

# Synthesis and Properties of Biodegradable Network Poly(ether-urethane)s from L-Lysine Triisocyanate and Poly(alkylene glycol)s

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**ABSTRACT:** Biodegradable network poly(ether-urethane) films with different hydrophilicity were prepared from L-lysine triisocyanate (LTI) and poly(ethylene glycol) (PEG), poly(1,4-tetramethylene glycol) (PTMG) or poly(propylene glycol) (PPG) with the molecular weights of 250–2000 g mol<sup>-1</sup>. Prepolymers prepared by a melt-polycondensation were cast from tetrahydrofuran solution and heated at 65–80°C for 9 h, then postpolymerized at 150–180°C for 10–20 min to form a network. The resultant films were transparent to opaque and insoluble in water and organic solvents. These network films were fully characterized by FTIR, density measurement, wide-angle X-ray scattering (WAXS), differential scanning calorimetry, dynamic mechanical analysis, and tensile tests. WAXS intensity curves of LTI/PEG-1000 and LTI/PEG-2000 exhibited crystalline peaks due to PEG segments, while those of all other network films did amorphous halos. The molecular weights ( $M_w$ ) between cross-links increased, while the

cross-linking density decreased with increasing the  $M_w$ s of the poly(alkylene glycol)s. Mechanical properties were strongly affected by the type and molecular weights of poly(alkylene glycol)s used. The weight losses of the LTI/PEG series network films that were degraded in a phosphate buffer solution (pH 7.2) at 37°C and the equilibrium water content in distilled water at 20°C were much larger than those of LTI/PTMG and LTI/PPG series ones. In contrast, LTI/PTMG-1000 and LTI/PPG-1000 network films absorbed 150–216% of organic solvents such as benzene and toluene under equilibrium state at 20°C. The use of poly(alkylene glycol)s with different types and the  $M_w$ s allowed the preparation of novel network poly(ether-urethane) films with a broad range of properties. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** biodegradable; poly(ether-urethane)s; L-lysine triisocyanate; poly(alkylene glycol)s; networks

## INTRODUCTION

Polyurethanes are considered to be excellent biomedical materials that possess good mechanical and physical properties as well as blood compatibility, and the segmented polyurethanes with improved biostability have been used for long-term implanted biomedical devices, such as heart valves and dialysis membranes.<sup>1–4</sup> Recently, bioabsorbable segmented polyurethanes have been investigated for specialized biomedical applications including tissue engineering and drug delivery.<sup>5–11</sup> They have been mainly synthesized by reacting polyester diols or polyether diols with 4,4'-methylene diisocyanate (MDI) or 2,4-toluene diisocyanate (TDI), but their degradation products such as 2,4-diaminotoluene or 4,4'-methylene dianiline are toxic, mutagenic, and carcinogenic, which have limited their *in vivo* applications. The al-

iphatic diisocyanates including 4,4'-methylenedicyclohexyl diisocyanate (hydrogenated MDI) and hexamethylene diisocyanate have also been used as the corresponding diisocyanate, but the corresponding diamines are still more or less toxic. Recently, poly(ester-urethane) urea have been prepared from poly( $\epsilon$ -caprolactone), 1,4-diaminobutane, and 1,4-diisocyanatobutane, which released putrescine upon degradation; this polyamine is essential for cell growth and proliferation.<sup>12</sup> Nontoxic biodegradable polyurethanes or polyureas could be prepared if the urethane or urea segments hydrolyze completely into nontoxic and biocompatible degradation products. Lysine-based isocyanates such as diisocyanate and triisocyanate have been used for the synthesis of biodegradable polyurethanes,<sup>13–16</sup> because the urethane segments composed of these polyisocyanates can hydrolyze into the nontoxic compounds. Bruin et al. reported the synthesis of bioabsorbable polyurethane networks from ethyl 2,6-diisocyanatohexanoate (lysine diisocyanate; LDI), lysine-derived diisocyanate and poly( $\epsilon$ -caprolactone) triols<sup>13</sup> or hexafunctional hydroxyl-terminated star-shaped oligomers,<sup>14</sup> and glucose,<sup>15</sup> in which LDI did not

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produce adverse tissue reactions. Recently, the bioabsorbable poly(ester-ether urethane)s were prepared from LDI and block copolymers of PCL-PEG-PCL as macrodiols.<sup>16</sup> We reported the preparation of degradable, elastomeric poly(ester-urethane) networks from 2-isocyanatoethyl 2,6-diisocyanatehexanoate (*L*-lysine triisocyanate, LTI), lysine-derived triisocyanate, and poly( $\epsilon$ -caprolactone) diols with different molecular weights.<sup>17</sup>

In this work, we prepared biodegradable network poly(ether-urethane)s from LTI and poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG) or poly(1,4-tetramethylene glycol) (PTMG) with the number average molecular weights ( $M_{wS}$ ) of 200–2000 g mol<sup>-1</sup>. PEG is one of the most widely used biocompatible polymers and has excellent water solubility, low toxicity and immunogenicity. PEG is frequently used for precursors of hydrogels. When PEG is cross-linked, its network would form a hydrogel. PEG-based hydrogels have been widely investigated.<sup>18–24</sup> But, the poly(ether-urethane) hydrogels derived from PEG and LTI have not been described in the literature. In addition, the properties of gels from PTMG and PPG with LTI have not been reported up to now. The effects of the types and the molecular weights of these poly(alkylene glycol)s on the structure, thermal, dynamic-mechanical, and mechanical properties as well as hydrolytic degradation of the network films were examined.

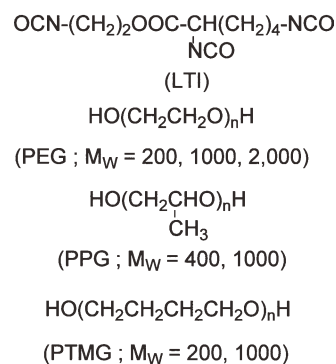
## EXPERIMENTAL

### Materials

The chemical structures and their codes of the starting materials are shown in Figure 1. The 2-isocyanatoethyl 2,6-diisocyanatehexanoate (Lysine triisocyanate, LTI) was gifted by Kyowa Hakko Kogyo. Poly(ethylene glycol) (PEG) with average  $M_{wS}$  of 200, 1000, and 2000 g mol<sup>-1</sup> as well as PPG with average  $M_{wS}$  of 400 and 1000 g mol<sup>-1</sup> were purchased from Wako Chemical. PTMG with average  $M_{wS}$  of 250, and 1000 g mol<sup>-1</sup> were purchased from Aldrich. These starting materials were used as received without an additional purification. Tetrahydrofuran was distilled prior to use.

### Preparation of prepolymers

Prepolymers were prepared from LTI and PEG, PPG or PTMG by a melt polycondensation, for example, a mixture of LTI and PEG-1000 (total amount of 4 g, molar ratio of LTI/PEG: 2/3) was heated in a stream of nitrogen at 120–140°C for 3–48 min, depending on the type and the molecular weights of poly(alkylene glycol)s used. Further heating caused the gelation of the prepolymers.



**Figure 1** Chemical structures and their codes of starting materials.

### Film preparation and postpolymerization

The obtained prepolymers were cast on an aluminum plate using about 17 wt % tetrahydrofuran solution. The cast films were heated at 65°C for 3 h, and then at 80°C for 6 h in nitrogen atmosphere. These films were successively postpolymerized at 150–170°C for 10–20 min in a stream of nitrogen. The postpolymerization conditions of all other films are summarized in Table I. The postpolymerized films were peeled off from the aluminum substrate and stored in a desiccator over silica gel prior to use.

### Characterization

Wide angle X-ray scattering (WAXS) was performed with a Bruker MX-Labo X-ray diffractometer with nickel-filtered Cu K $\alpha$  radiation on about 0.2 mm thin film specimens with a smooth surface. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC 2920 differential scanning calorimeter at a heating rate of 10°C min<sup>-1</sup> in a nitrogen atmosphere. Each film was preheated from room temperature to 150°C and rapidly cooled down to –100°C so that all films had the same thermal history. Then a DSC scan was recorded by heating from –100 to 150°C. A dynamic mechanical analysis (DMA) was performed using a TA Instruments DMA-2980 dynamic mechanical analyzer. Measurements were carried out in a temperature range of –100–150°C. All measurements were carried out at a heating rate of 5°C min<sup>-1</sup> and at a frequency of 1 Hz. The density of the films was measured at 25°C by a sink and float method using potassium iodide aqueous solution. Tensile tests were conducted using a Shimadzu AG-1 autograph at a strain rate of 100%/min at room temperature for polymer strips (20 × 2 × 0.2 mm<sup>3</sup>). The sample was elongated to failure. The ultimate tensile strength, Young's modulus, and maximum strain were measured, and the averaged value for 5–10 film specimens was employed.

**TABLE I**  
**Postpolymerization Conditions, Degree of Reaction ( $D_R$ ), Density ( $\rho$ ), and Glass Transition Temperature ( $T_g$ ) of the Network Films**

| Polymer code  | Temp <sup>a</sup><br>(°C) | Time <sup>b</sup><br>(min) | $D_R$<br>(%) | $\rho^c$<br>(g cm <sup>-3</sup> ) | $T_g^d$<br>(°C) | $T_g^e$<br>(°C) |
|---------------|---------------------------|----------------------------|--------------|-----------------------------------|-----------------|-----------------|
| LTI/PEG-200   | 150                       | 10                         | 85           | 1.26                              | -7              | 11              |
| LTI/PEG-1000  | 160                       | 10                         | 76           | 1.20                              | -51             | -35             |
| LTI/PEG-2000  | 180                       | 20                         | 62           | 1.19                              | -58             | -28             |
| LTI/PTMG-250  | 160                       | 10                         | 83           | 1.19                              | 1               | 18              |
| LTI/PTMG-1000 | 170                       | 10                         | 64           | 1.16                              | -73             | -42             |
| LTI/PPG-400   | 160                       | 10                         | 81           | 1.18                              | -15             | 6               |
| LTI/PPG-1000  | 170                       | 10                         | 68           | 1.17                              | -57             | -29             |

<sup>a</sup> Postpolymerization temperature.

<sup>b</sup> Postpolymerization time.

<sup>c</sup> Values determined at 25°C.

<sup>d</sup> Determined from DSC second heating scans.

<sup>e</sup> Estimated from  $\tan \delta$  peak.

### Water uptake behavior and hydrolytic degradation

The dry film samples (20 mm × 20 mm × 0.2 mm) were weighed and placed in water at 20°C. They were removed after 24 h, blotted quickly with tissue paper to remove surface water, and weighed. The water uptake of the films was calculated by the following relation:

$$\text{Water uptake (\%)} = 100 \times (W_w - W_{24} - W_d) / (W_d - W_{24}) (\%)$$

Here  $W_w$  is the maximum weight of swollen specimen,  $W_{24}$  is the weight loss after 24 h in water at 20°C and  $W_d$  is the initial dry weight of the sample. The water uptake values of film specimens were calculated considering the weight loss caused by the hydrolysis during the dipping.

The *in vitro* degradation was performed in a small vial containing 10 mL of 1/15 mol phosphate buffer solution (pH 7.2) at 37°C. The vial was incubated for various periods of time. After incubation, the films were washed with water thoroughly and dried at room temperature *in vacuo* to constant weight. The degree of degradation was calculated from the differences between the dry weight after degradation and the initial weight.

$$\text{Weight loss (\%)} = 100 \times (W_0 - W_t) / W_0 (\%)$$

Here  $W_0$  is the initial weight of dry specimen and  $W_t$  is the dry sample weight after degradation of the sample.

## RESULTS AND DISCUSSION

### Preparation of network poly(ether-urethane) films

All prepolymers were prepared by heating a mixture of LTI and PEG, PPG or PBG at 120–140°C for 3–48 min in a stream of nitrogen, depending on the type

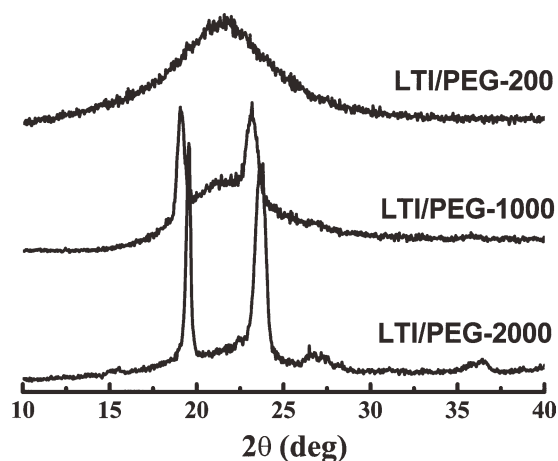
of poly(alkylene glycol)s. Further heating caused the gelation of the prepolymers. The postpolymerization was performed at 150–180°C for 10–20 min in nitrogen atmosphere to form a network. The postpolymerization conditions for each film were shown in Table I. After postpolymerization, the films were swollen in water or in organic solvents such as dichloromethane and *N,N'*-dimethylformamide, but did not dissolve in these solvents, suggesting the formation of a cross-linked structure. This network structure could be formed by the reaction of isocyanate group of LTI with hydroxyl group of the poly(alkylene glycol)s.

The degree of reaction ( $D_R$ ) was estimated by the procedures reported previously.<sup>25</sup> The network polymers showed infrared absorptions due to isocyanate group at 2270 cm<sup>-1</sup>, hydroxyl group at 3460 cm<sup>-1</sup> and methylene groups at 2875 cm<sup>-1</sup>. The both absorptions at 2270 and 3460 cm<sup>-1</sup> decreased with increasing postpolymerization time, while the absorption at 2875 cm<sup>-1</sup> remained unchanged. Because the postpolymerization proceeds through the reactions between the isocyanate group of LTI and hydroxyl group of poly(alkylene glycol), the change of absorption intensity ratio between -OH and >CH<sub>2</sub>,  $A_{OH} / A_{CH_2}$ , is a measure of the degree of reaction. For LTI/PEG-200, at the beginning of reaction, the ratio of hydroxyl and methylene groups in a monomeric unit, [OH]/[CH<sub>2</sub>], was 3/18 and varied with the progress of reaction to become (3 - 3)/18 when the network structure of film was completely developed. Thus, the following equation is defined:

$$[\text{OH}]/[\text{CH}_2] = (3 - y)/18$$

and

$$y = 3 - (18[\text{OH}]/[\text{CH}_2])$$



**Figure 2** WAXS profiles of network LTI/PEG series poly(ether-urethane) films.

Here  $y$  is the number of reacted hydroxyl groups. The degree of reaction ( $D_R$ ) is calculated as

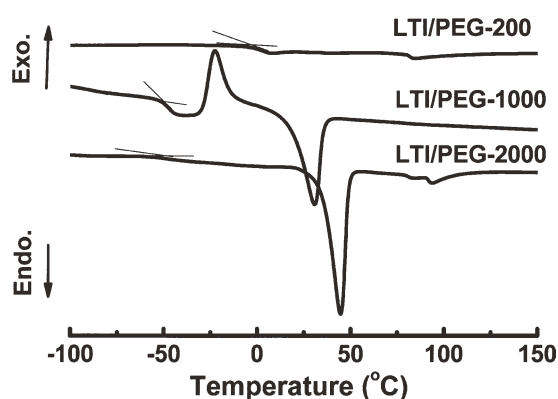
$$D_R = (y/3) \times 100 (\%)$$

To obtain the quantitative  $[\text{OH}]/[\text{CH}_2]$  ratio in network films, the calibration curve between  $A_{\text{OH}}/A_{\text{CH}_2}$  made by the known PEGs and PTMGs.

$D_R$  values of network films postpolymerized at 150–180°C, which leveled off for 10–20 min, are summarized in Table I.  $D_R$  values of the network films were in the range of 62–85%. Especially, the network films prepared from PPG-1000, PTMG-1000, and PEG-2000 show the lower  $D_R$  values between 62 and 68%, which may be responsible for the lower reactivity of the terminal hydroxyl group having the longer molecular chains.

#### Thermal, dynamic mechanical and tensile properties of network poly(ether-urethane) films

Figure 2 shows WAXS intensity curves of LTI/PEG series films. Two diffraction peaks were observed at around  $2\theta = 18\text{--}19^\circ$  and  $23\text{--}24^\circ$  for LTI/PEG-1000

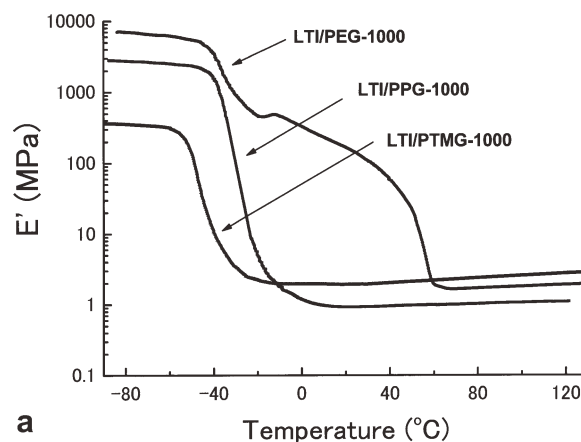


**Figure 3** DSC curves of network poly(ether-urethane) films.

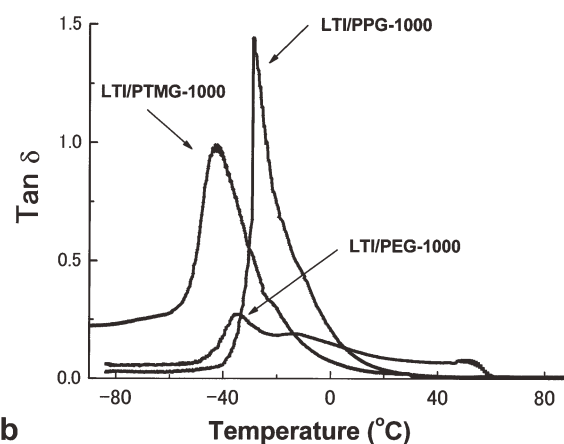
and LTI/PEG-2000, whereas LTI/PEG-200 showed only amorphous halos. These diffraction peaks were due to the crystallization of the PEG components. The crystallinity of LTI/PEG-2000 and LTI/PEG-1000 estimated by the WAXS was 49 and 21%, respectively. All the other network films were amorphous (WAXS curves are not shown).

Figure 3 shows DSC curves of LTI/PEG series films for the second heating run.  $T_g$  values are listed for LTI/PPG and LTI/PTMG series films in Table I.  $T_g$  of the network films decreased with increasing the  $M_w$ s of the poly(alkylene glycol)s, suggesting that the increase in the  $M_w$ s of them enhanced the molecular mobility of the networks. However  $T_g$  of LTI/PEG-2000 is higher than that of LTI/PEG-1000. The melting peaks of crystallites were observed at 44.6 and 30.7°C for LTI/PEG-2000 and LTI/PEG-1000, respectively, corresponding to the nature of crystalline structure which are clearly appeared as the diffraction peaks in the WAXS curves in Figure 2.

Figure 4(a,b) shows the typical dynamic-mechanical plots of LTI/PEG-1000, LTI/PTMG-1000 and



**a**



**b**

**Figure 4** Storage modulus (a) and  $\tan \delta$  plots (b) as a function of temperature of network poly(ether-urethane) films.

**TABLE II**  
**Modulus of Elasticity at the Rubbery Plateau ( $E'$ ), Molecular Weights Between Cross-Links ( $M_c$ ), Cross-Linking Density ( $n$ ), and Tensile Test Results of the Network Films**

| Polymer code  | $E'$ (MPa) | $M_c$ (g mol <sup>-1</sup> ) | $n$ (mol m <sup>-3</sup> ) | $\sigma_b^a$ (MPa) | $\epsilon_b^b$ (%) | $E^c$ (MPa) |
|---------------|------------|------------------------------|----------------------------|--------------------|--------------------|-------------|
| LTI/PEG-200   | 11.5       | 880                          | 1400                       | 4.3 ± 1.0          | 29 ± 10            | 26 ± 3.1    |
| LTI/PEG-1000  | 1.7        | 6100                         | 190                        | 7.2 ± 1.4          | 66 ± 15            | 91 ± 17     |
| LTI/PEG-2000  | 0.6        | 18,000                       | 66                         | 26 ± 4             | 42 ± 15            | 173 ± 61    |
| LTI/PTMG-250  | 6.2        | 1430                         | 830                        | 8.0 ± 1.1          | 92 ± 25            | 19 ± 2.6    |
| LTI/PTMG-1000 | 2.0        | 4100                         | 280                        | 2.1 ± 0.3          | 21 ± 5.4           | 13 ± 0.7    |
| LTI/PPG-400   | 1.2        | 7800                         | 150                        | 1.5 ± 0.4          | 32 ± 5.8           | 8.3 ± 1.1   |
| LTI/PPG-1000  | 0.9        | 9500                         | 120                        | –                  | –                  | –           |

<sup>a</sup> Ultimate tensile strength.

<sup>b</sup> Maximum strain.

<sup>c</sup> Young's modulus.

LTI/PPG-1000 network films. In the low-temperature region of the DMA curve, the storage modulus ( $E'$ ) decreased slightly with increasing temperature, as expected. A large decrease in  $E'$  due to glass transition was successively observed.  $T_g$  values evaluated from the  $\tan \delta$  peaks are also shown in Table II.  $T_g$  values estimated by DMA are higher than those by DSC. The similar behaviors have been reported by Helminen et al.<sup>26</sup>  $T_g$  value of LTI/PEG-2000 is higher than that of LTI/PEG-1000, which differs from the result determined by DSC described above. This would be probably caused by the experimental error. For LTI/PEG-1000 film, considerable amount of  $E'$  is maintained up to around melting point of 30.7°C, corresponding to the nature of crystalline structure.

The molecular weights between cross-links is often related to  $E'$  at the rubbery plateau according to the theory of rubber elasticity,<sup>27</sup>

$$M_c = 3\rho RT/E' \quad (1)$$

Here  $M_c$  represents the molecular weight between cross-links,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $E'$  is the modulus of elasticity at the rubbery plateau, and  $\rho$  is the density. The  $M_c$  values of the network films calculated with  $E'$  measured using eq. (1) are shown in Table II. These values were much larger than those theoretically calculated from the  $M_w$  of the poly(alkylene glycol)s, implying the incomplete formation of the network structure. The cross-linking density is expressed by  $n$  (moles of network chains per unit volume), which is calculated using the following equations<sup>27</sup>

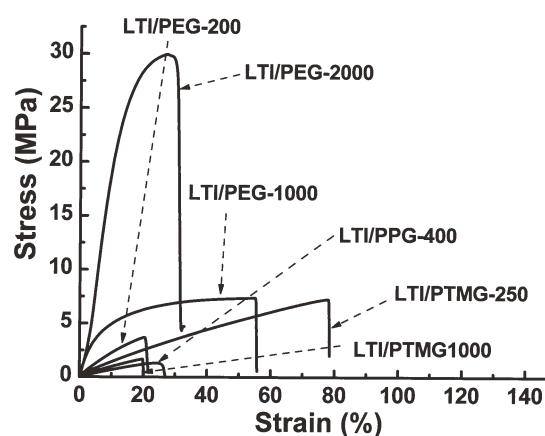
$$n = \rho/M_c \quad (2)$$

where all symbols have the same definitions as those in eq. (1). The  $n$  values estimated using eq. (2) are also listed in Table II. As expected,  $n$  decreased with the increasing  $M_w$ s of the poly(alkylene glycol)s.

Figure 5 shows representative strain–stress plots of the network films at room temperature. Table II summarizes the results of stress–strain data such as the ultimate tensile strength, Young's modulus, and maximum strain. The LTI/PEG-2000 showed the largest ultimate tensile strength of 26 MPa and Young's modulus of 173 MPa irrespective of the lowest  $n$  value, which would be ascribed to the higher crystalline nature (degree of crystallinity; 49% mentioned above) of the polymer. The  $\sigma_b$  and  $E$  of semi-crystalline LTI/PEG-1000 film (degree of crystallinity; 21% mentioned above) is also larger than those of non-crystalline LTI/PPG series films. The tensile properties of LTI/PPG-1000 film could not be determined because of its brittleness.

#### Water uptake and hydrolytic degradation of LTI/PEG series network films

The equilibrium water content (EWC) of LTI/PEG series gel films are listed in Table III. The gels swelled rapidly and appeared to be complete within 2 h, and EWC was almost constant after 24 h dipping. As expected, EWC of LTI/PEG series films is



**Figure 5** Stress–strain curves of network poly(ether-urethane) films.

**TABLE III**  
Absorption of Water and Some Organic Solvents of the Network Films<sup>a</sup>

| Polymer code  | Water (%) | Benzene (%) | Toluene (%) |
|---------------|-----------|-------------|-------------|
| LTI/PEG-200   | 55        | –           | –           |
| LTI/PEG-1000  | 330       | –           | –           |
| LTI/PEG-2000  | 393       | –           | –           |
| LTI/PTMG-250  | 1.5       | 25          | 21          |
| LTI/PTMG-1000 | 2.3       | 150         | 83          |
| LTI/PPG-400   | 2.7       | 82          | 148         |
| LTI/PPG-1000  | 3.9       | 92          | 216         |

<sup>a</sup> Measured at 25°C.

much larger than that of LTI/PPG and LTI/PTMG. EWC increases pronouncedly with increasing the  $M_{ws}$  of the PEGs. This abrupt increase of the EWC is probably due to the much higher content of hydrophilic PEG component in the network.

Figure 6(a) shows the weight loss profile of LTI/PEG series network films as a function of the degradation time immersed in PBS (pH 7.2) at 37°C. The weight losses of all network films increase with time. With increasing the  $M_{ws}$  of PEG, the degradation rates increase significantly, which is compatible with their increase of EWC. For LTI-PEG-2000, 77% of its weight is lost after 240 h (10 days) incubation. Figure 6(b) shows the weight loss profile of LTI/PTMG and LTI/PPG series network films as a function of time under the same condition as Figure 6(a). These network films lose their weight of 1–3% at early stage of degradation, then it degrades very slowly. The weight loss for LTI/PPG and LTI /PTMG series network films are much smaller than those LTI/PEG series one, which would be ascribed to the much lower EWC of them. The somewhat larger weight loss of LTI/PPG than that of LTI/PTMG would be due to the higher EWC of the former. The hydrolysis of the ester linkage in LTI moiety and that of the urethane linkage formed by the reaction of –OH group in PEG and –NCO group in LTI would lead to L-lysine and 2-aminoethanol. The analysis of degradation products of the network poly(ether-urethane) films is in progress.

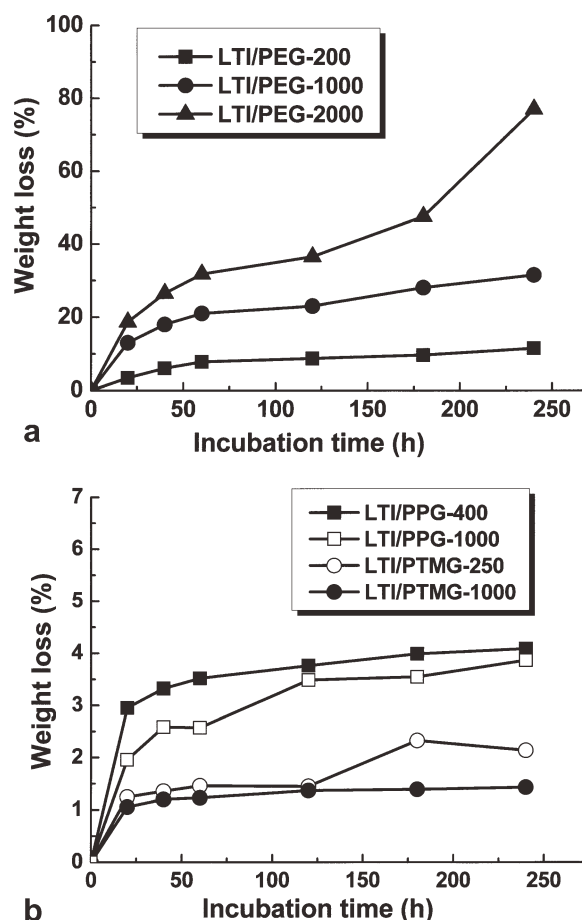
#### Swelling behavior in some organic solvents of LTI/PPG and LTI/PTMG series network films

The water content of LTI/PPG and LTI/PTMG network series films were much smaller than those of LTI/PEG ones as mentioned above. However, such network films are expected to absorb the organic solvents because of their hydrophobic properties. We examined swelling behavior in some organic solvents for LTI/PPG and LTI/PTMG series network

films. The results of solvent absorption in benzene and toluene are listed in Table III. LTI/PTMG series network films absorb benzene more than toluene, whereas LTI/PPG series network films absorb toluene than benzene. The organic solvents absorption increases with increasing the  $M_{ws}$  of poly(alkylene glycol)s corresponding to the increase of network size. LTI/PTMG and LTI/PPG have the properties as a lyogel.

#### CONCLUSIONS

Network poly(ether-urethane)s were prepared from L-lysine triisocyanate (LTI) and poly(ethylene glycol) (PEG), poly(propylene glycol) or poly(1,4-tetramethylene glycol) with the molecular weights of 250–2000 g mol<sup>-1</sup>. Dynamic mechanical analysis showed that the molecular weights between cross-links increased, while the cross-linking density decreased with increasing the  $M_{ws}$  of poly(alkylene glycol)s. The LTI/PEG-2000 showed the best tensile properties of the maximum strength of 26 MPa and



**Figure 6** Weight loss profiles of network poly(ether-urethane) films degraded in PBS at 37°C. (a) LTI/PEG series network films (b) LTI/PTMG and LTI/PPG network films.

Young's modulus of 173 MPa among the network films prepared because of the highest degree of crystallinity. The hydrolytic degradation rate of the LTI/PEG series network films were much faster than those of LTI/PTMG and LTI/PPG series ones, corresponding to the higher water content of PEG containing network films. LTI/PEG series films showed the properties of a hydrogel, whereas LTI/PTMG and LTI/PPG series one had the properties of a lipogel.

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