

# UV-Curable Poly(ethylene glycol)-Based Polyurethane Acrylate Hydrogel

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**ABSTRACT:** Poly(ethylene glycol) (PEG) with molecular weight ( $M_n$ ) of 1000, 2000, 3000, and 4000 g/mol, four types of diisocyanate [hexamethylene diisocyanate (HDI), 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI), isophorone diisocyanate (IPDI), and toluene diisocyanate (TDI)], two types of comonomers [acrylamide (AAM) and acrylic acid (AAc)] that comprised up to 60% of the total solid were used to prepare UV-curable PEG-based polyurethane (PU) acrylate hydrogel. The gels were evaluated in terms of mechanical properties, water content as a function of immersion time and pH, and X-ray diffraction profiles of dry and swollen films. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 2703–2709, 1999

**Keywords:** polyurethane hydrogel; pH sensitivity; mechanical properties

## INTRODUCTION

Polyurethanes (PU) are a unique class of polymers that have a wide range of applications because their properties can be readily tailored by the variations of their components. Conventionally, PUs are extensively used as foams, coatings, adhesives, elastomers, and fibers.<sup>1</sup> PUs are also widely used as biomedical materials; rapid growth is expected because scientists and manufacturers are capable of tailoring the basic PU products to suit their intended applications.<sup>2</sup> In fact, PU is the most important polymer used in the biomedical area. PU hydrogels are reported to have applications as contact lenses, surgical implants, and separation membranes.<sup>3–6</sup>

UV curing saves energy and reduces or eliminates solvent emission in comparison with solvent-based systems because most formulations are 100% reactive oligomers and diluents.<sup>3,7–11</sup>

UV-curable urethane hydrogel is not only free of toxic solvent, but also minimizes possible side reactions upon application and has excellent optical properties.<sup>12–16</sup>

A UV-curable system is typically composed of reactive urethane oligomers, reactive diluents, and photoinitiators. Reactive urethane oligomer is the most important component in determining the ultimate physical properties of UV-cured coatings. Typically, it is a segmented PU oligomer tipped with acrylic functionality, such as 2-hydroxyethylacrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA). The reactive diluents are acrylic monomers that are added to modify the properties and to reduce the viscosity of the precursor liquids.

In this study, UV-curable PU acrylates were prepared from poly(ethylene glycol) (PEG), aliphatic, cycloaliphatic, and aromatic diisocyanates, acrylamide (AAM), and acrylic acid (AAc). Effects of the PEG molecular weight ( $M_n$ ), the type of diisocyanate, and the content of AAM and AAc were studied in terms of mechanical properties, water content as a function of immersion time and pH, and X-ray diffraction profiles of dried and swollen films.

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## EXPERIMENTAL

## Raw Materials

PEG was dried and degassed at 80°C, 1–2 mmHg until no bubbling was observed. Extra pure grade of 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI), hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), isophorone diisocyanate (IPDI; Scholven), dibutyltin dilaurate (DBTDL), benzophenone as photoinitiator, and *N*-methyldiethanol amine (MDEA) as photosensitizer were used without further purification. AAc was purchased from Junsei (Japan), distilled at reduced pressure after removal of the inhibitor, and the middle fraction was used. AAm was purchased from Junsei (Japan), recrystallized, and used.

## Synthesis

PEG and diisocyanate (1 : 2 by mol) were charged into a 500-mL round-bottom, separable flask equipped with a mechanical stirrer, thermometer, and condenser with drying tube. Approximately 300 ppm of DBTDL was added. The urethane forming reaction proceeded at 80°C for over 1 h, and the progress of reaction was determined by using a standard di-*n*-butylamine back titration method.<sup>9</sup> Upon obtaining the theoretical NCO value, the reaction mixture was cooled down to 40°C and HEMA was added dropwise. Tipping of the NCO-terminated prepolymer with HEMA was done for 3 h below 45°C and for 30 min at 60°C. The progress of reaction was also detected by measuring the NCO value.

The mixture of urethane acrylates, 2 wt % benzophenone (initiator), 2 wt % MDEA (accelerator), and reactive diluents were heated slightly above the ambient temperature to ensure homogeneous mixing, followed by casting on a glass plate. Films were approximately 1 mm in thickness for tensile specimens, and 0.3–0.4 mm for dynamic mechanical testing. Samples were irradiated from one side with an 80 W-UV (365 nm) lamp for 10 min at 40°C. Basic formulations are given in Table I.

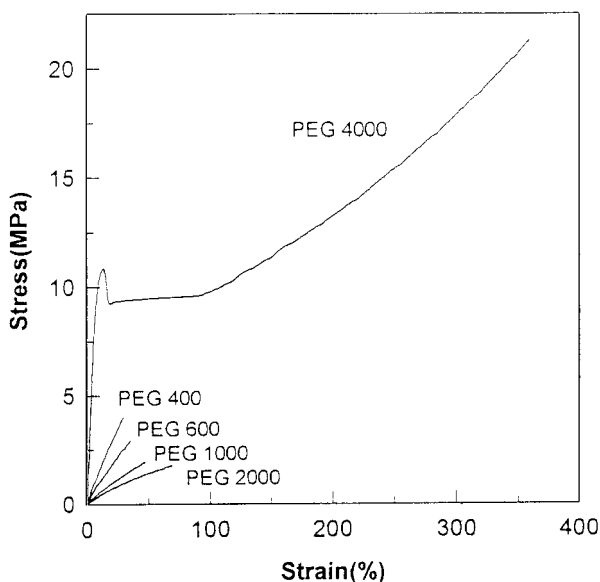
## Characterizations

Tensile tests at room temperature were performed following ASTM D-1822 with the use of a tensile tester (Tinius Olsen 1000) at a crosshead speed of 5 mm/min; an average of at least five measurements was taken to report. Thermal properties at the equilibrium swollen state were

**Table I.** Formulations of UV-curable PU Acrylate

| A. Effect of PEG Molecular Weights<br>PU Prepolymer End-Capped with HEMA  |                    |                       |                 |               |
|---------------------------------------------------------------------------|--------------------|-----------------------|-----------------|---------------|
| Run #                                                                     | PEG<br>(mol %)     | HDI<br>(mol %)        | HEMA<br>(mol %) |               |
| PEG 400                                                                   | 1                  | 2                     | 2               |               |
| PEG 600                                                                   | 1                  | 2                     | 2               |               |
| PEG 1000                                                                  | 1                  | 2                     | 2               |               |
| PEG 2000                                                                  | 1                  | 2                     | 2               |               |
| PEG 4000                                                                  | 1                  | 2                     | 2               |               |
| B. Effect of Isocyanate Types<br>PU Prepolymer End-Capped<br>with HEMA    |                    |                       |                 |               |
| Run #                                                                     | PEG2000<br>(mol %) | Isocyanate<br>(mol %) | HEMA<br>(mol %) |               |
| HDI                                                                       | 1                  | 2                     | 2               |               |
| IPDI                                                                      | 1                  | 2                     | 2               |               |
| TDI                                                                       | 1                  | 2                     | 2               |               |
| $H_{12}$ MDI                                                              | 1                  | 2                     | 2               |               |
| C. Effect of AAm Contents<br>PU Prepolymer End-Capped<br>with HEMA (wt %) |                    |                       |                 |               |
| Run #                                                                     | PEG2000<br>(mol %) | HDI<br>(mol %)        | HEMA<br>(mol %) | AAm<br>(wt %) |
| AAm 0                                                                     | 1                  | 2                     | 2               | 0             |
| AAm 10                                                                    | 1                  | 2                     | 2               | 10            |
| AAm 20                                                                    | 1                  | 2                     | 2               | 20            |
| AAm 40                                                                    | 1                  | 2                     | 2               | 40            |
| AAm 60                                                                    | 1                  | 2                     | 2               | 60            |
| D. Effect of AAc Contents<br>PU Prepolymer End-Capped<br>with HEMA (wt %) |                    |                       |                 |               |
| Run #                                                                     | PEG2000<br>(mol %) | HDI<br>(mol %)        | HEMA<br>(mol %) | AAc<br>(wt %) |
| AAc 0                                                                     | 1                  | 2                     | 2               | 0             |
| AAc 10                                                                    | 1                  | 2                     | 2               | 10            |
| AAc 20                                                                    | 1                  | 2                     | 2               | 20            |
| AAc 40                                                                    | 1                  | 2                     | 2               | 40            |
| AAc 60                                                                    | 1                  | 2                     | 2               | 60            |

performed with a heating rate of 10°C/min by using a differential scanning calorimeter (Seiko DSC 220). Crystal structures were investigated



**Figure 1.** Stress-strain behavior of the UV-curable PU acrylates that are based on PEGs with different molecular weights.

with an X-ray diffractometer by using nickel-filtered  $\text{CuK}\alpha$  radiation (40 kV/40 mA,  $2^\circ\text{C}/\text{min}$ ).

Swelling behavior was investigated for all compositions after removing the unreacted materials in water at room temperature. Swell of the film was measured in buffer solutions ( $\text{NaOH}/\text{HCl}$ ) of broad pH (2-9) and temperature ( $4$ - $80^\circ\text{C}$ ) ranges, and are reported in terms of water content defined below.

Water content (wt %)

$$= \frac{(\text{Weight of swollen gel} - \text{weight of dried gel})}{\text{Weight of swollen gel}} \times 100$$

To determine the rate of swell, water contents were measured as a function of time.

## RESULTS AND DISCUSSION

### Mechanical Properties

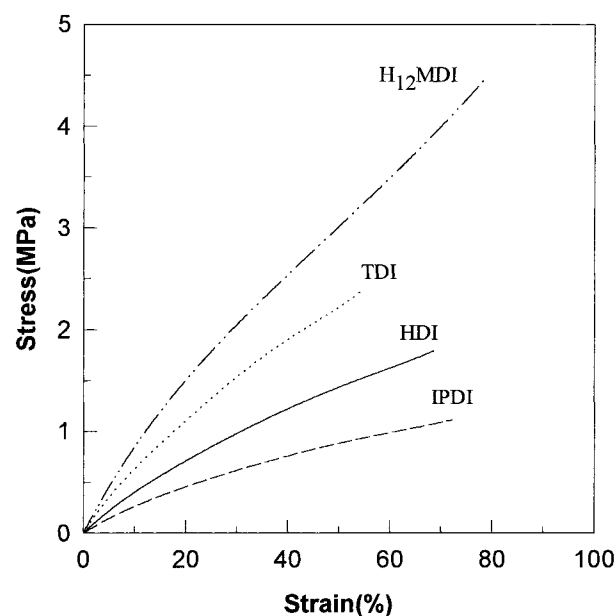
Stress-strain behavior of the UV-curable PU acrylates that are based on PEGs with different molecular weights is given in Figure 1. When the  $M_n$  of PPG is not long enough for crystallization ( $\leq 2000$ ), both the initial modulus ( $E$ ) and the strength ( $\sigma_b$ ) decrease and elongation at the break ( $\epsilon_b$ ) increases with increasing  $M_n$  of PEG.

Because the isocyanate-terminated PU prepolymers were encapped with HEMA,  $M_n$  of PEG is directly proportional to the molecular weight between crosslinks ( $M_c$ ). Therefore, the decrease in modulus and strength with increasing  $M_n$  of PEG is expected. However, PEG 4000 shows necking and by far the highest  $E$ ,  $\sigma_b$ , and  $\epsilon_b$ . This is simply due to crystallization of PEG segments to be discussed later.

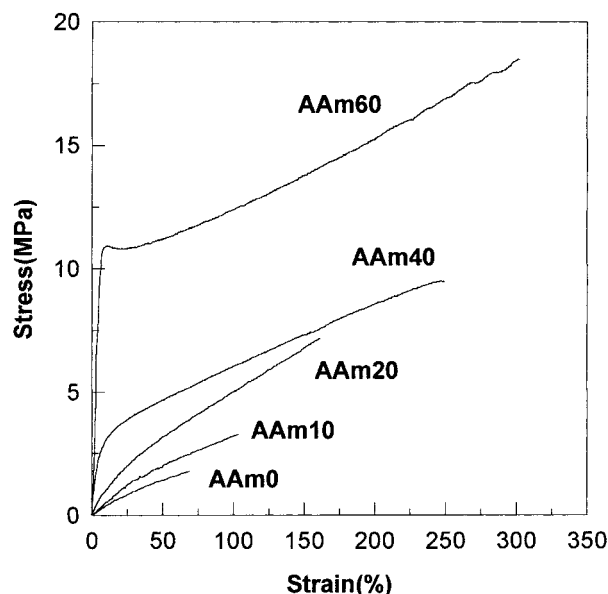
Figure 2 shows stress-strain behavior of the UV-curable PU acrylates that are based on PEG 2000 with various types of diisocyanate.  $E$ ,  $\sigma_b$ , and  $\epsilon_b$  increase with the order of  $\text{IPDI} < \text{HDI} < \text{TDI} < \text{H}_{12}\text{MDI}$ . It seems that the symmetrical structure of  $\text{H}_{12}\text{MDI}$  gives the highest, and the flexible aliphatic chain of HDI gives lower, tensile properties. Figures 3 and 4 show stress-strain behavior of UV-curable PU acrylates that are based on PEG 2000 with different AAm and AAc contents, respectively. In both series,  $E$ ,  $\sigma_b$ , and  $\epsilon_b$  increase with increasing reactive diluent contents. The increase of  $E$  and  $\sigma_b$  is caused by the incorporation of rigid chains. Notably, PU acrylate containing high AAm (40 and 60%) shows yield and necking, probably because of the crystallization of polyacrylamide (PAAm) block.

### Swelling Behavior

Figure 5 shows equilibrium water content of the UV-curable PU acrylates that are based on PEGs



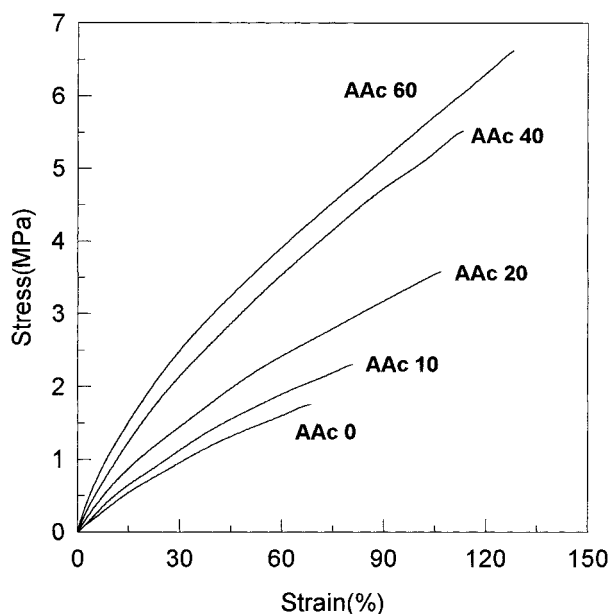
**Figure 2.** Stress-strain behavior of the UV-curable PU acrylates that are based on PEG 2000 with various types of diisocyanate.



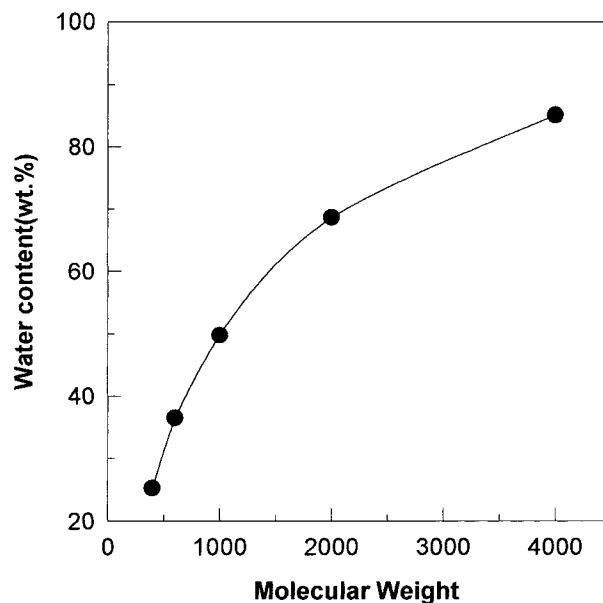
**Figure 3.** Stress-strain behavior of the UV-curable PU acrylates that are based on PEG 2000 with different AAm contents.

with different  $M_n$ . Swell of the PEG-based PU acrylate gels depends mainly on the crosslinking density. It was found that the ability to swell in water increased with increasing  $M_n$  of PEG due to the decreased crosslinking density.

Figure 6 shows the effect of the diisocyanate

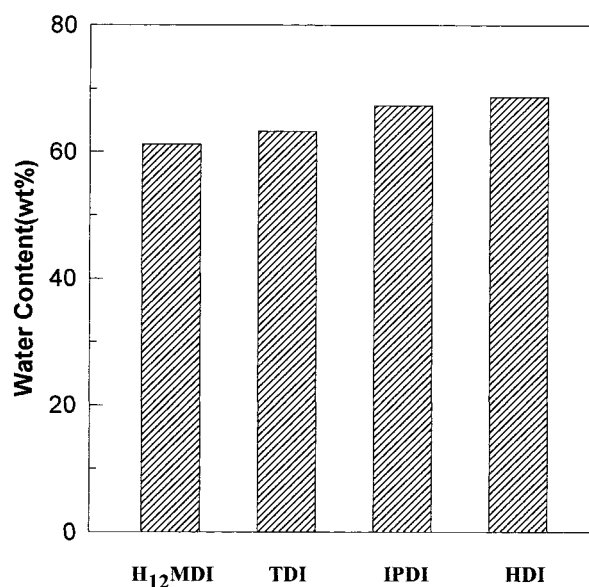


**Figure 4.** Stress-strain behavior of the UV-curable PU acrylates that are based on PEG 2000 with different AAc contents.

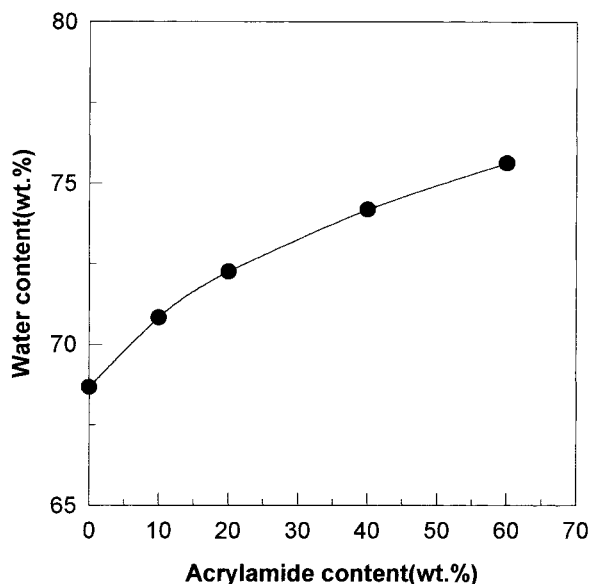


**Figure 5.** Equilibrium water content of the UV-curable PU acrylates that are based on PEGs with different molecular weights.

type on the swell of the gel. It is seen that HDI gives the highest water swell, probably because of the linear and flexible nature of the hard domains, whereas  $H_{12}$ MDI gives the lowest, perhaps because of the symmetrical and cohesive structure of its hard domains.

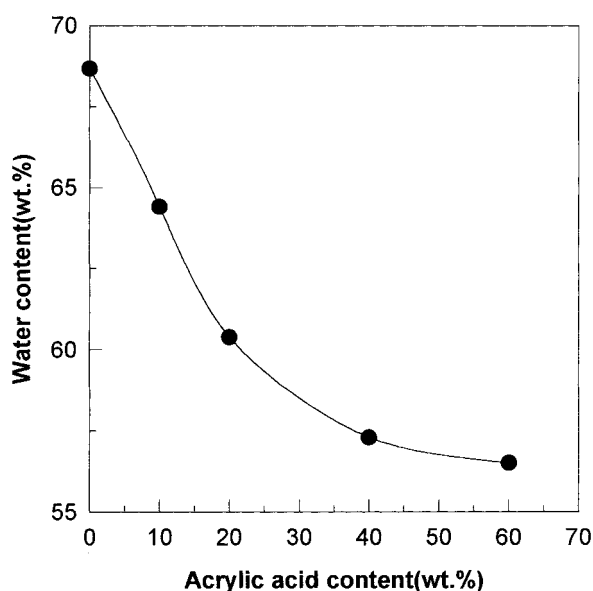


**Figure 6.** Equilibrium water content of the UV-curable PU acrylates that are based on PEG 2000 with various types of diisocyanate.

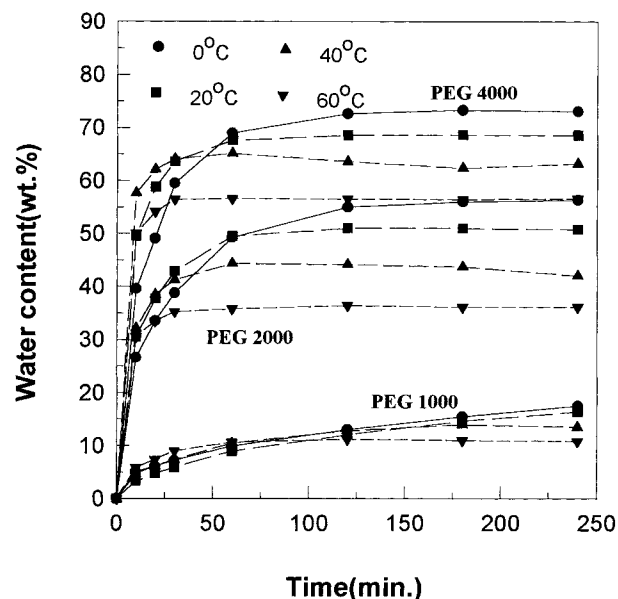


**Figure 7.** Equilibrium water content of the UV-curable PU acrylates that are based on PEG 2000 with different AAm contents.

Figures 7 and 8 show swell of PEG 2000-based PU acrylates with different AAm and AAc contents, respectively. In the case of AAm, equilibrium water content increases with increasing AAm content caused by the increased hydrophilicity and the decreased overall crosslinking density. On the other hand, equilibrium water content decreases



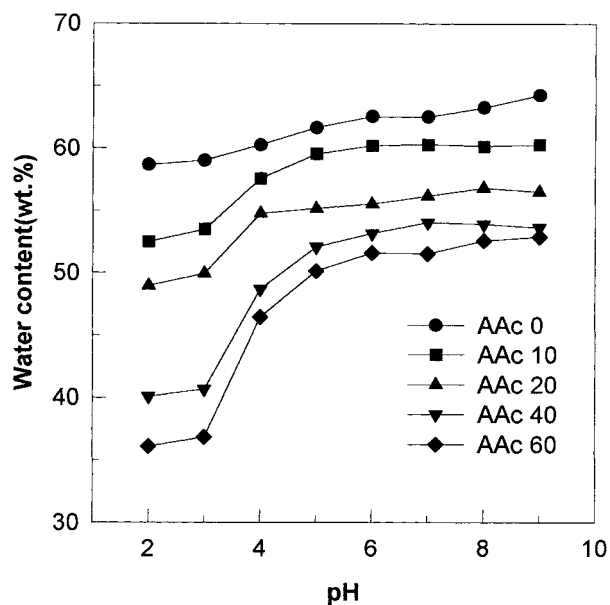
**Figure 8.** Equilibrium water content of the UV-curable PU acrylates that are based on PEG 2000 with different AAc contents.



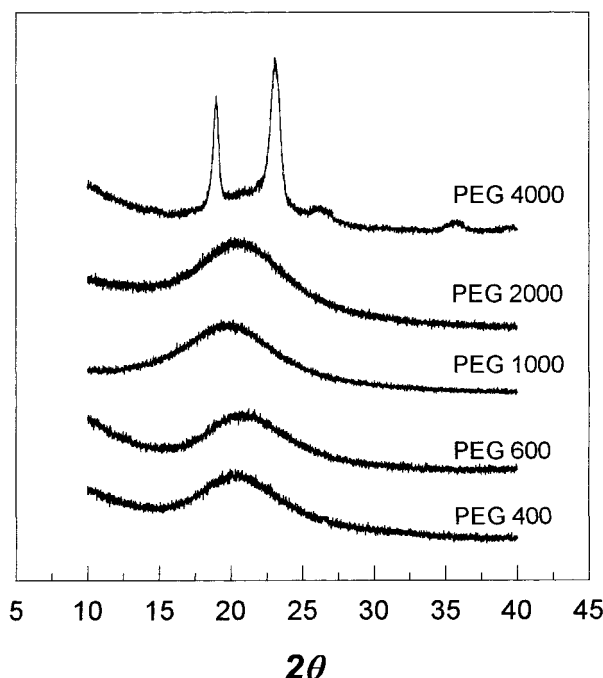
**Figure 9.** Time- and temperature- dependent water content of the UV-curable PU acrylates that are based on PEGs with different molecular weights.

with increasing AAc contents because of the formation of hydrogen bonds between PEG and polyacrylic acid (PAAc) segments in water.<sup>17,18</sup>

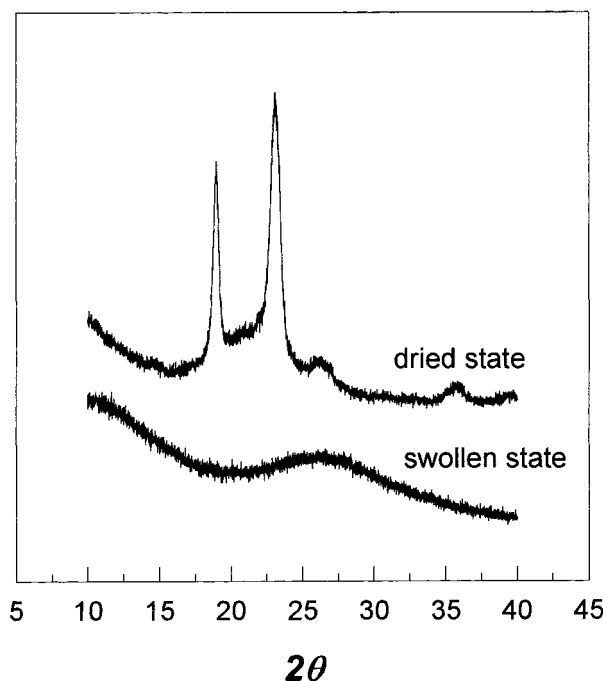
Figure 9 shows time- and temperature-dependent swell of UV-curable PU acrylates that are based on different  $M_n$  of PEG. As the temperature



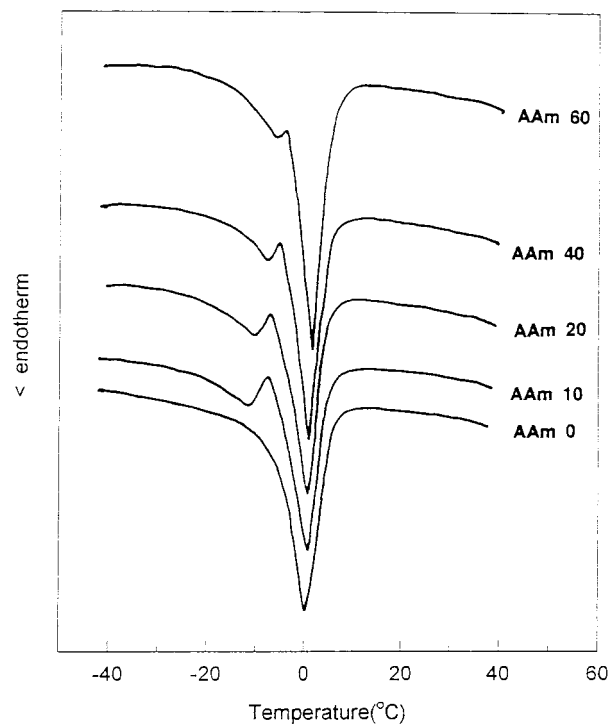
**Figure 10.** pH-dependent swelling behavior of the UV-curable PU acrylates that are based on PEGs with different AAc contents.



**Figure 11.** X-ray diffraction profile for the UV-curable PU acrylates that are based on PEGs with different molecular weights.



**Figure 12.** X-ray diffraction profile of swollen and dried films of the UV-curable PU acrylates that are based on PEG 4000.



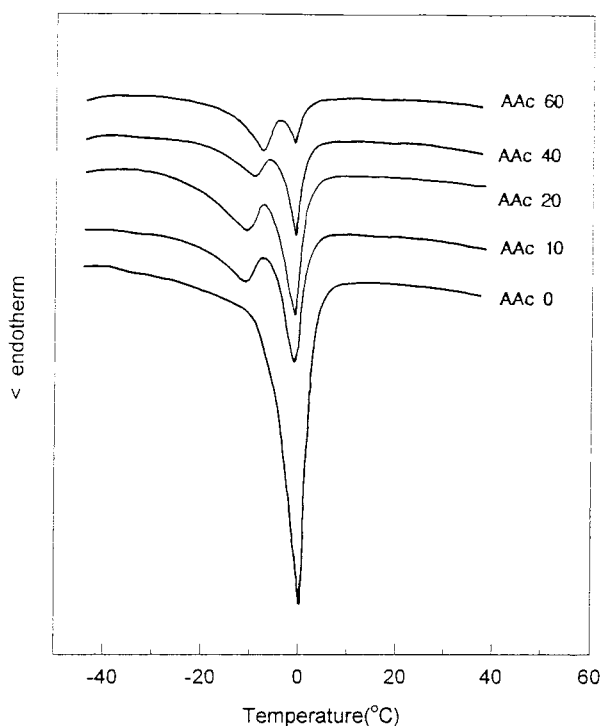
**Figure 13.** DSC thermograms of the UV-curable PU acrylates that are based on PEG 2000 with different AAm contents.

increases, the initial rate of swell increases because of the increased activity of water, whereas equilibrium water content decreases because of the low critical solution temperature (LCST) behavior of PEG.<sup>19-22</sup>

Figure 10 shows pH-dependent swell of the UV-curable PU acrylates based on different AAc contents at 20°C. Water content of the hydrogel decreases with increasing AAc contents, and transition from low to high water content is obtained at about pH 4. As the pH of water increases >4, COOH groups of AAc are ionized and repulsions between networks act as swelling forces, leading to a significant increase in the water swell of the gel.

#### X-ray Diffraction

Figure 11 shows X-ray diffraction profiles for the UV-curable PU acrylates that are based on different  $M_n$ 's of PEG. Only with the PEG 4000, the diffraction profile shows a sharp peak, indicative of PEG segment crystallization. Figure 12 shows the X-ray diffraction profile for the UV-curable PU acrylate in swollen and dried states. It is seen that the crystalline structure of PEG 4000 is broken down by water.



**Figure 14.** DSC thermograms of the UV-curable PU acrylates that are based on PEG 2000 with different AAc contents.

### Thermal Properties

Figures 13 and 14 show DSC thermograms of the UV-curable PU acrylates that are based on PEG 2000 with different AAm and AAc contents. Heat of fusion ( $\Delta H_f$ ) and the crystalline melting temperature ( $T_m$ ) of water slightly increase with increasing AAm content because of the increasing water content. However, with the increase of AAc contents,  $\Delta H_f$  of water decreases due to the decreasing water content in hydrogel. Because of the hydrogen bondings between PEG and PAAC networks, hydrogels collapse with increasing AAc content and  $\Delta H_f$  of water decreases.

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