synthesized via two-step condensation reaction and the molecular characteristics were summarized in Table 1. DSC was used to study the melting behavior of the samples. Small angle X-ray scattering and wide angle X-ray scattering (Synchrotron SAXS and WAXS, PALS) were also employed to investigate the microphase separation behavior and the crystalline structure for the samples, respectively. RMS 800 (Rheometrics Inc.) was used in oscillatory mode with parallel-plate fixtures (25 and 50 mm in diameter). Dynamic frequency sweep experiments were carried out to measure both storage and loss moduli (G' and G'') as a function of angular frequency (ω) ranging from 0.1 to 100 rad/s at various temperatures

Results and Discussion

DSC and WAXS measurements show that the microphase of MPUs in solid state is dominantly affected by the PEO crystalline phase (Figure 1 and Figure 2). Figure 3 shows the SAXS patterns of MPU55 at temperatures from 25 °C to 215 °C. As compared with the PEO homopolymer, a broader scattering peak at 0.271 nm^{-1} is obtained at room temperature, but the high order peaks are not observed even at elevated temperatures due to the random distribution of PEO and PTMO segments and the polydispersity of constituent chains. Figure 4 represents the logarithmic plot of dynamic storage modulus G' versus dynamic loss modulus G'' for MPU55 at various temperatures. Although the crystalline structure of the MPU55 completely disappears above 100 °C, it is noted that the MPU55 still maintains high viscosity and the $\log G'$ versus $\log G''$ plot superimposes together into a single curve only above 200 °C. However, the slope in the terminal region is found to be 1.4. It has been well-documented for block copolymers that the $\log G'$ versus $\log G''$ plot becomes independent of temperature with a slope of 2 when a transition from an ordered state to a disordered state occurs. We are convinced with the rheological measurement that the homogeneous state, in which all the chains are free to move without any association into a mesostructure, is not obtained even after the melting of PEO segments in the MPU55, implying that the MPU is still in the microphase separated state. The microphase in melt state is induced by the hydrogen bonding between the NH group of hexamethylene diisocyanate (HDI) linkers and the ether oxygen of PEO or PTMO blocks. On the contrary, the SAXS patterns of a triblock polyurethane (TPU) show weak but broad second order peaks below the melting temperature of the PEO block (Figure 5). Compared with the MPU55, the ordering of the TPU crystalline lamellar stacks is enhanced because of the high sequence regularity and the low hydrogen bonding density.

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Table 1. Molecular characteristics of homopolymers and PUs used in present study

Sample	M_n	M_w/M_n	mole % of PEO	T_m (°C)
PEO	3,400b	-	100	62
Monomethoxy PEO	2,000b	-	100	54
PTMO	2,000b	-	0	28
MPU64	42,000	1.30	58	48
MPU55	26,400	1.37	52	45
MPU37	23,400	1.50	31	42
MPU19	29,500	1.30	12	36, 18
TPU	6,700	1.39	65	52

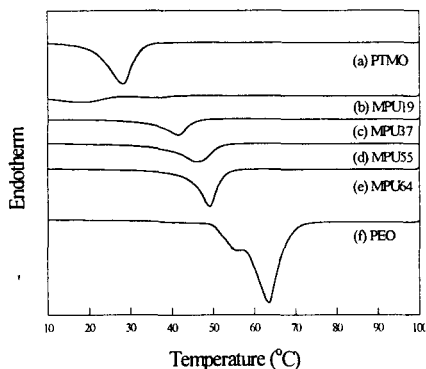


Figure 1. DSC thermograms for homopolymers and MPUs during heating at 10 °C/min.

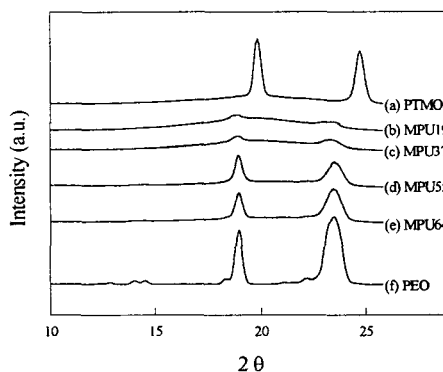


Figure 2. Synchrotron WAXS patterns for homopolymers and MPUs at room temperature.

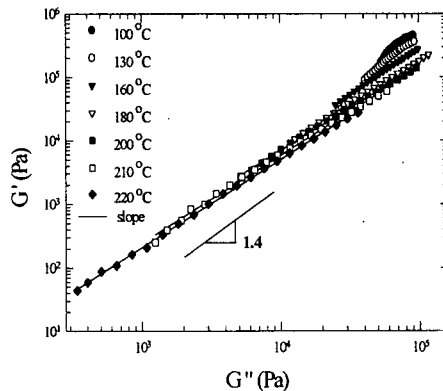
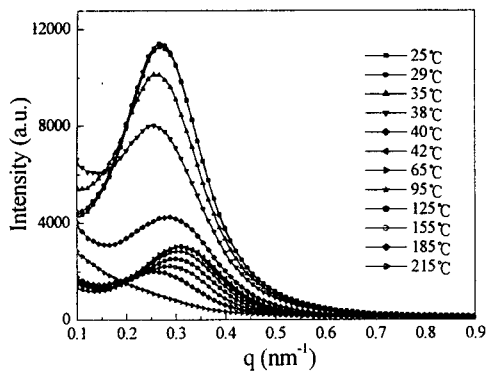


Figure 3. Synchrotron SAXS patterns for MPU55 at different temperatures.

Figure 4. log G' versus log G'' plot for MPU55 at different temperatures.

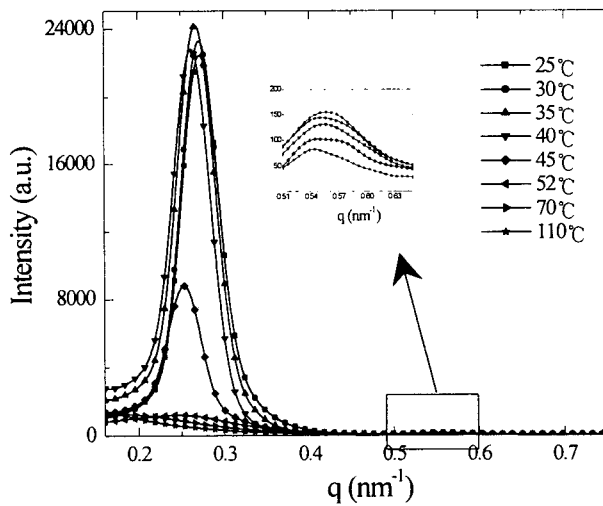


Figure 5. Synchrotron SAXS patterns for TPU at different temperatures.