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SHORT COMMUNICATION

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Mechanical properties of amphiphilic urethane acrylate ionomer hydrogels having heterophasic gel structure

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Abstract Amphiphilic urethane acryale hydrogels containing ionic groups (dimethylolpropionic acid) were prepared by varying the molecular weight of the soft segment (polyether type) and the type of diisocyanate, and their mechanical properties were examined. They showed heterophasic gel structure composed of ionic hard domains induced by aggregation of the ionic groups and polyether soft domains comprising the urethane acrylate network. This heterophasic structure could be confirmed by dynamic mechanical analysis (DMA) and by wide-angle X-ray scattering analysis (WAXS); the crystallinity detected by WAXS and the transition peak of the ionic hard domains detected by DMA strongly suggested that there were ionic aggregates. These ionic aggregates acted as reinforcing fillers in the network, which eventually enhanced the tensile strength of the hydrogels. Above all, the tensile properties of the hydrogels were of interest in that the trends of the stress-strain curves were consistent with the rubbery ones. It is believed that the higher purity of the polyether soft domains resulted from the heterophasic gel structure imparting further elastomeric properties on the network.

Key words Heterophasic gel structure – Ionic hard domains – Polyether soft domains – Crystallinity – Elastomeric properties

Introduction

Amphiphilic networks are random assemblages of hydrophilic and hydrophobic chains linked to three-dimensional crosslinked systems. Since these networks swell in both water and organic solvents, they may be regarded as a special class of hydrogels [1–4].

In previous work [4], we studied the preparation of amphiphilic urethane acrylate hydrogels containing ionic groups as a hydrophilic domain and a polyether soft segment as a hydrophobic domain in the same network. This peculiar network structure was achieved by the gelation of water-soluble urethane acrylate ionomers having a molecular structure with vinyl groups at both ends enabling crosslinking during gelation and carboxylated groups in the molecular backbone enabling sufficient hydration [4, 5]. Especially, when hydrogels were prepared, the heterophasic gel structure was observed by the phase separation of the ionic groups from the polyether soft domains in the urethane acrylate network. Owing to this heterophasic gel structure, strong mechanical properties were observed even in the wet state.

In this study, the mechanical properties of heterophasic hydrogels in a dried state were investigated. It is important to consider the mechanical properties of hydrogels in a dried state because these determine the processability in the course of manufacturing. As one component of the urethane acrylate hydrogels between two phases was the polyether soft domain, rubber-like network properties were expected even in the dried state. The effects of the molecular weight of the soft segment, the ion content, and the type of diisocyanate on the gel structure and the mechanical properties were studied.

Experimental

Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co.), toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co.), and 4,4′ diphenyl methane diisocyanate (MDI, Tokyo Chemical Industry Co.) were vacuum distilled before use. Polytetramethylene glycol (PTMG, 1.0×10^3, 1.4×10^3, and 2.0×10^4 g mol^{-1}, Hyosung BASF), α,α-dimethylolpropionic acid (DMPA, Aldrich), Ammonium persulfate (AMPS, Yakuri Pure Chemicals Co.), and 2-hydroxyethyl methacrylate(HEMA, Junsei Chemical Co.) were used as received.

Preparation of urethane acrylate ionomer hydrogels [4, 5]

The ingredients for the synthesis of urethane acrylate ionomers are listed in Table 1. The reaction procedure and molecular structure are presented in Scheme 1. Here, ID, TD, and MD are IPDI-, TDI- and MDI-based urethane acrylate ionomers, respectively. In the ID series, serial numbers 1, 2, and 3, correspond to molecular weights of PTMG of 1.0×10^3, 1.4×10^3, and 2.0×10^3 g mol^{-1}, respectively. Firstly, after dissolving 1 wt% dibutyltindilaurate (DBTDL), diisocyanate and DMPA dissolved in DMAc (2:1 mol) were reacted at 80 °C for 4 h in a four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. The change in NCO value during the reaction was determined using the dibutylamine back-titration method to find out the end point of the reaction. Secondly, 0.5 mol PTMG was added slowly into the reactor with the same method as the first step. Lastly, after dissolving 1 wt% DBTDL again, 2 mol HEMA was reacted with the residual NCO groups at 45 °C for 12 h, capping the molecular ends with reactive vinyl groups. The average molecular weights of urethane acrylate calculated on the basis of the molecular weight versus the retention volume curve of monodisperse polystyrene standards were $M_w = 8.3 \times 10^3$–1.4×10^4 g mol^{-1} and $M_n = 5.4 \times 10^3$–7.1×10^3 g mol^{-1}. The carboxylic acid groups were ionized with an appropriate amount of triethylamine at room temperature for 1 h.

The ingredients for the preparation of urethane acrylate hydrogels are given in Table 2. To carry out gelation, a mixture of ionomer (7 g) and DDI water (21 g) including AMPS (3 wt% based on total ionomer weight) was transferred into a mold (10 cm × 15 cm × 0.2 cm). Then, gelation was performed at 50 °C for 24 h. After gelation, all samples were fully washed with a large amount of DDI water and methanol and dried in vacuo. Here, HID, HTD and HMD are hydrogels prepared with ID, TD, and MD in water, respectively.

Measurements

Tensile properties were measured with an Instron (model no. 4460), at a crosshead speed of 50 mm min^{-1}, and an average of at least four measurements was taken. Dynamic mechanical analysis (DMA) was performed using a DMA 2980 (TA Instruments) at 2 Hz. Wide-angle X-ray scattering (WAXS) analysis was carried out in the reflection mode using a RINT 2000 goniometer (X-ray; Cu Kα radiation, wavelength; 0.1542 nm). The scattering intensity was monitored on a strip-chart recorder as a function of the scattering angle (2θ) between 2° and 50° using a goniometer arm speed of 2° min^{-1} at an operating voltage of 30 kW and a current of 50 mA.

Results and discussion

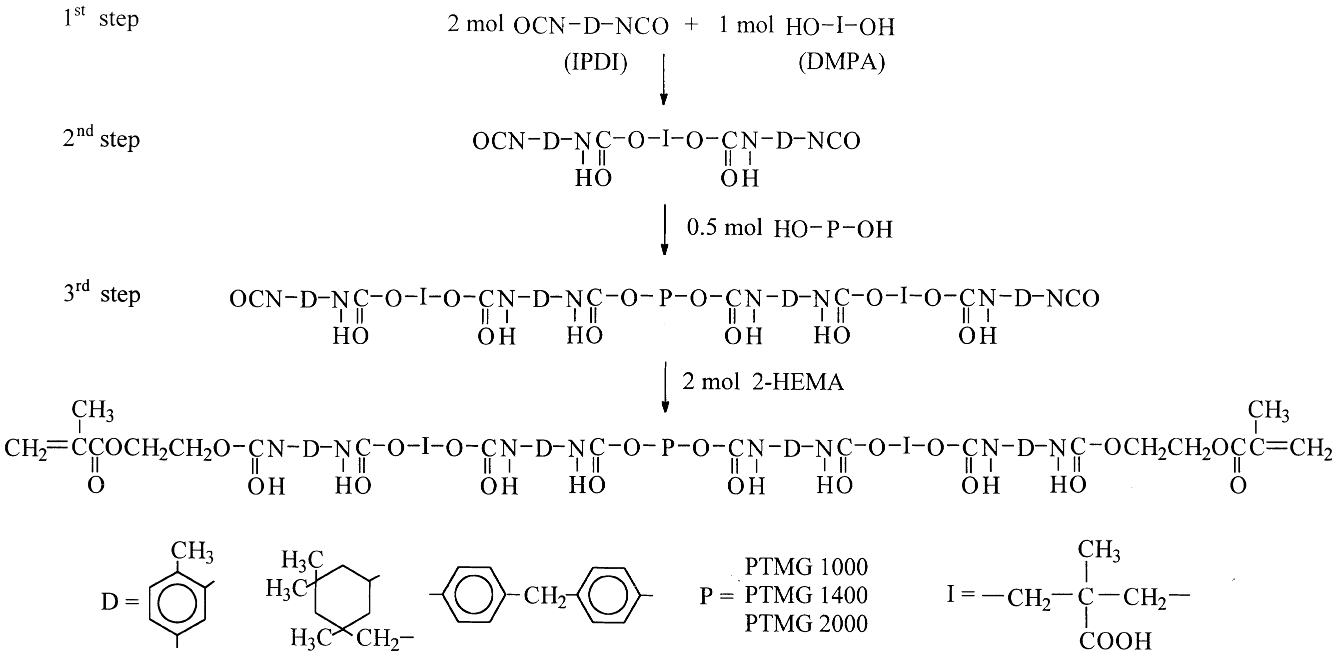
The stress-strain (S-S) curves for the hydrogels having different molecular weights of the soft segment (PTMG) are shown in Fig. 1. The tensile strength and the initial modulus increased with decreasing molecular weight of the soft segment while maintaining significant elongation at the break point. However, the tensile strength and the elongation of the HID3 gel decreased significantly compared with those of the HID1 and HID2 gels. This seemed to be attributed to the network structure which is not fully crosslinked because of the lower vinyl content (the gel fraction of the HID3 gel was only about 33.3%). In the S-S curves of the HID1 and HID2 gels, in particular, it was notable that differing from conventional urethane acrylate derivatives [6, 7], the gels displayed traditional rubbery properties as well as high tensile properties because of the incorporation of ionic groups into the network.

In order to confirm the effect of ionic groups in the network, the crystallinity of the HID1, 2, and 3 gels was observed by WAXS, (Fig. 2). The scattering intensity increased in the following order: HID1 > HID2 > HID3. This explains that the crystallinity increased with the content of the ionic groups (DMPA), as listed in Table 1. It has been generally accepted that due primarily to the great difference in polarity between the ionic groups and the polymer backbone, the ionic groups microphase-separate from the matrix [8–11]. The

Table 1 The ingredients for the synthesis of urethane acrylate ionomers[a]

Symbol	IPDI	TDI	MDI	DMPA	PTMG[b]			HEMA	TEA[c]	DMPA content (wt%)
					1.0×10^3	1.4×10^3	2.0×10^3			
ID1	20	–	–	6.03	22.49	–	–	5.85	4.54	10.24
ID2	20	–	–	6.03	–	31.49	–	5.85	4.54	8.88
ID3	20	–	–	6.03	–	–	44.98	5.85	4.54	7.41
TD2	–	20	–	7.70	–	40.19	–	7.47	5.80	10.22
MD2	–	–	20	5.36	–	27.97	–	5.20	4.04	9.15

[a] All units are in grams
[b] Molecular weight of PTMG
[c] Triethylamine was used as a neutralization agent



Scheme 1 The reaction procedure and molecular structure of urethane acrylate ionomers

Table 2 Gelation recipe of urethane acrylate hydrogels[a]

Symbol	Resin	DDI water	AMPS	Vinyl content (wt%)[b]	Gel fraction (%)
HID1	7	21	0.21	2.31	90.7
HID2	7	21	0.21	2.14	93.3
HID3[c]	7	21	0.21	1.78	33.3
HTD2	7	21	0.21	2.28	95
HMD2	7	21	0.21	2.06	95.7

[a] 50 °C; 24 h. All units are in grams

[b] Vinyl content means the weight percent of HEMA in the total composition weight

[c] HID3 was dispersed in water (droplet size: about 30 nm) before gelation

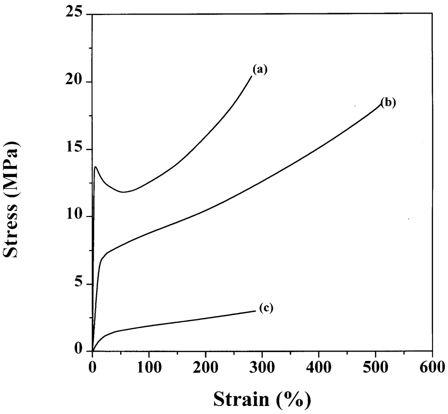


Fig. 1 Stress-strain curves for the urethane acrylate ionomer hydrogels in the dried state; *a* HID1, *b* HID2, and *c* HID3

degree of phase separation depends strongly on the interconnectivity of the ionic groups, which is achieved by the Coulombic force [11–13]. The urethane acrylate ionomer network contains a larger number of ionic groups than the polyurethane ionomer derivatives, as the reaction molar ratio of the ionic hard segment to the polyether soft segment was 2:1 (that of polyurethane ionomer derivatives is 1:1). This larger number of ionic groups seemed to lead to a favorable phase separation of the ionic groups from the network, resulting in the increased crystallinity of the network in WAXS measurements.

The phase separation of the urethane acrylate ionomer hydrogels was also confirmed by DMA. The temperature dependence of the storage modulus and the loss modulus for HID1 and HID3 gels is shown in Fig. 3. In the temperature dependence of the loss modulus, two distinct transition peaks for the HID1 gel were detected around −83.4 °C and 25.2 °C, corresponding to the glass transition temperature of polyether soft segment domains and the glass transition temperature of ionic hard segment domains (T_{gh}), respectively. This result verifies that HID gels of high ionic content were composed of two phases, the polyether soft segment domains and the ionic hard segment domains. Therefore, such rubber-like S-S curves in Fig. 1. were obtained, because the ionic hard segment domains, with a glass transition temperature above ambient, act as physical crosslinkers and as reinforcing fillers, and much purer polyether soft segment domains, with a glass

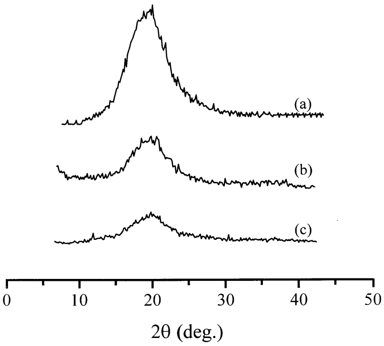


Fig. 2 Wide-angle X-ray scattering profiles of the urethane acrylate ionomer hydrogels in the dried state; *a* HID1, *b* HID2, and *c* HID3

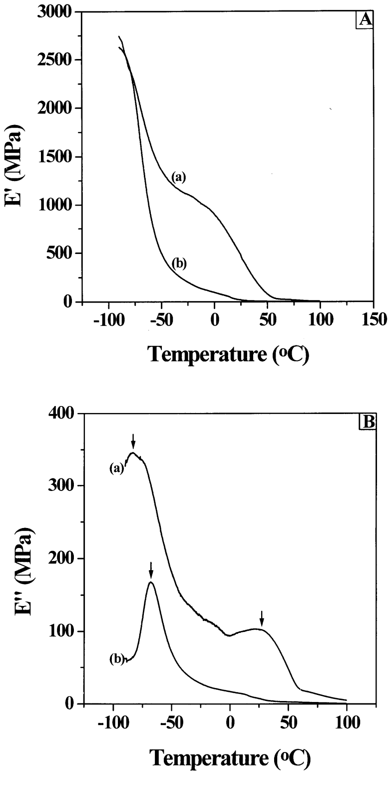


Fig. 3A, B Dynamic mechanical properties for the urethane acrylate ionomer hydrogels in the dried state; *a* HID1 and *b* HID3. **A** Temperature dependence of the storage modulus and **B** temperature dependence of the loss modulus

transition temperature below ambient, impart elastomeric character on the network. In contrast, for HID3 of low ionic content, T_{gh} could not be found. It appears that the ionic groups of the HID3 gel did not form ion aggregates and just mixed with the polyether soft segment domains, because of the charge density reduction caused by the increase in the phase volume of soft segment domains [4].

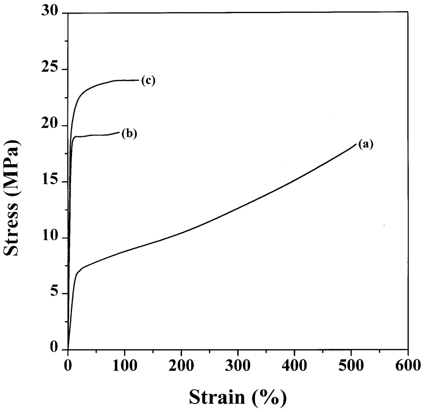


Fig. 4 Stress-strain curves for the urethane acrylate ionomer hydrogels having different kinds of diisocyanate in the dried state; *a* HID2, *b* HTD2, and *c* HMD2

The S-S curves of the hydrogels having different kinds of diisocyanate in the dried state are shown in Fig. 4. The tensile strengths of the hydrogels increased in the following order: HID2 < HTD2 < HMD2. The MDI- and TDI-based hydrogels had higher tensile strengths and initial moduli and lower elongation than the IPDI-based one. This result can be explained as a consequence of the presence of the aromatic ring which gives rise to π-electron interactions in the urethane acrylate network [12]. Therefore, the HMD2 and HTD2 gels showed higher tensile strengths and initial moduli, compared with the HID2 gel. Moreover, the HMD2 gel showed much higher tensile strength than the HTD2 gel. As Chen and coworkers reported [14, 15], MDI-based polyurethane ionomers have an ordered hard domain, i.e., semicrystalline, because of their symmetric molecular structure, while TDI-based polyurethane ionomers have a disordered hard domain, because TDI has asymmetric 2,4-isomers. With the above results, it can be said that the HMD2 gel displayed superior tensile properties to the HTD2 gel.

From these results, it is concluded that the urethane acrylate ionomer hydrogels in the dried state formed a heterophasic gel structure composed of ionic hard domains induced by ionic aggregation, and polyether soft domains. Their mechanical properties depended considerably on the ion content, the molecular weight of the soft segment, and the sort of diisocyanate.

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