

# Vinyl ether-based polyacetal polyols with various main-chain structures and polyurethane elastomers prepared therefrom: Synthesis, structure, and functional properties

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**ABSTRACT:** Novel acid degradable polyacetal polyols and polyacetal polyurethanes able to controlled acid degradation were developed. Polyacetal polyols with various main-chain structures were synthesized by polyaddition of various vinyl ethers with a hydroxyl group [4-hydroxy butyl vinyl ether ( $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$ ), 2-hydroxy ethyl vinyl ether ( $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{OH}$ ), diethylene glycol monovinyl ether ( $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{OH}$ ), and cyclohexanedimethanol monovinyl ether ( $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-\text{OH}$ )] with *p*-toluenesulfonic acid monohydrate (TSAM) as a catalyst in the presence of the corresponding diols [1,4-butanediol ( $\text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$ ), ethylene glycol ( $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$ ), diethylene glycol ( $\text{HO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{OH}$ ), and 1,4-cyclohexanedimethanol ( $\text{HO}-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-\text{OH}$ )], respectively. Polyacetal polyurethanes were prepared by a two-step polymerization, using the synthesized polyacetal polyols, 4,4'-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BD) as a chain extender. Depending on the main-chain structures, these polyurethanes had different glass transition temperature (from  $-44$  to  $19^\circ\text{C}$ ) and properties such as hydrophobic or hydrophilic. Polyurethanes containing the hydrophilic main-chain exhibited the thermoresponsiveness and had the certain volume phase transition temperature (VPPT). The polyacetal polyurethanes were flexible elastomers around room temperature ( $\sim 25^\circ\text{C}$ ) and thermally stable ( $T_d \geq 310^\circ\text{C}$ ) and additionally exhibited smooth degradation with a treatment of aqueous acid in THF at room temperature to give the corresponding raw material diols.

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## INTRODUCTION

Acetals are commonly employed as a protecting group for aldehydes and ketones, because the acetal linkages  $[-\text{O}-\text{C}(\text{R})(\text{R}')-\text{O}-]$  are stable to bases, reducing agents, and various nucleophiles, but easily converted into the corresponding carbonyl compounds  $[\text{O}=\text{C}(\text{R})(\text{R}')] ]$  and alcohols  $[\text{R}''-\text{OH}$  and  $\text{R}'''-\text{OH}]$  via hydrolysis degradation of acetal linkages by treatment with aqueous acid. Hydrolysis rates under acidic conditions increased in the order  $\text{R}''-\text{O}-\text{CH}_2-\text{O}-\text{R}''' < \text{R}''-\text{O}-\text{CH}(\text{R}')-\text{O}-\text{R}''' < \text{R}''-\text{O}-\text{C}(\text{R})(\text{R}')-\text{O}-\text{R}'''$  as would be expected for the stability of a carbocation intermediate.<sup>1</sup> Commercially manufactured polyacetals are polyoxymethylenes (POM)  $[-(\text{CH}_2\text{O})_n-]$ ; their acetal linkages are  $-\text{O}-\text{CH}_2-\text{O}-$ , thus the most stable to acid) obtained by polymerization based on formaldehyde or trioxane monomers and are widely used as engineering plastics.<sup>2-4</sup> In contrast, polyacetals of  $-\text{O}-\text{CH}(\text{CH}_3)-\text{O}-$  linkages, which are more sensitive to acid-hydrolysis, were primarily synthesized by polycondensation of

acetaldehyde and diols.<sup>5</sup> In the polycondensation method, by-product water should be removed from the reaction mixture to obtain high-molecular-weight polymers. As an entirely different and more straightforward route, polyaddition of divinyl ethers and diols<sup>6</sup> and self-polyaddition of vinyl ethers with a hydroxyl group<sup>7,8</sup> are effective, where the acid-catalyzed addition reaction between a vinyl ether group and a hydroxyl group of these monomers produces polyacetals in the stepwise manner without the elimination of a small molecule and hence would be more applicable for industry manufacturing (Table I).

Chemistry of vinyl ether-based polyacetal could lead to commodity polymer materials with suitable degradability for chemical recycling. Our previous study was directed toward the development of environmentally friendly, chemically recyclable polymers with polyacetal segments. Acetal linkages-incorporated polyurethanes<sup>9,10</sup> and epoxy resins<sup>11,12</sup> undergo smooth degradation to produce raw materials for chemical recycling. In this

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**Table I.** List of Used Abbreviations in This Study

HBVE	4-Hydroxy butyl vinyl ether
HEVE	2-Hydroxy ethyl vinyl ether
DEGV	Diethylene glycol monovinyl ether
CHMVE	Cyclohexanedimethanol monovinyl ether
BD	1,4-Butandiol
EG	Ethylene glycol
DEG	Diethylene glycol
CHDM	1,4-Cyclohexanedimethanol
PTMG	Poly(tetramethylene ether) glycol
MDI	4,4'-Diphenylmethane diisocyanate
TSAM	<i>p</i> -Toluenesulfonic acid monohydrate
MALDI-TOF-MS	Matrix-assisted laser desorption ionization time of flight mass spectrometry
TG-DTA	Thermogravimetry-differential thermal analysis
DMA	DMA
VPTT	Volume phase transition temperature

study, we aim to provide thermoplastic polyurethane elastomers with a wide range of properties like hydrophobicity to hydrophilicity, flexibility to rigidity, and specific functions as well as degradability or chemical recyclability. For this, we employed four vinyl ethers with a hydroxyl group ( $\text{CH}_2=\text{CH}-\text{O}-\text{R}-\text{OH}$ ) and a different central R chain, 4-hydroxybutyl vinyl ether (HBVE), 2-hydroxyethyl vinyl ether (HEVE), diethylene-glycol monovinyl ether (DEGV), and cyclohexanedimethanol monovinyl ether (CHMVE), for self-polyaddition reaction leading to polyacetal polyols with various main structures in the presence of the corresponding diols [1,4-butanediol (BD), ethylene glycol (EG), diethylene glycol (DEG), and 1,4-cyclohexanedimethanol (CHDM)] (Scheme 1) and new polyurethanes derived from them (Scheme 2). Depending on their repeating

main chains [ $-\text{OCH}(\text{CH}_3)\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ;  $-\text{OCH}(\text{CH}_3)\text{O}-\text{CH}_2\text{CH}_2-$ ;  $-\text{OCH}(\text{CH}_3)\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ;  $-\text{OCH}(\text{CH}_3)\text{O}-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-$ ], the obtained polyurethanes exhibit different glass transition temperature, hydrophilicity, and thermoresponsive behavior, and similar degradability or stability.

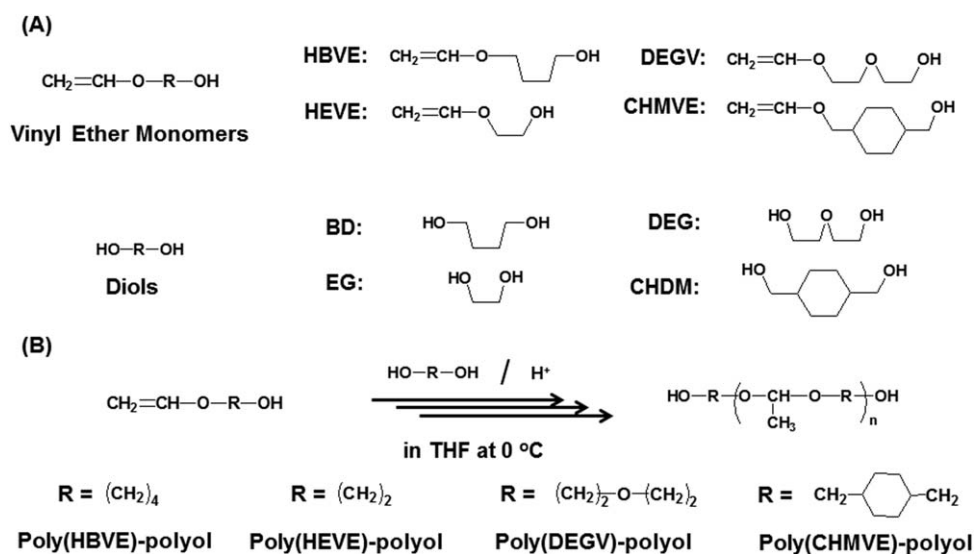
## EXPERIMENTAL

### Materials

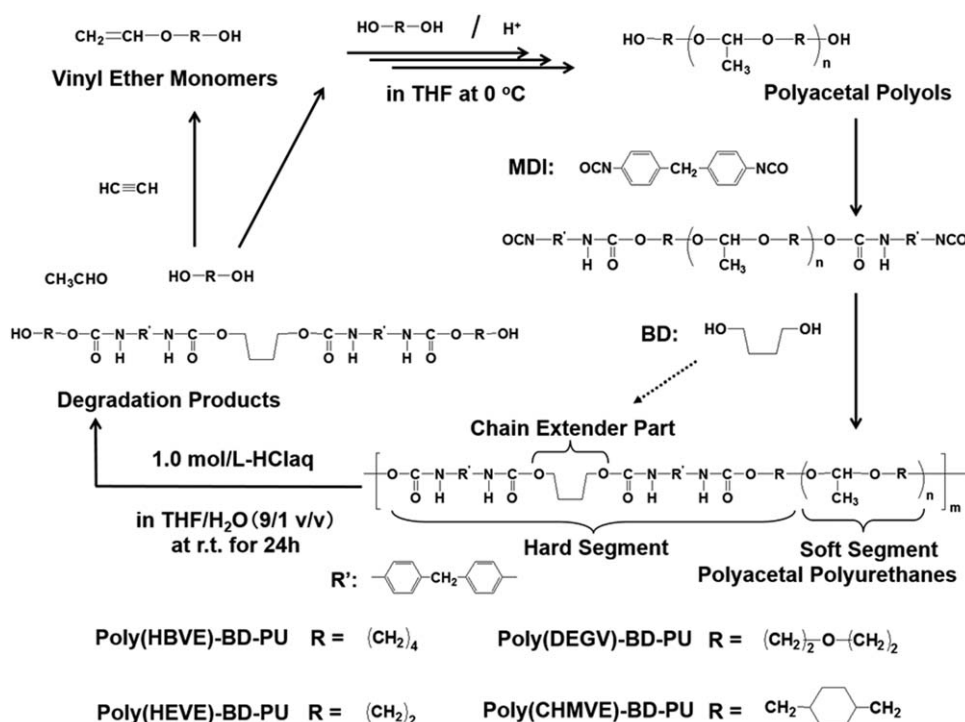
HBVE, HEVE, DEGV, and CHMVE (isomer mixture *cis:trans* = 20:80) were obtained from Nippon Carbide Industries (Tokyo, Japan), dried with potassium carbonate overnight, and doubly distilled over calcium hydride under reduced pressure before use. BD, EG, and DEG were purchased from Wako Pure Chemical (Tokyo, Japan), dehydrated with calcium chloride for several days, and doubly distilled over calcium hydride under reduced pressure. CHDM was purchased from Wako Pure Chemical (Tokyo, Japan) and dried under reduced pressure (5 mmHg) at 40 °C for 2 h before use. Tetrahydrofuran (THF; Kishida Chemical, Osaka, Japan) and *N,N*-dimethylformamide (DMF; Wako Pure Chemical, Tokyo, Japan) were dehydrated with molecular sieves (3A 1/16) for several days and doubly distilled over lithium aluminum hydride under atmospheric pressure and over calcium hydride under reduced pressure (20 mmHg), respectively. Poly(tetramethylene ether) glycol (PTMG) was purchased from Aldrich and dried with bubbling dry nitrogen gas under reduced pressure (5 mmHg) at 40 °C for 6 h. Other materials were used without further purification.

### Polymerization Procedures

**Synthesis of Polyacetal Polyols.** Synthesis of polyacetal polyols was conducted by polyaddition of HBVE, HEVE, DEGV, and CHMVE with *p*-toluenesulfonic acid monohydrate (TSAM) as a catalyst in the presence of the corresponding diols (BD, EG, DEG, and CHDM, respectively) in THF at 0 °C maintained by a methanol bath.<sup>8</sup> A glass flask equipped with three-way stopcock was baked at about 400 °C on a heat gun just before the reaction. As a typical example, synthesis of poly(HEVE)-polyol is



**Scheme 1.** (A) Structures of vinyl ether monomers and diols. (B) Synthesis of polyacetal polyols: poly(HBVE)-polyol, poly(HEVE)-polyol, poly(DEGV)-polyol, and poly(CHMVE)-polyol.



**Scheme 2.** Synthesis and chemical recycling of polyacetal polyurethanes: poly(HBVE)-BD-PU, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, and poly(CHMVE)-BD-PU.

described below. HEVE (31.10 mL, 0.347 mol) and EG (0.92 mL, 0.0165 mol) were dissolved in THF (62.98 mL) in a glass flask of 200 mL (monomer solution). The reaction was initiated by adding the solution of a catalyst (5 mL) to the monomer solution (95 mL) at  $0^\circ\text{C}$ , stirred for 4 h at the same temperature, and terminated by adding ammoniacal methanol:  $[\text{HEVE}]_0 = 3.47 \text{ M}$ ;  $[\text{EG}]_0 = 0.165 \text{ M}$ ;  $[\text{TSAM}]_0 = 5.0 \text{ mM}$ . The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with 10% sodium carbonate aqueous solution, and saturated aqueous sodium chloride to remove the residual acid catalyst, evaporated to remove  $\text{CH}_2\text{Cl}_2$  and THF, and vacuum-dried to give the product polymers. For further purification, the obtained polyols were dried by bubbling dry nitrogen gas under reduced pressure (5 mmHg) at  $40^\circ\text{C}$  for 6 h. For the synthesis of poly(HBVE)-polyol, poly(DEGV)-polyol, and poly(CHMVE)-polyol, the similar procedures were employed and the concentrations of the reagents in each system were as follows:  $[\text{HBVE}]_0 = 3.47 \text{ M}$ ,  $[\text{BD}]_0 = 0.225 \text{ M}$ ,  $[\text{TSAM}]_0 = 5 \text{ mM}$ ;  $[\text{DEGV}]_0 = 3.46 \text{ M}$ ,  $[\text{DEG}]_0 = 0.260 \text{ M}$ ,  $[\text{TSAM}]_0 = 5 \text{ mM}$ ;  $[\text{CHMVE}]_0 = 3.47 \text{ M}$ ,  $[\text{CHDM}]_0 = 0.350 \text{ M}$ ,  $[\text{TSAM}]_0 = 5 \text{ mM}$ . Using the following formula, the feed ratio of vinyl ether monomers and diols were determined to obtain polyacetal polyols with  $M_n$  of 2000.

$$X_n = (r + 1)/(r - 2rp + 1)$$

$X_n$  is number-average degree of polymerization,  $r$  is molar ratio of functional groups ( $[\text{vinyl ether group}]_0/[\text{hydroxyl group}]_0$ ), and  $p$  is extent of reaction ( $p = 1$ )

**Synthesis of Polyacetal Polyurethanes.** Polyacetal polyurethanes were synthesized by a two-step polymerization at one atmospheric pressure. The polymerization was conducted under an

inert dry nitrogen atmosphere in the four-necked separable flask of 500 mL equipped with a mechanical stirrer, a reflux condenser, a calcium chloride guard tube, and a nitrogen inlet tube. The molar ratio of polyol:MDI:BD was 1:2:1. As a typical example, synthesis of poly(HEVE)-BD-PU is described below. In the first step, MDI (4.97 g, 0.020 mol) as a diisocyanate (hard segment part) was placed in the flask, and poly(HEVE)-polyol (the hydroxyl content,  $[\text{OH}] = 1.19 \text{ mmol/g}$  measured by acetylation method; 16.7 g, 0.010 mol) as a polyol (soft segment part) was added dropwise at  $85^\circ\text{C}$  for 3 h under smooth stirring. Before the second step of the synthesis, the isocyanate content of the reaction solution containing the prepolymer was measured by the secondary amine addition method using dibutylamine as an addition reagent, hydrochloric acid as a titration reagent, and bromophenol blue as an indicator. On the basis of the measured isocyanate content, BD (0.79 g, 0.009 mol) as a chain extender (hard segment part) was added, and the resulting reaction mixture was stirred for 2.5 h at the same temperature. During the polymerization reaction, DMF (prewarmed at  $60^\circ\text{C}$ ) as a solvent was added for smooth stirring. After cooling the resulting solution to room temperature, the produced polymer was precipitated into a large amount of methanol (ca. 1 L). The recovered polymer was washed with methanol and vacuum-dried for several days. Film specimens of polyurethanes were prepared through the casting of 5 wt % polymer solutions in THF onto a Teflon mold at room temperature for three days and vacuum drying for several days. Poly(HBVE)-BD-PU (the hydroxyl content of poly(HBVE)-polyol,  $[\text{OH}] = 1.23 \text{ mmol/g}$ ), poly(DEGV)-BD-PU (the hydroxyl content of poly(DEGV)-polyol,  $[\text{OH}] = 0.869 \text{ mmol/g}$ ), and poly(CHMVE)-BD-PU (the hydroxyl content of poly(CHMVE)-polyol,  $[\text{OH}] = 0.995 \text{ mmol/g}$ )

g) were synthesized by the similar way described above. PTMG-BD-PU (the hydroxyl content of PTMG,  $[\text{OH}] = 0.960 \text{ mmol/g}$ ) was also synthesized using commercial PTMG (Aldrich TERA-THANE 2000 polyether glycol) as a control sample of polyacetal polyurethanes.

### Measurements

$^1\text{H}$  (500 MHz) NMR spectra were recorded on a Jeol JNM-ECX500II FT-NMR instrument in toluene- $d_8$ , dimethyl sulfoxide- $d_6$  or THF- $d_8$  at room temperature with tetramethylsilane as an internal standard. The molecular weight distributions (MWDs) of polyacetal polyols and the degradation products of polyurethanes were measured by GPC in THF (at a 1.0 mL/min flow rate) at room temperature on a Shimadzu LC-10AD chromatograph equipped with one polystyrene gel precolumn (Shodex A-800P), three polystyrene gel columns (two Shodex A-80M and one KF-802.5) and a Shimadzu RID-6A refractive index detector. The number-average molecular weight ( $M_n$ ), the weight-average molecular weight ( $M_w$ ), and polydispersity ratio [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] were calculated from chromatograms on the basis of a polystyrene calibration obtained with six polystyrene standards whose  $M_n$ 's were 8,420,000, 775,000, 168,000, 50,000, 17,700, and 2,800. The MWDs of polyurethanes were measured by gel permeation chromatography (GPC) in chloroform (at a 1.0 mL/min flow rate) at 40 °C on a Shimadzu LC-10AD chromatograph equipped with one polystyrene gel guard column (TOSOH TSK guard column), three polystyrene gel columns (Shodex K-807L, K-805L and K-804L) and a Shimadzu RID-6A refractive index detector. The  $M_n$ ,  $M_w$ , and  $M_w/M_n$  were calculated from chromatograms on the basis of a polystyrene calibration obtained with the same set of six polystyrene standards described above. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed with a Bruker Daltonics autoflex spectrometer (reflector mode) equipped with a 337 nm nitrogen laser. In general, mass spectra from 50 shots were accumulated to produce a final spectrum. Peptide calib standard mono was used as inter standards to calibrate the mass scale. Samples were dissolved in THF with 1,8,9-trihydroxyanthracene (dithranol) as a matrix and sodium trifluoroacetate as an added salt (polymer sample/dithranol/sodium trifluoroacetate = 1/8/1 weight ratio). Thermogravimetry-differential thermal analysis (TG-DTA) was conducted with a Rigaku TG-DTA 8078G1 under a nitrogen atmosphere. The temperature range was room temperature to 650 °C, and heating rate was at 10 °C/min. The thermal decomposition temperature ( $T_d$ ) was defined as the temperature of 5% weight loss of sample. Differential scanning calorimetry (DSC) was performed with a Rigaku Thermo Plus DSC8230L under a nitrogen atmosphere. The temperature range was -120 to +150 °C, and the heating and cooling rate was 5 °C/min. Glass transition temperature ( $T_g$ ) was defined as the temperature of the midpoint of the change in heat capacity on second heating scan. Weight of samples was 0.01 g in both TG-DTA and DSC measurement. The hydroxyl content of the polyols was measured by acetylation method. A polymer sample (0.3 g) was dissolved in 5 mL-3 vol % of acetic anhydride in pyridine (acetylating agent) and the mixture was heated at 95 °C for 2 h.

After addition of water of 15 mL, the remaining acetic acid was back-titrated with 0.05 mol/L ethanolic potassium hydroxide using phenolphthalein as an indicator. The isocyanate content in the polymerization system for polyurethane formation was measured by secondary amine addition method. A product sample (0.2 g) in the reaction system was dissolved in 10 mL benzene solution of 1.7 vol % of dibutylamine (secondary amine addition reagent) and the mixture was heated at 60 °C for 30 min. After cooling the reaction solution to room temperature, the remaining dibutylamine was back-titrated with 0.10 mol/L ethanolic hydrochloric acid using bromophenol blue as an indicator. The cloud point of the polymers in aqueous solutions (1 wt %) was measured with a Jasco V-550 UV/Vis spectrometer equipped with a Peltier-type thermostatic cell holder ETC-505T. The transmittance at 500 nm was monitored at a 1.0 °C/min heating rate. The dynamic mechanical analysis (DMA) was carried out with a UBM Rheogel-E4000 viscoelastic analyzer. Temperature scans at a frequency of 1 Hz were carried out at heating rate of 2 °C/min. The temperature range was -120 to +150 °C. The film specimens used for the measurement were 20 mm long, 5.0 mm wide, and about 0.5 mm thick.

## RESULTS AND DISCUSSION

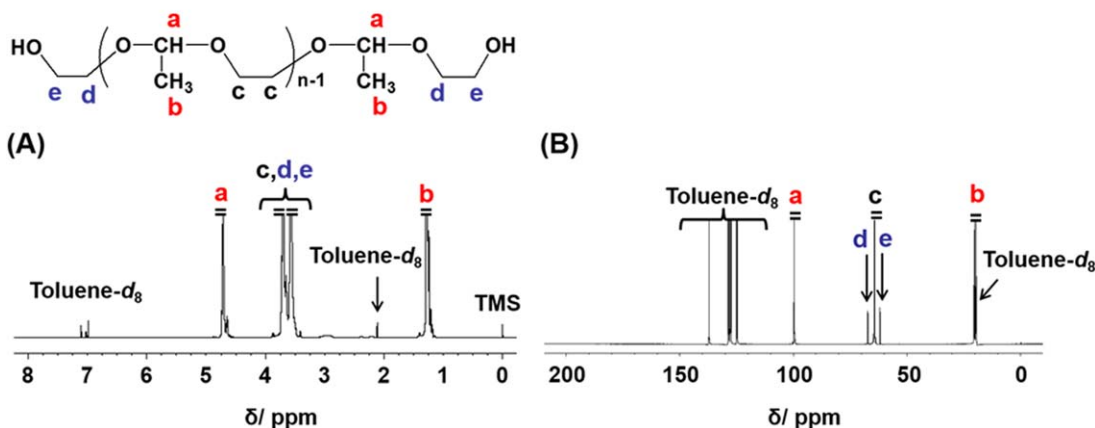
### Synthesis of Polyacetal Polyols and Polyacetal Polyurethanes

The mechanism of the polyaddition reaction (Scheme 1) is described below.<sup>7,8</sup> The catalyst first adds the vinyl ether group of monomer and the generated carbocation electrophilically and selectively adds the hydroxy group (not vinyl ether group) of another monomer to form an acetal linkage and regenerate a catalyst proton. This addition reaction occurs repeatedly in stepwise manner to give the polyacetal chain. The diol also reacts with the terminal carbocation and led to the hydroxy groups at both the chain ends. Under the present reaction conditions, the cationic chain polymerization does not take place at all and the polyaddition reaction exclusively occurs.

Figure 1(A,B) illustrate  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of poly(HEVE)-polyol, respectively. The  $^1\text{H}$  NMR spectrum exhibits the characteristic signals of the polyacetal chain generated by polyaddition of HEVE; the signals of the acetal methine (peak **a**;  $\delta$  4.72), the main-chain methylene (peak **c**;  $\delta$  3.58, 3.70), and the pendant methyl (peak **b**;  $\delta$  1.28) are observed. The peaks **d** and **e** due to the two methylene units adjacent to the terminal hydroxyl group are overlapped with those of the main-chain methylene groups (peak **c**). To detect these key terminal signals, therefore,  $^{13}\text{C}$  NMR spectrum of the same polyol was measured. In the  $^{13}\text{C}$  NMR spectrum, the signals of the terminal methylene carbons (peak **d** and **e**) are clearly observed:  $^{13}\text{C}$  NMR ( $\delta$  in toluene- $d_8$ , ppm): 19.5 (peak **b**;  $-\text{OCH}(\text{CH}_3)\text{O}-$ ), 61.8 (peak **e**;  $-\text{OCH}_2\text{CH}_2\text{OH}$ ), 64.3 (peak **c**;  $-\text{O}-\text{CH}_2\text{CH}_2-$ ), 67.2 (peak **d**;  $-\text{O}-\text{CH}_2\text{CH}_2\text{OH}$ ), 99.7 (peak **a**;  $-\text{OCH}(\text{CH}_3)\text{O}-$ ). Signals indicative of other terminal groups are not seen. These results indicate the formation of the target polyol, poly(HEVE)-polyol with two hydroxyl end groups.

The other polyacetal polyols were also characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (their spectra are not shown) and they were consistent with each target structure; poly(HBVE)-polyol:  $^1\text{H}$  NMR (in toluene- $d_8$ , ppm) the signals of the acetal

## Poly(HEVE)-polyol



**Figure 1.**  $^1H$  NMR and  $^{13}C$  NMR spectra of poly(HEVE)-polyol [ $M_n$  (Tit.) = 1,680,  $M_w/M_n$  = 2.09] in toluene- $d_8$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

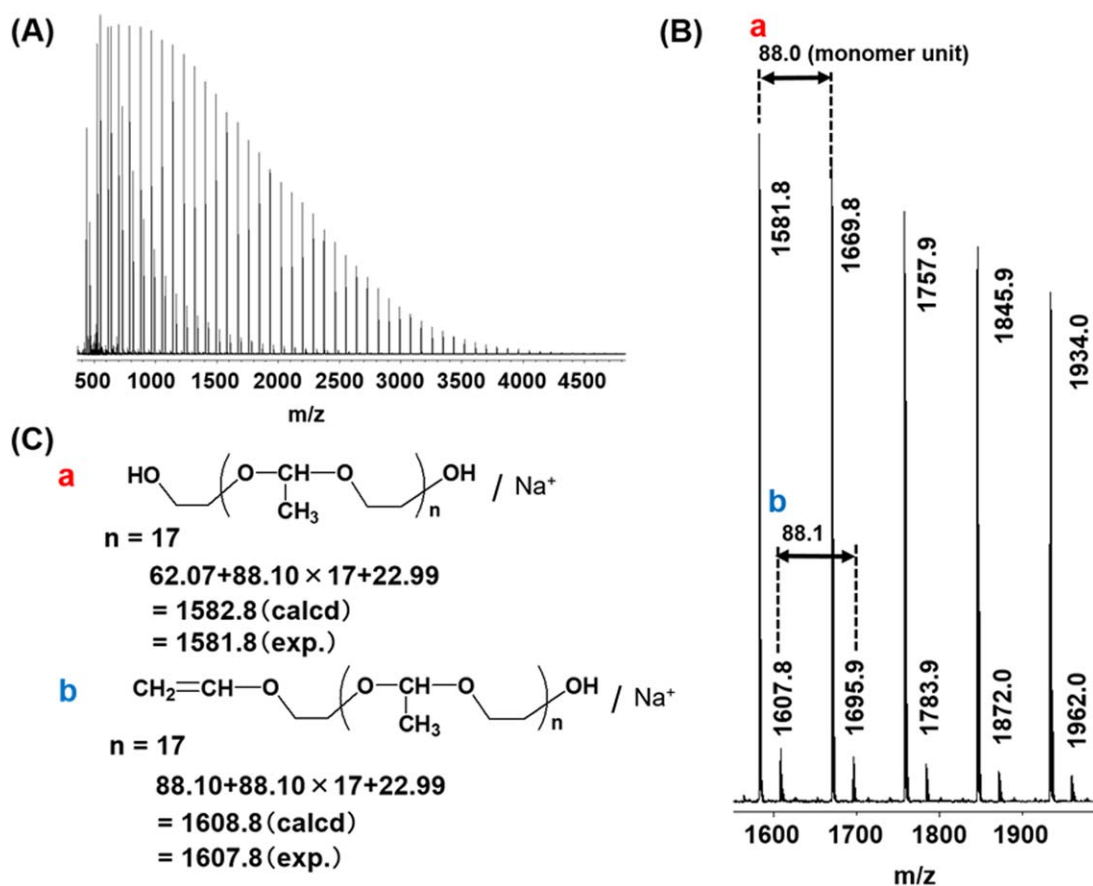
methine ( $\delta$  4.57), the main-chain methylene ( $\delta$  1.64, 3.34, 3.52), the pendant methyl ( $\delta$  1.23);  $^{13}C$  NMR ( $\delta$  in toluene- $d_8$ , ppm): 20.1 ( $-OCH(CH_3)O-$ ), 27.1 ( $-O-CH_2-CH_2-CH_2-CH_2-$ ), 30.1 ( $-O-CH_2-CH_2-CH_2-CH_2OH$ ), 62.0 ( $-O-CH_2-CH_2-CH_2-CH_2OH$ ), 64.6 ( $-O-CH(CH_3)O-$ ); poly(DEGV)-polyol:  $^1H$  NMR (in toluene- $d_8$ , ppm) the signals of the acetal methine ( $\delta$  4.72), the main-chain methylene ( $\delta$  3.54, 3.68), the pendant methyl ( $\delta$  1.27);  $^{13}C$  NMR ( $\delta$  in toluene- $d_8$ , ppm): 19.6 ( $-OCH(CH_3)O-$ ), 61.6 ( $-O-CH_2-CH_2-OCH_2-CH_2OH$ ), 64.3 ( $-O-CH_2-CH_2-OCH_2-CH_2-$ ), 70.7 ( $-O-CH_2-CH_2-OCH_2-CH_2-$ ), 72.9 ( $-O-CH_2-CH_2-OCH_2-CH_2OH$ ), 99.8 ( $-OCH(CH_3)O-$ ); poly(CHMVE)-polyol,  $^1H$  NMR (in toluene- $d_8$ , ppm): the signals of the acetal methine ( $\delta$  4.61), the main-chain cyclohexanedimethylene ( $\delta$  0.99, 1.52, 1.86, 3.17, 3.27, 3.38, 3.51), the pendant methyl ( $\delta$  1.27);  $^{13}C$  NMR ( $\delta$  in toluene- $d_8$ , ppm): 20.2 ( $-OCH(CH_3)O-$ ), 29.8, 38.6 ( $-O-CH_2-C_6H_{10}-CH_2-$ ), 68.1 ( $-O-CH_2-C_6H_{10}-CH_2OH$ ), 70.4 ( $-O-CH_2-C_6H_{10}-CH_2-$ ), 99.6 ( $-OCH(CH_3)O-$ ).

To analyze the terminal structure of the polyols further, MALDI-TOF-MS analysis of the polyacetal polyols was conducted. Figure 2 shows MALDI-TOF-MS spectra of poly(HEVE)-polyol. The major peaks (e.g., peak a) values agree well with the calculated mass of the poly(HEVE) with two hydroxyl terminal groups. Peak a (1581.8 g/mol), one of the major peaks, very fits the calculated molecular weight with  $Na^+$  (1582.8 g/mol,  $n = 17$ ). The distance between individual peaks (88.0) corresponds to the molar mass of the HEVE unit (88.10). The smaller peaks with the similar repeating distance (88.1) (e.g., peak b) are in good agreement with the calculated mass of the poly(HEVE) with one hydroxyl terminal group and one vinyl ether terminal group. Peak b (1607.8 g/mol), for example, is consistent with the calculated molecular weight with  $Na^+$  (1608.8 g/mol,  $n = 17$ ). Therefore, very minor amount of the vinyl ether-capped polymers are present in the obtained poly(HEVE)-polyol.

The other polyacetal polyols were also characterized by MALDI-TOF-MS spectra (their spectra are not shown). In MALDI-TOF-MS spectrum of poly(HBVE)-polyol, the major peaks values agree well with the calculated mass of the poly(HBVE) with

two hydroxyl terminal groups. One of the major peaks (1622.0 g/mol) very fits the calculated molecular weight with  $Na^+$  (1623.2 g/mol,  $n = 13$ ). The distance between individual peaks (116.1) corresponds to the molar mass of the HBVE unit (116.2). The smaller peaks with the similar repeating distance (116.1) are in good agreement with the calculated mass of the poly(HBVE) with one hydroxyl terminal group and one vinyl ether terminal group. One of the smaller peaks (1648.0 g/mol), for example, is consistent with the calculated molecular weight with  $Na^+$  (1649.2 g/mol,  $n = 13$ ). In MALDI-TOF-MS spectrum of poly(DEGV)-polyol, the major peaks values agree well with the calculated mass of the poly(DEGV) with two hydroxyl terminal groups. One of the major peaks (2243.1 g/mol) very fits the calculated molecular weight with  $Na^+$  (2243.6 g/mol,  $n = 16$ ). The distance between individual peaks (132.1) corresponds to the molar mass of the DEGV unit (132.2). The smaller peaks with the similar repeating distance (132.1) are in good agreement with the calculated mass of the poly(DEGV) with one hydroxyl terminal group and one vinyl ether terminal group. One of the smaller peaks (2269.1 g/mol), for example, is consistent with the calculated molecular weight with  $Na^+$  (2269.7 g/mol,  $n = 16$ ). In MALDI-TOF-MS spectra of poly(CHMVE)-polyol, the major peaks values agree well with the calculated mass of the poly(CHMVE) with two hydroxyl terminal groups. One of the major peaks (1869.2 g/mol) very fits the calculated molecular weight with  $Na^+$  (1869.7 g/mol,  $n = 10$ ). The distance between individual peaks (170.1) corresponds to the molar mass of the CHMVE unit (170.2). The smaller peaks with the similar repeating distance (170.1) are in good agreement with the calculated mass of the poly(CHMVE) with one hydroxyl terminal group and one vinyl ether terminal group. One of the smaller peaks (1895.3 g/mol), for example, is consistent with the calculated molecular weight with  $Na^+$  (1895.7 g/mol,  $n = 10$ ). Overall, although very minor amount of the vinyl ether-capped polymers are present in the products, the polyacetal polyols with two hydroxyl terminal groups are the main product polymers.

Table II shows the number-average molecular weight, glass transition temperature ( $T_g$ ), and the solvent solubility of



**Figure 2.** (A) MALDI-TOF-MS spectrum of poly(HEVE)-polyol [ $M_n$  (Titr.) = 1,680,  $M_w/M_n$  = 2.09]. (B) Expanded region of the spectrum (A). (C) Chemical structures for the products detected by MALDI-TOF-MS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

poly(HBVE)-polyol, poly(HEVE)-polyol, poly(DEGV)-polyol, poly(CHMVE)-polyol, and PTMG (commodity polyol). The number-average molecular weight measured by acetylation method [ $M_n$  (Titr.); with respect to the hydroxyl contents of the polyols] of the polyols were  $\sim 2,000$ . The  $T_g$ 's of poly(HBVE)-polyol, poly(HEVE)-polyol, poly(DEGV)-polyol, and poly(-CHMVE)-polyol were observed at  $-76^\circ\text{C}$ ,  $-62^\circ\text{C}$ ,  $-62^\circ\text{C}$ , and  $-24^\circ\text{C}$ , respectively, and thus, a wide range of variation in  $T_g$  of the polyols was obtained depending on main-chain structures. Poly(HBVE)-polyol, poly(HEVE)-polyol, and poly(-DEGV)-polyol exhibited good solubility in various solvents (from toluene to methanol) like PTMG. In particular, poly(-HEVE)-polyol and poly(DEGV)-polyol were soluble even in water at room temperature. In contrast, poly(CHMVE)-polyol was less soluble in polar solvents such as methanol.

Table III shows results of characterization of poly(HBVE)-BD-PU, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, poly(CHMVE)-BD-PU, and PTMG-BD-PU (commodity polyurethane). All polyurethanes had relatively high molecular weights ( $M_n > 40,000$ ). As an example, the MWD curve (obtained by GPC) and  $^1\text{H}$  NMR spectrum of poly(HEVE)-BD-PU are illustrated in Figures 3(A) and 4(A), respectively. In the  $^1\text{H}$  NMR spectrum (in THF- $d_6$ ) of poly(HEVE)-BD-PU, the signals (peak a–e) coming from the soft segment part are remained, the new signals (peak f–k)

coming from the incorporated hard segment part are observed:  $\delta$  1.72 [peak k; the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  3.82 [peak f; the isocyanate methylene ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )],  $\delta$  4.11 [peak j; the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  4.19 [peak e; the methylene adjacent to urethane linkage ( $-\text{NH}-\text{C}(\text{O})\text{O}-\text{OCH}_2\text{CH}_2\text{O}-$ )],  $\delta$  7.04, 7.36 [peak g, h; the isocyanate phenyl ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )] and  $\delta$  8.61, 8.69 [peak i; the urethane hydrogen ( $-\text{NH}-\text{C}(\text{O})\text{O}-$ )]. The other polyurethanes were also characterized by  $^1\text{H}$  NMR spectra (their spectra are not shown). In the  $^1\text{H}$  NMR spectrum (in THF- $d_8$ ) of poly(-HBVE)-BD-PU, the signals coming from the soft segment part are remained, the new signals coming from the incorporated hard segment part are observed:  $\delta$  1.72 [the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  3.81 [the isocyanate methylene ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )],  $\delta$  4.09 [the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ) and the methylene adjacent to urethane linkage ( $-\text{NH}-\text{C}(\text{O})\text{O}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  7.03, 7.35 [the isocyanate phenyl ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )] and  $\delta$  8.58 [the urethane hydrogen ( $-\text{NH}-\text{C}(\text{O})\text{O}-$ )]. In the  $^1\text{H}$  NMR spectrum (in THF- $d_8$ ) of poly(-DEGV)-BD-PU, the signals coming from the soft segment part are remained, the new signals coming from the incorporated hard segment part are observed:  $\delta$  1.71 [the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  3.83 [the isocyanate

**Table II.** Characterization of Polyacetal Polyols and PTMG

	$M_n$ (GPC) <sup>a</sup>	$M_w/M_n$ (GPC) <sup>a</sup>	$M_n$ (Titr.) <sup>b</sup>	$M_n$ (Calc.) <sup>c</sup>	$T_g$ (°C) <sup>d</sup>	Solubility <sup>e</sup>			
						Toluene	Chloroform	Methanol	Water
Poly(HBVE)-polyol	1710	2.30	1630	2000	-76	○	○	○	×
Poly(HEVE)-polyol	1350	2.09	1680	2000	-62	○	○	○	○
Poly(DEGV)-polyol	1800	2.28	2400	2000	-62	○	○	○	○
Poly(CHMVE)-polyol	2230	2.25	2010	2000	-24	○	○	△	×
PTMG	2760	2.46	2090	2000	-	○	○	○	×

<sup>a</sup>Determined by GPC with polystyrene calibration.

<sup>b</sup>Measured by acetylation method.

<sup>c</sup>Calculated by the equation  $X_n = (r + 1)/(r - 2rp + 1)$ ;  $X_n$  is number-average degree of polymerization,  $r$  is molar ratio of functional groups ([vinyl ether group]<sub>0</sub>/[hydroxyl group]<sub>0</sub>), and  $p$  is extent of reaction ( $p = 1$ ).

<sup>d</sup>Glass transition temperature; measured by DSC on second heating scan.

<sup>e</sup>Polymer concentration, 0.5 wt %; ○, soluble; △, partially soluble; ×, insoluble.

methylene ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ ),  $\delta$  4.01 [the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ),  $\delta$  7.03, 7.36 [the isocyanate phenyl ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )] and  $\delta$  8.62, 8.73 [the urethane hydrogen ( $-\text{NH}-\text{C}(\text{O})\text{O}-$ )]. In the <sup>1</sup>H NMR spectrum (in chloroform-*d*) of poly(CHMVE)-BD-PU, the signals coming from the soft segment part are remained, the new signals coming from the incorporated hard segment part are observed:  $\delta$  1.64 [the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ),  $\delta$  3.74 [the isocyanate methylene ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ ),  $\delta$  4.19 [the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ),  $\delta$  6.64 [the urethane hydrogen ( $-\text{NH}-\text{C}(\text{O})\text{O}-$ ), and  $\delta$  7.10, 7.30 [the isocyanate phenyl ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )].

### Thermal Properties

The  $T_g$ 's (measured by DSC) of poly(HBVE)-BD-PU, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, poly(CHMVE)-BD-PU, and PTMG-BD-PU were observed at  $-44$  °C,  $-24$  °C,  $-38$  °C,  $19$  °C, and  $-62$  °C, respectively, depending on main-chain structures (Table III). In comparison of the  $T_g$  of these polyurethanes with those of the polyols from which they are derived, the  $T_g$ 's were about  $30$  °C higher for the polyurethanes than for the polyols, because of the incorporation of hard urethane segments in the polymer chains. The thermal decomposition behavior of all polyurethanes were measured by thermogravimetric analysis.

The thermal decomposition temperatures ( $T_d$ 's) of poly(HBVE)-BD-PU, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, and poly(CHMVE)-BD-PU were observed at  $310$  °C,  $312$  °C,  $314$  °C, and  $320$  °C, respectively. Thus, the acetal-containing polyurethanes have high thermal stability ( $T_d \geq 310$  °C) and their  $T_d$ 's are comparable to that of commodity polyurethane, PTMG-BD-PU ( $T_d = 314$  °C).

Figure 5(A,B) show the temperature dependence of storage modulus ( $E'$ ) of the hydrophobic polyurethanes [poly(HBVE)-BD-PU, poly(CHMVE)-BD-PU, and PTMG-BD-PU] and the hydrophilic polyurethanes [poly(HEVE)-BD-PU and poly(DEGV)-BD-PU], respectively, in DMA. Poly(HBVE)-BD-PU exhibited a glassy state below  $-60$  °C, decrease of  $E'$  from  $-50$  °C, and a rubbery plateau from  $-20$  to  $120$  °C. Poly(CHMVE)-BD-PU exhibited a glassy state below  $-20$  °C, decrease of  $E'$  from  $-10$  °C, and a rubbery plateau from  $20$  to  $120$  °C. Thus, Poly(HBVE)-BD-PU had wider range of temperature for elastomeric property than Poly(CHMVE)-BD-PU. PTMG-BD-PU showed the shoulder of  $E'$  observed between  $-60$  and  $10$  °C due to cold crystallization of the PTMG-based soft segments<sup>9,13</sup> and hence the temperature range of rubbery plateau (from  $10$  to  $120$  °C) rather limited. Poly(HEVE)-BD-PU exhibited a glassy state below  $-30$  °C, decrease of  $E'$  from

**Table III.** Characterization of Polyacetal Polyurethanes and PTMG-Based Polyurethane

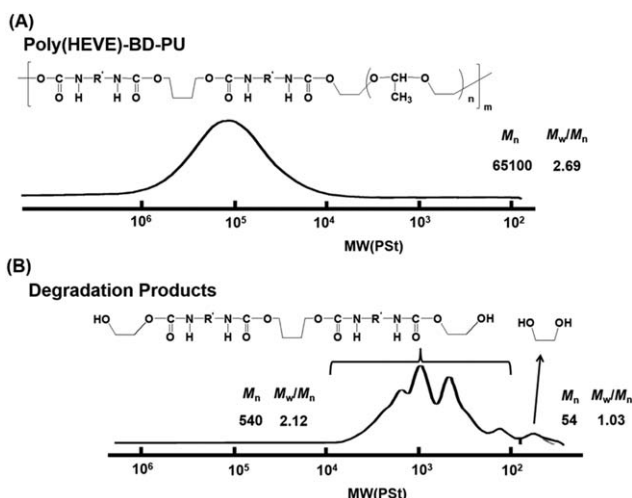
	$M_n$ (GPC) <sup>a</sup>	$M_w/M_n$ (GPC) <sup>a</sup>	Rubbery <sup>b</sup> plateau (°C)	Tan $\delta$ Peak Temp (°C) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>	$T_d$ (°C) <sup>d</sup>	Property	Reproduced Diols	
								Yield (%)	
Poly(HBVE)-BD-PU	45,100	2.75	$-20 \sim 120$	$-33$	$-44$	$310$	Hydrophobic	1,4-Butanediol	32
Poly(HEVE)-BD-PU	65,100	2.69	$-10 \sim 100$	$-18$	$-24$	$312$	Hydrophilic	Ethylene glycol	3
Poly(DEGV)-BD-PU	72,400	2.66	$-20 \sim 100$	$-34$	$-38$	$314$	Hydrophilic	Diethylene glycol	34
Poly(CHMVE)-BD-PU	40,700	2.06	$20 \sim 120$	$2$	$19$	$320$	Hydrophobic	1,4-Cyclohexanedimethanol	66
PTMG-BD-PU	90,400	1.89	$10 \sim 120$	$-58$	$-62$	$314$	Hydrophobic	–	–

<sup>a</sup>Determined by GPC with polystyrene calibration.

<sup>b</sup>Measured by DMA.

<sup>c</sup>Glass transition temperature, measured by DSC on second heating scan.

<sup>d</sup>Thermal decomposition temperature, measured by TG-DTA with 5% weight loss.



**Figure 3.** A: GPC curve of poly(HEVE)-BD-PU ( $M_n = 65,100$ ,  $M_w/M_n = 2.69$ ). B: GPC curve of the degradation products ( $M_n = 540$ ,  $M_w/M_n = 2.12$  and  $M_n = 54$ ,  $M_w/M_n = 1.03$ ).

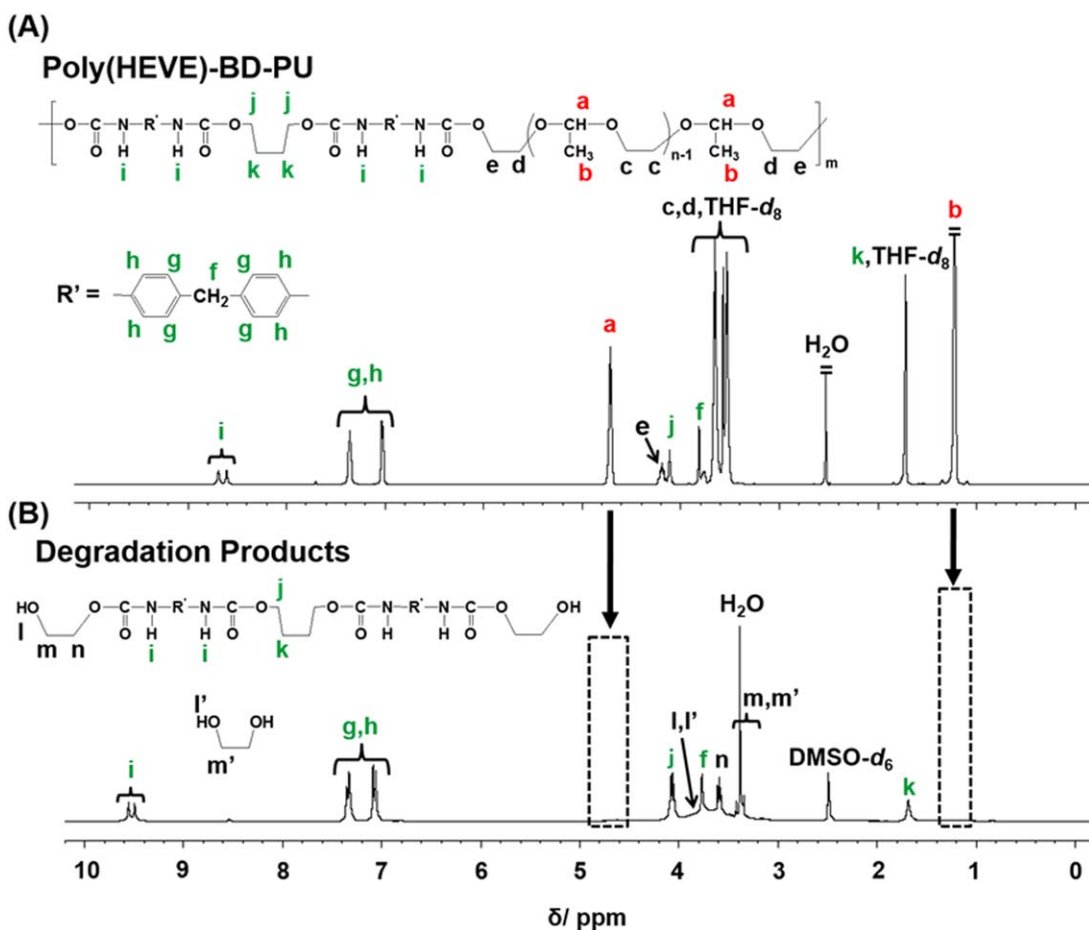
$-20^\circ\text{C}$ , and a rubbery plateau from  $-10$  to  $100^\circ\text{C}$ . Poly(-DEGV)-BD-PU showed a glassy state below  $-50^\circ\text{C}$ , decrease of  $E'$  at  $-40^\circ\text{C}$ , and a rubbery plateau from  $-20$  to  $100^\circ\text{C}$ . All

the polyacetal polyurethanes were flexible elastomers around room temperature ( $\sim 25^\circ\text{C}$ ). The  $\tan \delta$  peak temperatures observed by DMA as a glass transition temperature for all the polyurethanes were shown in Table III. The  $T_g$ 's ( $\tan \delta$  peak temperature measured by DMA) of poly(HBVE)-BD-PU, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, poly(CHMVE)-BD-PU, and PTMG-BD-PU were observed at  $-33^\circ\text{C}$ ,  $-18^\circ\text{C}$ ,  $-34^\circ\text{C}$ ,  $2^\circ\text{C}$ , and  $-58^\circ\text{C}$ , respectively. These values were slightly lower than but close to the  $T_g$  values measured by DSC.

#### Thermoresponsive Function

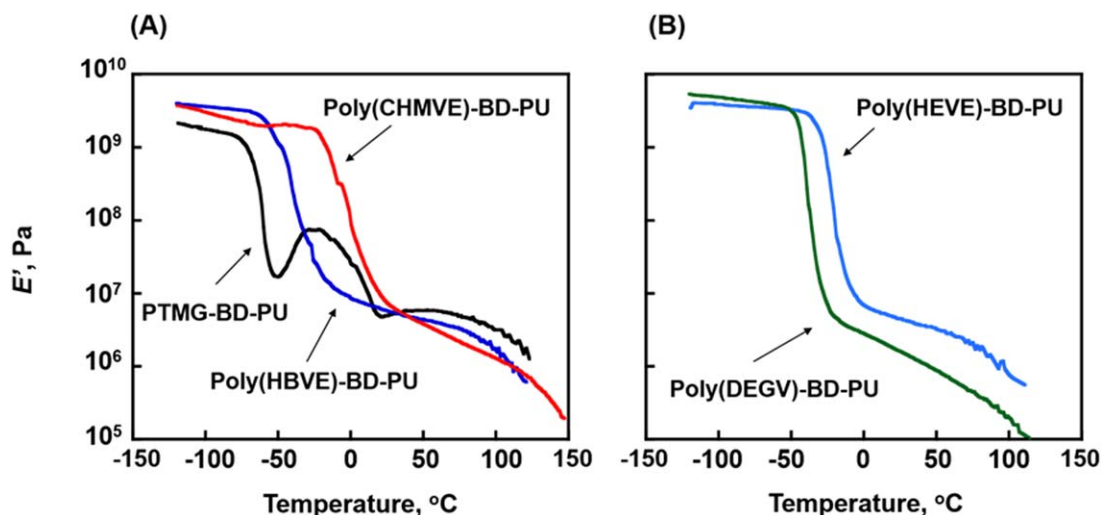
Recently, thermoresponsive polymers are paid much attention to develop controlled drug release systems.<sup>14</sup> Typical examples are poly(ethylene oxide) (PEO) and poly(*N*-isopropylacrylamide).<sup>15</sup> During course of study, we found that the poly(HEVE)-polyol and poly(DEGV)-polyol containing the hydrophilic main-chains [ $-\text{O}-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}_2-$  and  $-\text{O}-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ , respectively] showed thermally induced precipitation from their aqueous solution.

Figure 6 shows the temperature dependence of the transmittance at 500 nm for the aqueous solutions of poly(HEVE)-polyol. The transmittance of the poly(HEVE)-polyol solution decreased very sharply at  $38^\circ\text{C}$  because of polymer precipitation



**Figure 4.** (A)  $^1\text{H}$  NMR spectra of poly(HEVE)-BD-PU ( $M_n = 65,100$ ,  $M_w/M_n = 2.69$ ) in  $\text{THF}-d_8$ . (B)  $^1\text{H}$  NMR spectra of the degradation products ( $M_n = 540$ ,  $M_w/M_n = 2.12$  and  $M_n = 54$ ,  $M_w/M_n = 1.03$ ) in  $\text{DMSO}-d_6$ . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





**Figure 5.** Temperature dependence of storage modulus ( $E'$ ) of (A) hydrophobic polyurethanes: poly(HBVE)-BD-PU ( $M_n = 45,100$ ,  $M_w/M_n = 2.75$ ), poly(CHMVE)-BD-PU ( $M_n = 40,700$ ,  $M_w/M_n = 2.06$ ) and PTMG-BD-PU ( $M_n = 90,400$ ,  $M_w/M_n = 1.89$ ), and (B) hydrophilic polyurethanes: poly(HEVE)-BD-PU ( $M_n = 65,100$ ,  $M_w/M_n = 2.69$ ) and poly(DEGV)-BD-PU ( $M_n = 72,400$ ,  $M_w/M_n = 2.66$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

from the aqueous solution. Poly(DEGV)-polyol also exhibited a similar polymer precipitation at the temperature higher than 90 °C or near to boiling point of water, and hence an exact phase separation temperature could not be determined by the present apparatus.

Since poly(HEVE)-polyol had thermoresponsiveness in aqueous solution, water-based thermoresponsive function of poly(HEVE)-BD-PU was investigated. As shown in Figure 7(A), its film specimen ( $1.0 \times 1.0 \text{ cm}^2$ ) was immersed in deionized water at 5 °C and allowed to swell for 24 h. The obtained swollen film ( $1.3 \times 1.3 \text{ cm}^2$ ) was then heated at 30 °C on hot plate, at which the absorbed water was observed to release from the specimen and the film size reached  $1.1 \times 1.1 \text{ cm}^2$ . After the specimen was heated at 30 °C for 30 min, the absorbed water was released completely and the film reached the original film size ( $1.0 \times 1.0 \text{ cm}^2$ ). Reversible swelling-dewelling behavior of poly(HEVE)-BD-PU was observed repeatedly.

Another thermoresponsive function of the hydrophilic polyacetal polyurethanes was observed by temperature dependence of water content, where poly(HEVE)-BD-PU and poly(DEGV)-BD-PU were examined to have their volume phase transition temperature (VPTT).<sup>16</sup> The films ( $1.0 \times 1.0 \text{ cm}^2$ ) of poly(HEVE)-BD-PU and poly(DEGV)-BD-PU were immersed in deionized water at the certain temperature and allowed to swell for 3 days to reach equilibrium state. Water uptake of the polyurethane is defined as the follows:

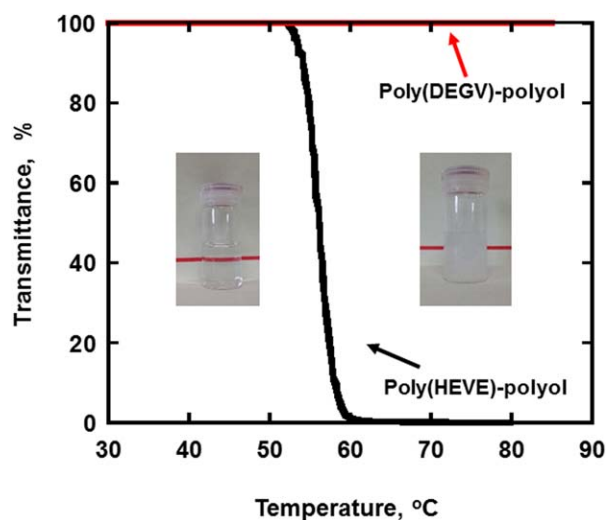
$$\text{Water uptake} = [(W_s - W_d)/W_d] \times 100\%$$

where  $W_s$  is the weight of the equilibrium swollen polyurethanes,  $W_d$  is the weight of dry polyurethane. The change in water uptake of poly(HEVE)-BD-PU and poly(DEGV)-BD-PU in the temperature range 3–65 °C are displayed in Figure 7(B). The temperature at which the water uptake with 50% loss is defined as VPTT. A remarkable difference was seen between the water uptakes below and above VPTT. VPTTs of poly(HEVE)-

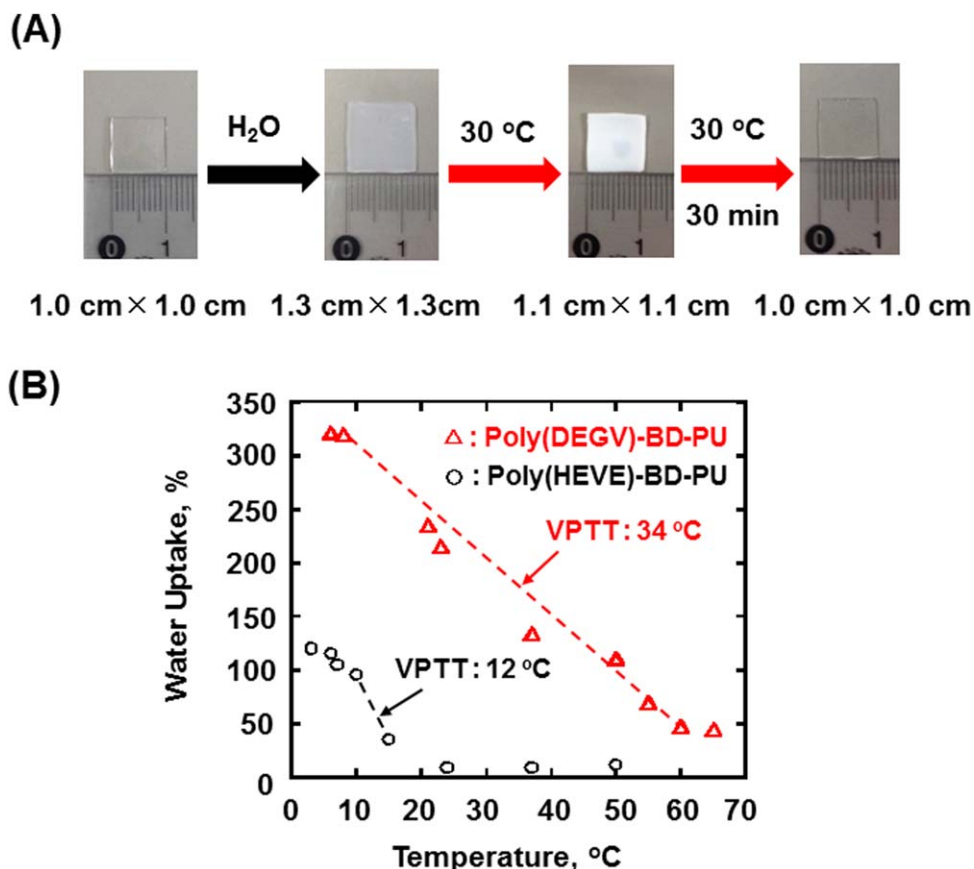
BD-PU and poly(DEGV)-BD-PU were 12 and 29 °C, respectively. Thus, poly(HEVE)-BD-PU and poly(DEGV)-BD-PU have the thermoresponsive nature and can be expected to use as thermoresponsive materials.

#### Acid-Induced Degradation and Stability toward Acid

An acid-induced degradability test of polyacetal polyurethanes was conducted as follows. A polymer (0.20 g) in 3 mL of a mixed solvent (THF/H<sub>2</sub>O = 9/1) containing 1.0 mol/L-hydrochloric acid was stirred at room temperature for 24 h. The resulting solution was evaporated to dryness, and the resultant products were analyzed by GPC and <sup>1</sup>H NMR. Yield of the obtained diols was formally obtained from the area of the diol fraction in the total degradation product on their GPC curves.



**Figure 6.** Thermoresponsive behavior of the aqueous solutions of poly(HEVE)-polyol [ $M_n$  (Titr.) = 1,680,  $M_w/M_n = 2.09$ ] and poly(DEGV)-polyol [ $M_n$  (Titr.) = 2,400,  $M_w/M_n = 2.28$ ]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

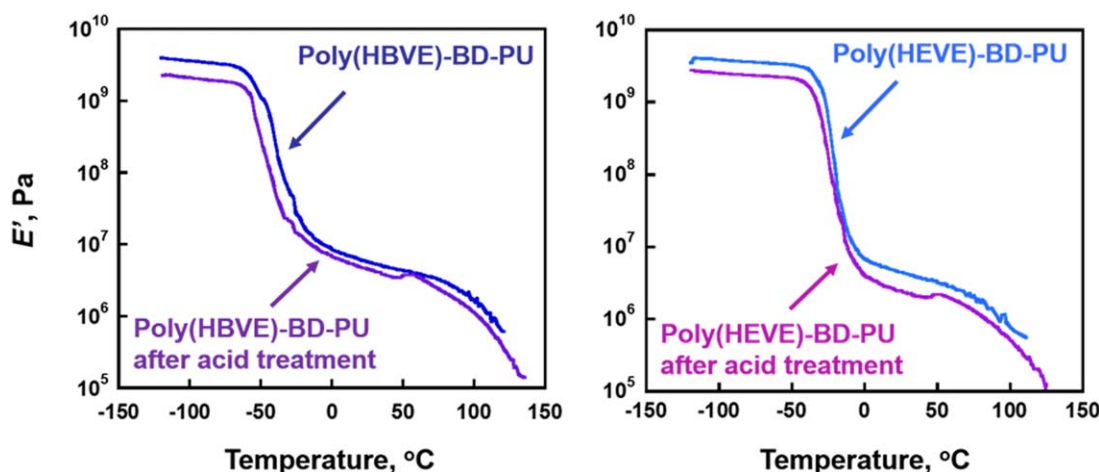


**Figure 7.** (A) Thermoresponsive behavior of poly(HEVE)-BD-PU ( $M_n = 65,100$ ,  $M_w/M_n = 2.69$ ). (B) Temperature dependence of water content of poly(HEVE)-BD-PU and poly(DEGV)-BD-PU ( $M_n = 72,400$ ,  $M_w/M_n = 2.66$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The MWD curve (obtained by GPC) and  $^1\text{H}$  NMR spectrum of degradation products of poly(HEVE)-BD-PU were illustrated in Figures 3(B) and 4(B), respectively. After the acid treatment, the peak of poly(HEVE)-BD-PU [Figure 3(A)] completely disappeared, and new peaks with their  $M_n = 540$  and 54 were detected in the lower molecular weight region. The possible products are ethylene glycol, urethane linkage-containing compounds, and acetaldehyde (Scheme 2). In  $^1\text{H}$  NMR spectrum of the degradation products [Figure 4(B)], the signals of the acetal methine [peak **a**;  $\delta$  4.71 in Figure 4(A)] and the pendant methyl [peak **b**;  $\delta$  1.22 in Figure 4(A)] completely disappeared, and the signals of ethylene glycol and urethane compounds were observed:  $\delta$  1.70 [peak **k**; the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  3.39 [peak **m**, **m'**; the terminal methylene of ethylene glycol and urethane compound ( $\text{HOCH}_2-$ )],  $\delta$  3.60 [peak **n**; the terminal methylene of urethane compound ( $\text{HOCH}_2\text{CH}_2-$ )],  $\delta$  3.78 [peak **f**; the isocyanate methylene ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )],  $\delta$  3.50–3.90 [broad peak **l**, **p**; the terminal hydroxyl hydrogen of ethylene glycol and urethane compound ( $\text{HOCH}_2-$ )],  $\delta$  4.11 [peak **j**; the chain extender methylene ( $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ )],  $\delta$  7.10, 7.34 [peak **g**, **h**; the isocyanate phenyl ( $-\text{C}_6\text{H}_6-\text{CH}_2-\text{C}_6\text{H}_6-$ )] and  $\delta$  9.51, 9.57 [peak **i**; the urethane hydrogen ( $-\text{NH}-\text{C}(\text{O})\text{O}-$ )]. Therefore, the degradation reaction occurred at room

temperature and ethylene glycol was regenerated. However, yield of ethylene glycol was low (3%; Table III) due to loss during evaporation in a workup procedure. The other polyacetal polyurethanes, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, and poly(CHMVE)-BD-PU, were also smoothly degraded in the same procedure and the corresponding diols were reproduced in relatively high yield (Table III); 1,4-butanediol, 32%; diethylene glycol, 34%; 1,4-cyclohexanedimethanol, 66%.

However, stability toward acid is otherwise important for practical use of the polyacetal polyurethanes in the environment. To study this, the film specimens of poly(HEVE)-BD-PU and poly(HEVE)-BD-PU were immersed in 0.1 mol/L aqueous acetic acid solution [pH = 2.8; slightly more acidic than rain in Japan (pH = 4.77)<sup>17</sup>] at room temperature for 24 h. After washing the films with deionized water and vacuum-drying overnight, GPC analysis, tensile test, and DMA were conducted. There were virtually no changes in the appearance of the polymer films and in their  $M_n$  before and after the acid treatment. Figure 8 shows the temperature dependence of storage modulus ( $E'$ ) of poly(HEVE)-BD-PU and poly(HEVE)-BD-PU before and after the acid treatment. There were virtually no changes in these mechanical properties before and after treatment of the acid and the observed  $\tan \delta$  peak temperatures after the acid treatment were  $-33$  and  $-18$  °C, respectively, which were the same values as



**Figure 8.** Temperature dependence of storage modulus ( $E'$ ) of poly(HBVE)-BD-PU ( $M_n = 45,100$ ,  $M_w/M_n = 2.75$ ) and poly(HBVE)-BD-PU after acid treatment ( $M_n = 50,600$ ,  $M_w/M_n = 2.91$ ), and poly(HEVE)-BD-PU ( $M_n = 65,100$ ,  $M_w/M_n = 2.69$ ) and poly(HEVE)-BD-PU after acid treatment ( $M_n = 75,800$ ,  $M_w/M_n = 2.14$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

those before the acid treatment (Table III). These results indicate that the polyacetal polyurethanes are stable at least in acidity (pH = 2.8) or in the normal living environment.

## CONCLUSIONS

In this study, acid-degradable polyurethane elastomers [poly(HBVE)-BD-PU, poly(HEVE)-BD-PU, poly(DEGV)-BD-PU, and poly(CHMVE)-BD-PU] were developed by the incorporation of acetal linkage in the main-chain structures into polyols [poly(HBVE)-polyol, poly(HEVE)-polyol, poly(DEGV)-polyol, and poly(CHMVE)-polyol]. The polyacetal polyurethanes were flexible elastomer at room temperature and had good thermal stability. Depending on the main-chain structures, the polyacetal polyurethanes were different in thermal and mechanical properties. In particular, poly(HEVE)-BD-PU and poly(DEGV)-BD-PU containing hydrophilic main-chain possessed water-based thermoresponsive functions. The polyacetal polyurethanes underwent smooth degradation with a treatment of aqueous acid in THF at room temperature to give the corresponding raw material diols (BD, EG, DEG, CHDM). Thus, polyacetal polyol-based polyurethanes are a new type of environmentally friendly functional materials in which degradation sites are embedded into the polymers at design stage.

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