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SHORT COMMUNICATIONS

Phase Separation Structure of Poly(urethane-urea)s Prepared from Different Manufacturing Methods

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Segmented poly(urethane-urea)s (PURs) are generally prepared by the following two-step polymerization method in an organic solvent such as *N,N*-dimethylacetamide (DMAc) or *N,N*-dimethylformamide(DMF)[1]: (1) preparation of an isocyanate-terminated prepolymer obtained by a reaction of an excess amount of an aromatic isocyanate with an oligomeric glycol in bulk or in solution and (2) a diffusion limited reaction of the prepolymer with a diamine.

A PUR consisting of urethane-linked segments (soft segment) and urea-linked segments (hard segment) gives unique elastic properties[2] which are directly associated with the microphase-separated structures owing to the thermodynamical incompatibility between the hard and the soft segments.[3] Quite recently, Itoh *et al.* have found that PURs in a concentrated solution aggregate molecularly, giving some network-like structures by using light scattering technique.[4] And Nakano *et al.* revealed that these structures were formed between urethane and/or urea groups in the both segments of the PUR through hydrogen bonding.[5] The dissolved state of PUR is definitely influenced by primary structures such as chemical structures, volume and weight fractions of hard and soft segments, their molecular weights and molecular weight distributions. Thus, the higher order structures originated from the dissolved state of PUR give rise to even more complexity in clarifying the primary structure/morphology property relationships for the products.

Recently, the manufacturing method to obtain PURs directly without using any common solvents by the reaction of an isocyanate-terminated prepolymer with reaction products from acetone and ethylenediamine, was proposed by authors.[6]

Authors have found morphological and structural differences between the above two PUR films by scanning probe microscopy (SPM) with force modulation technique and thermally stimulated depolarized current (TSDC) analysis. The results are presented in this paper briefly.

EXPERIMENTAL

Materials and Preparation of PUR Films

Extra pure grade (99.5%) acetone and ethylenediamine (EDA), and diethylamine (DEA) were supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and they were distilled before use. Deuterated chloroform (99.95%) and deuterated acetone (99.95%) were also supplied from Wako Pure Chemical Industries, Ltd. and used with no further purification. Fiber-grade methylene-bis(4-phenylisocyanate) (MDI), manufactured by Nippon Polyurethane Industry Co., Ltd., Tokyo, was freshly distilled at 185°C/400 Pa. The purity of MDI thus prepared was higher than 99.9% as determined by the conventional titration method.[7] Poly(tetramethylene-oxide) (PTMO) manufactured by Asahi Chemical Industry Co., Ltd., Tokyo was dehydrated at 90°C/400 Pa for 4 h. The water content was reduced to 15 ppm as measured by a moisture meter, Model CA-2 manufactured by Mitsubishi Chemical Industry Co., Ltd., Tokyo. The number-average molecular weight, $\overline{M}_n$ of PTMO was 2010 as determined by the end-group analysis.[8]

Poly(urethane-urea) films obtained by the conventional solution polymerization (PURsp) were prepared in the following manner: PTMO (201 g, 0.100 mol) with the number-average molecular weight $\overline{M}_n = 2010$ was mixed with MDI (40.0 g, 0.160 mol) in DMAc (241 g) at 15°C for 2.5 h with a small amount of sulfuric acid to avoid side reactions[9] under N_2 atmosphere, then the mixture of MDI (27.5 g, 0.110 mol) and DMAc (400 g) was added to the prepolymer solution. After complete mixing, the prepolymer including MDI was reacted with the mixture of EDA (10.3 g, 0.171 mol), DEA (1.89 g, 0.0258 mol), and DMAc (500 g) at 15°C for 0.5 h. The resultant dope was cast on a glass plate and dried under vacuum at 70°C for 10 h, giving a PUR film with a thickness of 100 μm.

PUR films without the solvent (PURrm)[6] were prepared as follows: A mixture of EDA (14.4 g, 0.240 mol) and acetone (20.9 g, 0.360 mol) was reacted at 50°C for 1 h under N_2 atmosphere. After this reaction water (2.16 g, 0.120 mol) was added to the mixture and the 'new' mixture was kept at the same temperature for another one hour. A prepolymer composing of PTMO (201 g, 0.10 mol) and MDI (67.8 g, 0.271 mol) was prepared at 70°C for 3 h in bulk. The isocyanate content of the prepolymer was 1.24 mol kg^{-1} determined by the titration method.[7] After the prepolymer was cooled down to 30°C, the prepolymer (100.0 g, 0.124 mol as the isocyanate group concentration) was mixed with the

reaction products from EDA, acetone, and water (9.35 g, 0.124 mol with respect to the amino group concentration calculated based on EDA used) in addition to acetic acid (0.0180 g, 3.00×10^{-4} mol) under vigorous stirring for 10 s at 30°C and this mixture was immediately placed on a glass plate to obtain a PUR film (*ca.* 100 μm thickness). The polymerization was completed within 200 s at room temperature, followed by vacuum-drying for 10 h to remove small amounts of acetone and water. It is noted here that the roll of water and the acid added is to avoid the formation of the by-product.

Scanning Probe Microscopy (SPM)

Phase separated morphology of PUR films was observed using SPM unit connected with a SPM instrument (Digital Instruments Corp., Model Nano Scope III) under the following operating conditions: cantilever (single crystal silicone; length 125 μm; frequency 7—8 kHz; Fooke's modulus 0.18 N m^{-1}; resolution 0.2—1 nm), scanning range 3000 nm; measuring temperature 298 K in an atmospheric pressure. This novel microscopy mode is possible to visualize two dimensional images of soft and hard regions on a film.

As a preliminary attempt, viscoelastic measurements of the PUR samples were performed by a SPM, Model SPI 3700 manufactured by Seiko Instruments Inc., Japan. The principles and theories of measurements are described in detail elsewhere.[10] An elastic force constant of a commercially available silicon cantilever was determined to be 1.9 N m^{-1} based on the samples with known moduli of elasticity at room temperature; PMMA (4 GPa), polycarbonate (2.5 GPa), and silicon rubber (10 MPa).

The resultant images were analyzed by an imaging analyzer (Model IP-1000, Asahi Chemical Industries Co., Ltd.) to estimate the size and the relative area for the detected domains with relatively higher modulus. The bright and dark regions were divided into 10 even parts according to their contrasts and the images with above 40% from the darkest part in the tested region were regarded as the relatively higher modulus domain.

Thermally Stimulated Depolarized Current (TSDC) Analysis

TSDC measurements[11,12] were made using TSC/RMA spectrometer 91000 (Solomat) on the two PUR films under He atmosphere. Groval and thermal window measurements were carried out as follows.

Groval Measurements. The samples were polarized at polarizing temperature T_p of 75°C by charging a polarizing voltage V_p of 1800 V mm^{-1} for a given polarizing time t_p of 2 min and then quenched down to −150°C under V_p so that the polarized state of the polymer molecules holded. Subsequently, depolarization of samples was carried out at a depolarizing temperature T_d of −150°C for a depolarizing time t_d of 2 min and the samples were heated at a rate of 7°C min^{-1}. TSDC curves (depolarized current J *vs.* heating temperature T) were obtained by recording J values generated on the heating process.

Thermal window measurements: This is a technique to polarize only certain molecules possessing a particular relaxation time among molecules with different relaxation time. In these experiments, the polarizing temperature range ($\Delta T = T_p - T_d$) was fixed to be 5°C. Under V_p of 1800 V mm^{-1} the polarization at T_p was made for 2 min and the sample was depolarized at T_d for 2 min. At this instant, the most of dipolar molecules having relaxation time less than 2 min deem to be depolarized. Then, the sample was further cooled down to the temperature lower than T_p by 50°C so that the remaining polarized moiety was frozen, and the TSDC curve was obtained by heating to T_p plus 50°C with the heating rate of 7°C min^{-1}. These series of procedures were performed at every 5°C between −100 and −5°C of T_p in order to obtain the relaxation map with a unique relaxation mechanism.

According to the Bucci–Fieschi–Guidi (BFG) analysis,[13] the depolarization current density of dielectric with a single relaxation time can be written

$$J(t) = -\mathrm{d}P(t)/\mathrm{d}t = P(t)/\tau \tag{1}$$

where $P(t)$ is the decay of polarization after removal of the electric field at $t = \infty$ and τ denotes the dipolar relaxation time. In order to obtain the current density by the progressive decrease in polarization in the course of a TSDC experiment, where time and temperature are simultaneously varied, the differentiation must be performed in terms of the new variable T. Then, eq 1 is rewritten as eq 2 by using the rate of increase in temperature β ($\mathrm{d}T/\mathrm{d}t$).

$$\ln \tau(T) = \ln\left[(1/\beta)\int_T^{\infty} J(T)\mathrm{d}T\right] - \ln J(T) \tag{2}$$

By using the first and second terms of right hand side of eq 2 which can be integrated experimentally, the left hand side is obtained. On the other hand, the relaxation time $\tau(T)$ is approximately described by the absolute rate theory equation as follows:

$$\tau(T) = h/kT\exp(\Delta G^*/RT) \tag{3}$$

$$= h/kT\exp(\Delta H^*/RT)\exp(-\Delta S^*/R) \tag{4}$$

$$\ln \tau - \ln h/kT = \Delta H^*/RT - \Delta S^*/R \tag{5}$$

Here, k is Boltzman constant and h is Planck constant. And ΔG^*, ΔH^*, and ΔS^* are free energy, enthalpy, and entropy of activation, respectively. Equation 5 indicates that within a relaxation map a plot of the logarithm of relaxation as a function of inverse temperature should give a straight line with a slope, $\Delta H^*/R$ and an intercept, ($\ln h/kT - \Delta S^*/R$).

RESULTS AND DISCUSSION

Figure 1 shows the SPM photographs of PURsp and PURrm. Judging from the shade in the photographs, the former exhibits a net-work structure with a relatively higher modulus and the latter is characterized by almost clearly isolated domains. This result is indicative of distinctive phase separation nature of PURrm. Although the dimensions of hard domains of PURrm are diverged in the wide range, the average size of the ellipsoidal domains (black parts) calculated from the image analysis is ranged from 80 nm to 140 nm long. The total area occupies *ca.* 30% over the observed area

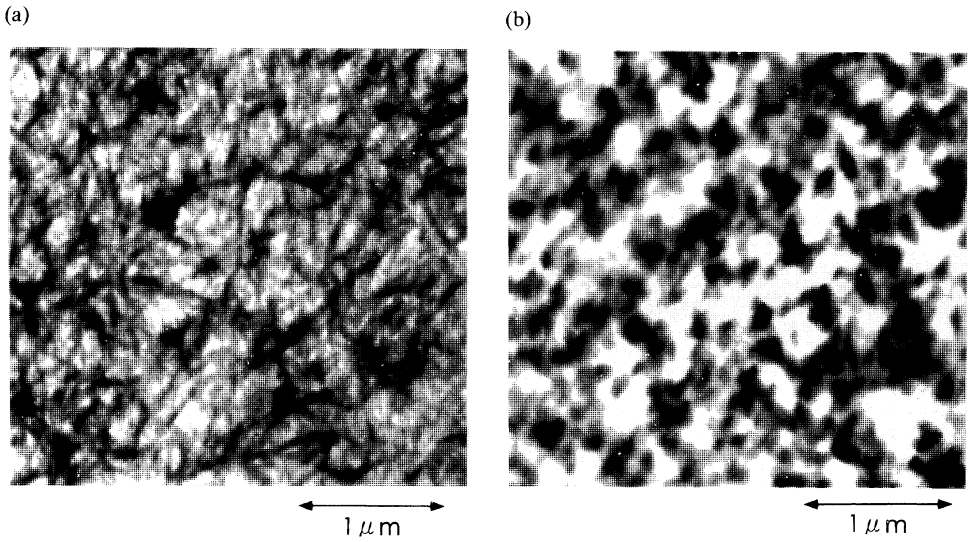

Figure 1. The SPM micrographs of PURsp (a) and PURrm (b) by an imaging analyzer. (Black parts were regarded as relatively higher modulus.)

Table I. The modulus of elasticity of PURsp and PURrm

Sample	Sea part	Island part
PURsp	25—40	50—300
PURrm	20—35	80—2000

Unit = MPa.

($9\,\mu m^2$), which is considerably larger than the hard segment content (18.6%) of the PURrm. The difference seems to be associated with an interface of the PUR film and will be described in the next section.

Table I compiles the moduli of elasticity of the sea part and the island part for the two PUR films, respectively. The sea part possesses values in range 20—40 MPa for both films. Taking into account of the model hard segment ($\fallingdotseq$2 GPa) arising from the reaction of one mole of MDI with two moles of *n*-butylamine,[14] we may at least say that the sea parts for both samples are rich in soft segments. For the island part of PURsp there observed no significant difference in modulus from the sea part. This result may be associated with the poor phase separation nature of PURsp, leading to phase mixing between the two segment regions within the order of the curvature radius (10 nm) of the silicon cantilever. On the contrary, the island part of PURrm exhibits significantly higher moduli in spite of wide distribution (80—2000 MPa) than those of the sea part, indicating that the relative degree of phase mixing is less for this sample than for PURsp. The wide distribution is also associated with the existence of the hard segment domain boundary which consists of the urethane groups adjacent to the domains and less mobile than those in the soft segments.[15] It is noted here that the depth profile of the hard segment domains might affect the distribution as well and an attempt for the preparation of ultra thin membrane is now underway. These results just mentioned are consistent with TSDC results (described later) for both samples with respect to the interface.

Grobal TSDC spectra measured in range −150—250°C, as shown in Figure 2, clearly picture the characteristic patterns of the depolarized current *I* as a function of temperature for the two films. Three relaxation peaks

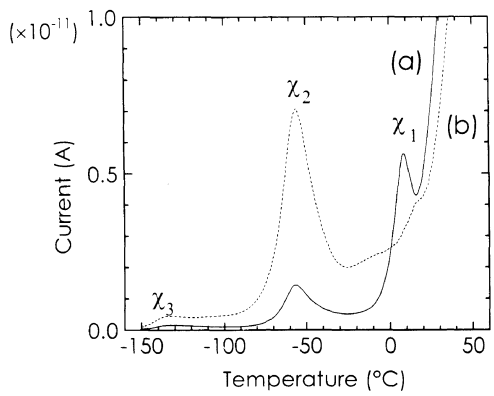

Figure 2. Characteristic patterns of depolarized current as a function of temperature for the two films. (a, PURsp; b, PURrm.)

are observed around −130°C, −60°C, and 8—15°C, and also a strong upswing over 30°C is seen. For convenience, these peaks besides the upswing are termed as χ_1, χ_2, and χ_3 from the higher temperature. χ_1, χ_2, and χ_3 are associated with segmental motions of the interfacial region between the hard and soft segment, the segmental motion of the soft segment, and the motion of the methylene moiety in the soft segment, respectively.[16] χ_2 corresponds to α dispersion peak of the soft segment, related to the glass transition of the segment observed in a mechanical analysis. For PURsp χ_1 peak is far larger than that of χ_2 and χ_3 peak seems not to appear practically. In contrast to this, for PURrm χ_2 peak is a major peak and χ_1 peak appears only as a shoulder peak on the strong upswing curve. And χ_3 peak of this film is relatively more distinct compared with that for PURsp. The comparison of these results between the two samples indicates that the PURrm consists of far larger fractions of mobile segments in the soft segments and less interfacial regions than those for PURsp.

Figure 3 shows the results on thermal window analyses on χ_1 and χ_2 peaks, reducing to ΔS^*–ΔH^* relationship.[17,18] The amorphous region of PURsp consists of at least five domains with different relaxation mechanisms and that of PURrm contains only two domains. This result, together with the comparison of SPM images as well as of global peaks between PURrm

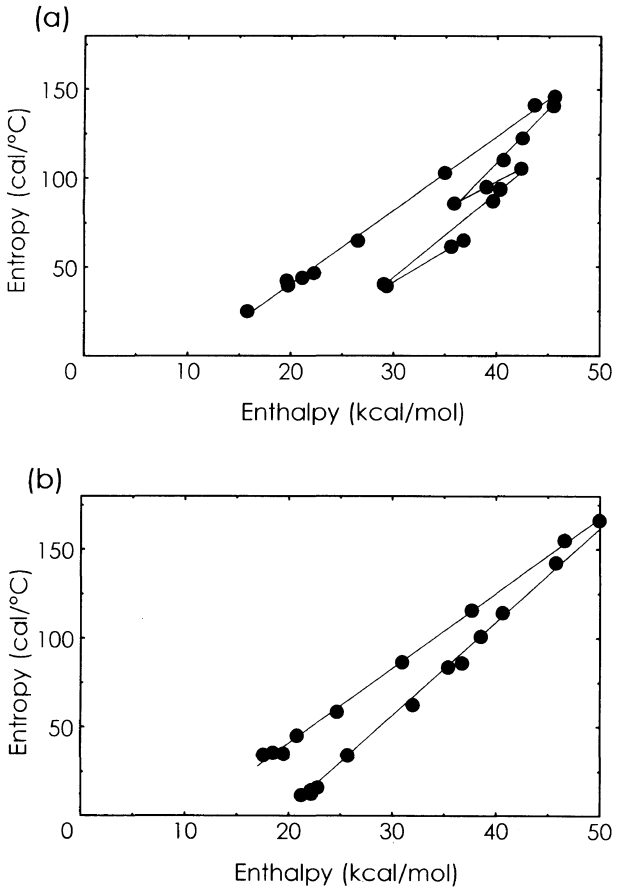

Figure 3. The relationships between the activation entropy ΔS^* and the activation enthalpy ΔH^* by the thermal window analysis. (a, PURsp; b, PURrm.)

and PURsp clearly indicates that the entire PURrm sample is characteristic of the relatively higher order of the phase separation nature, compared with PURsp. The relatively poor phase separation nature of the PURsp is probably associated with, as described before, the molecularly aggregated network structure of the polymer in the concentrated solution. The detailed study relating to these matters is under way and will be published soon.

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