Synthesis and Physical Properties of Poly(urethane)s Using Vicinal Diols Derived from Acrylate and Styrene Monomers

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ABSTRACT: We describe the utilization of four kinds of diol derivatives, representing structural similarity to the well-known and commercially available vinyl monomers such as acrylate, acrylamide, styrene, and N-substituted maleimide. The vinyl monomers are readily converted by dihydroxylation reaction to afford the vicinal diol. The synthesis of poly(urethane)s was performed by the reaction of the vicinal diol with two model diisocyanates, including methylene diphenyl isocyanate (MDI) and hexamethylene diisocyanate (HDI) in the presence of dibutyltin dilaurate to form a series of poly(urethane)s, and the effect of vicinal diol containing a side chain inherited from vinyl monomers on their thermal and mechanical properties was investigated using thermogravimetric analysis, differential scanning calorimetry, and tensile test. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: polyaddition; poly(urethane); vicinal diol; thermal and mechanical properties

INTRODUCTION Poly(urethane)s elastomer has constituted one of the most versatile classes of polymeric materials because of remarkable properties including flexibility, rigidness, thermal stability, diverse utility, and relatively low-cost production. Thus, polyurethanes have been used in a broad range of applications including foams,[1,2] coatings,[1,2] adhesives,[1,2] elastomers,[1,2] furniture,[2] sealants,[1] synthetic leathers,[2] membranes,[1,3] and heat insulators to the biomedical products.[1,3] Generally, poly(urethane) elastomer was synthesized using the polyaddition of diol (HO—R—OH) and diisocyanates (NCO—R′—NCO) derivatives. The selection of monomer structure is important to achieve the desired property of poly(urethane). From the viewpoint of the synthesis of functional poly(urethane), the design of a new type of diol or diisocyanate is the most important, because the specific function is provided by control over the primary structure of the monomers. Therefore, numerous efforts are devoted to the preparation of functional diol and diisocyanate to improve the properties of poly(urethane).[4–7]

In the field of polymer synthesis, a series of vinyl monomers are widely used to produce a synthetic polymer through conventional radical, anionic, and cationic polymerization approach. These vinyl monomers are considered as one of the promising raw materials, which are readily converted into vicinal diols by dihydroxylation reaction to being used for the synthesis of poly(urethane) elastomer. Additionally, to date, various vinyl monomers were not only commercially available but also were prepared as one of the key parts for the production of polymeric materials.

Herein, we present a new approach for preparing new types of poly(urethane)s by the use of vicinal diol derivatives, which have a similar structure with the well-known commercial vinyl monomers for typical polymerization, such as acrylate, acrylamide, styrene, and N-substituted maleimide with a unique difference on the side chain. The polymerizations proceeded based on a conventional synthesis of poly(urethane) procedure. Four kinds of vicinal diols were successfully incorporated in poly(urethane) main chain by the reaction of commercially available diisocyanate derivatives, methylene diphenyl isocyanate (MDI), and hexamethylene diisocyanate (HDI), in the presence of dibutyltin dilaurate (DBTDL) catalyst. Our interests in this work are to evaluate the structural effect of vinyl monomer-based diol structure on the thermal and mechanical properties of poly(urethane).

EXPERIMENTAL

Measurements

Nuclear magnetic resonance (NMR) spectra (400 MHz for ^{1}H and 100 MHz for ^{13}C) were recorded with a JEOL ECS-400 spectrometer (JEOL Ltd, Tokyo, Japan), and chemical shifts were recorded in ppm units using tetramethylsilane (TMS) as an internal standard. Column chromatography was carried out using Kanto Silica Gel 60 N (spherical, neutral, 63–210 μm). Fourier transform infrared spectroscopy (FTIR) analysis was carried out on a Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc, Tokyo, Japan) in the range of 600–4000 cm^{-1} ranges. Size

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exclusion chromatography (SEC) was carried out at 40 °C on a TOSOH HLC-8220 system (Tosoh corporation, Tokyo, Japan) equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion limited molecular weight); super-AW4000 (6 μm, > 4×10^5), super-AW3000 (4 μm, > 6×10^4), and super-AW2500 (4 μm, > 2×10^3)] and refractive index and ultraviolet detectors. This system was operated using DMF containing 10 mM LiBr as the eluent at a flow rate of 0.5 mL min^{-1}. Polystyrene standards were used for the calibration. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument DSC-6200 (Seiko Instrument Inc, Chiba, Japan) using an aluminum pan under nitrogen flow at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed on TG/DTA6200 thermal analyzer (Seiko Instrument Inc, Chiba, Japan) with aluminum pan under nitrogen flow at a heating rate of 10 °C min^{-1}. The mechanical properties of thin films (approximately 130 μm) were evaluated on a Shimadzu EZ Test EZ-LX (SHIMADZU CORPORATION, Kyoto, Japan) at a crosshead speed of 200 mm/min. Young's modulus was estimated by the initial rising slope of stress–strain curve. The film was cut into dumbbell-shaped test pieces according to the Japan Industrial Standards (JIS) K6251, No.7, and the tensile tests were repeated at least four times to obtain the average values. Geometry optimized energy was estimated by using density functional theory (DFT) calculation with B3LYP/6-31G* method (Wavefunction, Inc., Spartan'06 Windows version 1.1.0).

Materials

Tert-butyl acrylate, *N*-isopropyl acrylamide and potassium permanganate (KMnO$_4$) were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Styrene oxide, L-tartaric acid, *n*-octylamine, benzyltriethylammonium chloride (TEBAC), dibutyltin dilaurate (DBTDL), methylenediphenyl 4,4′-diisocyanate (MDI), and HDI were purchased from Tokyo Chemical Industry C., Ltd. (Tokyo, Japan). All other solvents were purchased from KANTO Chemical Co., INC. (Tokyo, Japan) and used as received without further purification unless otherwise described.

Synthesis of tert-butyl 2,3-dihydroxypropanoate (diol-1) and 2,3-dihydroxy-N-isopropylpropanamide (diol-2)

TEBAC (13.7 g, 60 mmol) and KMnO$_4$ (9.5 g, 60 mmol) were mixed in acetone (400 ml) and the mixture were stirred at r.t. for 3 h, then cooled to 0 °C. To this mixture, a solution of *tert*-Butyl acrylate or *N*-isopropyl acrylamide (50 mmol) in 100 ml acetone was added dropwise over 15 min at 0 °C and stirred for 10 min after addition completed. Aqueous solution of NaHSO$_3$ (25 g, 240 mmol in 100 mL water) was added in one portion to quench the reaction mixture, then filtered through Celite by washing with acetone. Acetone in the filtrate was evaporated and the aqueous residue was extracted with excess ethyl acetate. The organic phase was dried (MgSO$_4$), filtered, and solvent evaporated. The crude oily product was purified by column chromatography (silica gel, hexane: ethyl acetate (2:1 for **diol-1**) to yield 50% as colorless oil and (silica gel, hexane: ethyl acetate (1:1 for **diol-2**)) to yield 60% as light-yellow oil).

diol-1: ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.36 (s, 9H), 3.59–3.35 (m, 2H), 3.96–3.74 (m, 1H), 4.66 (t, *J* = 5.9 Hz, 1H), 5.05 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 28.27, 64.31, 72.88, 80.55, 172.46. FT-IR (neat, cm^{-1}): 1728, 2940, 2990, 3420.

diol-2: ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.02 (dd, *J* = 6.6, 2.2 Hz, 6H), 3.38 (dd, *J* = 11.1, 6.2 Hz, 1H), 3.58–3.46 (m, 1H), 3.89–3.73 (m, 2H), 4.57 (t, *J* = 5.8 Hz, 1H), 5.36 (d, *J* = 5.6 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 22.84, 40.35, 64.48, 73.41, 171.53. FT-IR (neat, cm^{-1}): 1539, 1640, 2880, 2940, 2980, 3290, 3400.

Synthesis of 1-phenylethane-1,2-diol (diol-3)

The heterogeneous mixture of styrene oxide (6.0 g, 50 mmol) distillated water (100 mL) was refluxed for 24 h. Then, water was evaporated in rotary and the residue dissolved in ethyl acetate. Organic phase was dried on Mg$_2$SO$_4$, filtrated, and concentrated. Toluene (500 mL) was added and kept in refrigerator for overnight to perform recrystallization. Obtained white crystals was filtered and dried in vacuum at 100 °C overnight to yield 90%.

diol-3: ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.40 (t, *J* = 5.9 Hz, 2H), 4.51 (dd, *J* = 10.3, 5.9 Hz, 1H), 4.67 (t, *J* = 5.8 Hz, 1H), 5.17 (d, *J* = 4.2 Hz, 1H), 7.35–7.14 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 68.04, 74.37, 126.80, 127.30, 128.33, 143.95. FTIR (neat, cm^{-1}): 1345, 1454, 2865, 2930, 3200.

Synthesis of 3,4-dihydroxy-1-octylpyrrolidine-2,5-dione (diol-4)

L-tartaric acid (25 g, 166.5 mmol) and octylamine (27.5 mL, (166.5 mmol) in 250 mL of *p*-xylene were refluxed at 150 °C for 24 h. The reaction mixture was cooled to ambient temperature and to resulting crystalline product, excess amount of hexane was added and stirred for 30 min, then filtered off. After successive washing with portions of hexane until the color of crystalline becomes light-yellow, then dried in vacuum at 100 °C overnight to yield 95%.

diol-4: ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 0.81 (dd, *J* = 8.7, 5.0 Hz, 3H), 1.55–0.99 (m, 12H), 3.41–3.16 (m, 2H), 4.27 (s, 2H), 6.20 (br, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 14.44, 22.58, 26.66, 27.56, 29.04, 31.71, 38.16, 74.86, 175.20. FTIR (neat, cm^{-1}): 1465, 1534, 1646, 2879, 2934, 2984, 3370.

Synthesis of Poly(urethane)s from Vicinal Diol and Diisocyanate

As described in Scheme 2, the polymers were synthesized in the solution of DMF, which was dried over 4 Å molecular sieves overnight. Briefly, the diol compound (3 mmol) and dibutyltin dilaurate (DBTDL) (36 μL, 0.06 mmol) were dissolved in half amount of total reaction solvent. To this solution MDI (3 mmol) or HDI (3 mmol) in DMF (1.5 mL) was added, then the mixture was degassed by nitrogen cycles. The polymerization was performed under nitrogen at 60 °C for 24 h. All of the polymers were precipitated in the mixture
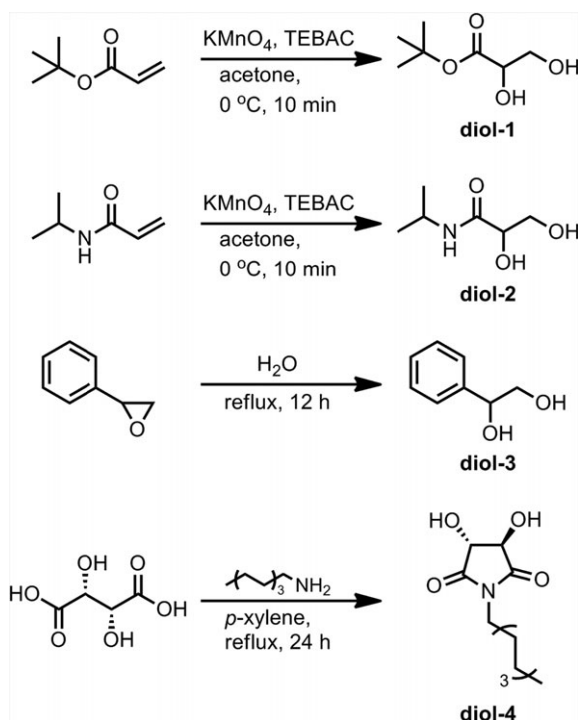
SCHEME 1 Synthetic routes to series of vicinal diols prepared from *tert*-butyl acrylate, *N*-isopropyl acrylamide, styrene oxide, and L-tartaric acid.

of hexane: ethyl acetate (1:1). After drying in vacuum at 100 °C for 24 h, the polymers are obtained.

Poly1: The reaction concentration is 0.5 M, white powder (92% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.34 (br, 9H), 3.74 (br, 1H), 4.59–4.23 (br, 2H), 5.13 (br, 2H), 7.49–6.39 (br, 8H), 9.61 (br, 1H), 9.81 (br, 1H). FT-IR (neat, cm^{-1}): 1205, 1305, 1520, 1595, 1720, 2970, 3320.

Poly2: Yellow powder (84% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26–0.90 (br, 6H), 3.78–3.67 (br, 1H), 3.90–3.77 (br, 1H), 4.40–4.20 (br, 2H), 5.16–5.06 (br, 2H), 7.40–6.95 (br, 8H), 7.98–7.91 (br, 1H), 9.66–9.66 (br, 1H), 9.81–9. 67 (br, 1H). FT-IR (neat, cm^{-1}): 1069, 1203, 1520, 1598, 1670, 1723, 2926, 2970, 3300.

Poly3: White powder (94% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.76–3.67 (br, 1H), 4.38–4.4.22 (br, 2H), 5.95–5.86 (br, 2H), 7.45–6.95 (br, 8H), 9.68–9.54 (br, 1H), 9.82–9.70 (br, 1H). FT-IR (neat, cm^{-1}): 1058, 1316, 1405, 1520, 1595, 1710, 2919, 2950, 3032, 3310, 3320.

Poly4: Yellow powder (61% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.6–0.6 (br, 14H), 3.5–3.30 (br, 2H), 3.85–3.68 (br, 1H), 5.75–5.65 (br, 2H), 7.4–6.9 (br, 8H), 10.2–9.8 (br, 2H).). FT-IR (neat, cm^{-1}): 1095, 1207, 1305, 1414, 1524, 1606, 1715, 2862, 2916, 3325.

Poly5: Yellow sticky solid (80%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.56–1.05 (br, 17H), 3.04–2.74 (br, 4H), 4.40–3.97 (br, 2H), 5.01–4.75 (br, 1H), 7.45–7.06 (br, 2H). FT-IR (neat, cm^{-1}): 1130, 1233, 1451, 1525, 1710, 2860, 2930, 3335.

Poly6: Yellow sticky solid (65% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.47–0.90 (br, 14H), 3.03–2.73 (br, 4H), 3.86–3.64 (br, 1H), 4.20–3.95 (br, 3H), 7.33–7.02 (br, 2H), 7.77–7.60 (br, 1H). FT-IR (neat, cm^{-1}): 1127, 1233, 1460, 1525, 1660, 1705, 2862, 2934, 3315.

Poly7: White powder (45% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.45–1.0 (br, 8H), 3.07–2.69 (br, 4H), 4.26–3.98 (br, 3H), 5.85–5.54 (br, 4H), 7.44–7.0 (br, 7H). FT-IR (neat, cm^{-1}): 1136, 1236, 1451, 1530, 1695, 2862, 2937, 3325.

Poly8: Yellow powder (65% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.57–0.7 (br, 23H), 3.08–2.76 (br, 4H), 3.49–3.22 (br, 2H), 5.55–5.29 (br, 2H), 7.66–7.42 (br, 2H). FT-IR (neat, cm^{-1}): 1053, 1118, 1242, 1351, 1413, 1444, 1525, 1705, 2856, 2924, 3335.

Preparation of Poly(Urethane)S Films for Tensile Test

Three hundred milligram of poly(urethane) was dissolved in 10 ml of THF by stirring at room temperature. The resultant solution was immediately transferred to a Teflon Petri dish (60 mm) and kept in ambient condition. After 24 h, the dried film separated from the Petri dish was then dried under vacuum at 80 °C for 12 h. The thickness of the obtained films was estimated at 127 ± 17 μm.

RESULTS AND DISCUSSION

Preparation of Vicinal Diols

The synthetic approaches to four kinds of vicinal diols used in this work are illustrated in Scheme 1. Dihydroxylation of olefins is a reliable way for the preparation of vicinal diol compounds. Highly efficient olefin dihydroxylation was performed
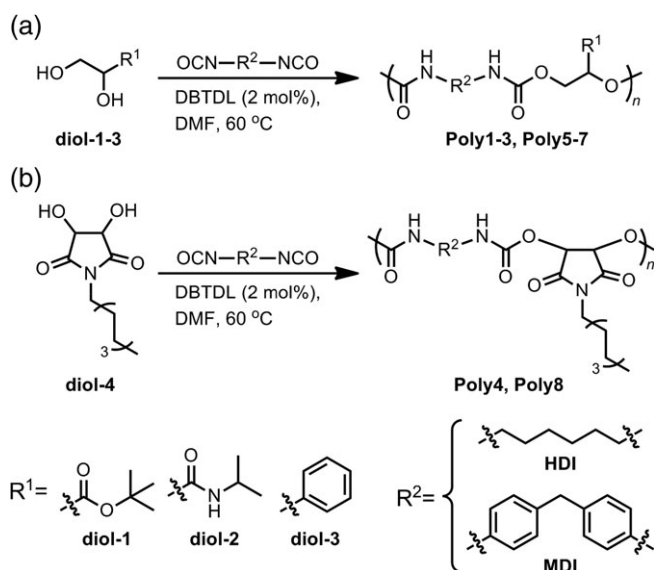
SCHEME 2 Synthesis of series of polyurethanes using (a) **diol-1**, **diol-2**, **diol-3**, and (b) **diol-4**, with MDI and HDI.

TABLE 1 Synthesis of Poly(urethane)s by Polyaddition of Vicinal Diol and Diisocyanate [a]

Poly	R^1	R^2	Conv.[b]	Yield[c]	M_n[d]	M_w/M_n[d]	T_{d5}[e]	T_g[f]
			(%)	(%)	($\times 10^{-4}$)		(°C)	(°C)
1	1	MDI	>99	92	3.2	2.02	171	62
2	2	MDI	>99	84	1.7	2.99	217	120
3	3	MDI	>99	94	3.0	1.70	225	128
4	4	MDI	>99	61	0.75	2.40	240	130
5	1	HDI	>99	80	3.3	2.76	188	15
6	2	HDI	>99	65	2.1	2.80	233	47
7	3	HDI	>99	45	1.6	1.90	239	50
8	4	HDI	>99	65	2.0	3.13	242	61

[a] conc. = [diol]$_0$ and [diisocyanate]$_0$ = 2.0 M in DMF with DBTDL catalyst (2 mol %) at 60 °C for 24 h.
[b] Conversations (%) were calculated by ^{1}H-NMR following the conversation of diisocyanate component.
[c] Calculated from insoluble part in the mixture of hexane:ethyl acetate (1:1).
[d] M_n and M_w/M_n are estimated by SEC [eluent: DMF solution of LiBr (10 mM), calibrated by polystyrene standards].
[e] Measured by TGA under flowing N_2 gas (50 mL min^{-1}, 10 °C min^{-1}).
[f] Measured by DSC under flowing N_2 gas (100 mL min^{-1}, 10 °C min^{-1}).

by osmium salts to form chiral vicinal diols and by the combination of potassium permanganate ($KMnO_4$) and quaternary ammonium salt.[8,9] By choosing $KMnO_4$ and ammonium salt system to achieve a simple preparation of vicinal diols from a vinyl monomer, we first synthesized two kinds of vicinal diols including *tert*-butyl 2,3-dihydroxy propanoate (**diol-1**), and 2,3-dihydroxy-*N*-isopropylpropanamide (**diol-2**) by the dihydroxylation of *tert*-butyl acrylate and *N*-isopropyl acrylamide, respectively. The benzyltriethylammonium chloride (TEBAC) (1.2 eq.) and $KMnO_4$ in acetone were suspended under stirring at room temperature for 3 h. Then the solution of *tert*-butyl acrylate or *N*-isopropyl acrylamide in acetone was added slowly to this reaction mixture at 0 °C. After the quenching with aqueous $NaHSO_3$, desired vicinal diol products (**diol-1** and **diol-2**) were obtained in moderate yield (50–60%). Second, styrene oxide that is commercially available low-cost monomer can be prepared by epoxidation of styrene with peroxybenzoic acid in the Prilezhaev reaction.[8] Thus, herein, the dihydroxylation of styrene was achieved by the one-step ring-opening reaction of styrene oxide with excess amounts of water to give a 1-phenylethane-1,2-diol (**diol-3**) (90%). Third, *N*-substituted maleimide-based vicinal diol, 3,4-dihydroxy-1-octylpyrrolidine-2,5-dione (**diol-4**) was conducted by a condensation reaction, where L-tartaric acid and *n*-octylamine was refluxed in xylene, instead of dihydroxylation of maleimide.[10,11]

All of the chemical structure of the obtained vicinal diols were confirmed by ^{1}H-NMR and ^{13}C-NMR analysis as shown in the Supporting Information Figure S1. These prepared diols have a chiral center, but the hydrolysis of racemic epoxide typically provided a corresponding diol as a racemic mixture. On the other hand, the diol, **diol-4** was synthesized from L-tartaric acid and a primary amine, where the configuration (*RR*) of product remained unchanged after condensation reaction. In all spectra, the characteristic alcohol peaks were disappeared by the addition of one drop of the deuterium oxide, to confirm the signal of alcohol group.

Preparation of Poly(Urethane)s by Polyaddition of Diols and Diisocyanate

To investigate polymerization behavior of the prepared vicinal diol monomers with MDI and HDI which are the most widely used diisocyanate derivatives for the synthesis of poly(urethane), we performed the polymerization reactions in the presence of dibutyltin dilaurate (DBTDL) catalyst (Scheme 2). The results of polymerization are summarized in Table 1. The conversions of diisocyanate during the reaction were tracked using ^{1}H NMR analysis. As a model reaction, we performed the polymerization of **diol-1** with MDI at room temperature. The reaction proceeded in high conversion of MDI to give a corresponding poly(urethane), **Poly1** (M_n = 8800, M_w/M_n = 2.62) (Supporting Information Scheme S1). Considering the possibility of remaining unreacted isocyanate or alcohol groups at the end of the polymer chain, we elevated the temperature of polymerization up to 60 °C. The molecular weight of **Poly1** (M_n = 32000, M_w/M_n = 2.02) (Poly1, in Table 1) became higher than in the case of polymerization at room temperature. It is worth noting that the reactivity of a distinct alcohol group for the case of **diol-1**, **diol-2**, and **diol-3** are asymmetric; it contains secondary and primary alcohol groups. Steric hindrance of the secondary alcohol group is likely to make them less reactive during polymerization reaction. Thus, the higher temperature was required to achieve a high molecular weight suitable for evaluating thermal and physical properties even though polymerization occurs at room temperature. On the basis of this optimized condition, the polymerization of other vicinal diols with MDI and HDI proceeded successfully to give a corresponding poly(urethane)s with high molecular weight and high yield. In the case of **diol-4**, the existence of two secondary alcohol groups and the rigid cyclic structure prevented a smooth formation of urethane linkage (Poly4, in Table 1), thereby providing lower molecular weight compared to the case of other poly(urethane)s (M_n = 7500, M_w/M_n = 2.40) (Scheme 2). When HDI was used for the reaction of **diol-4** (Poly8, in Table 1), the relatively higher molecular weight of poly(urethane) (M_n = 20000, M_w/M_n = 3.13) was formed due to less hindrance of alkyl isocyanate even in same reaction
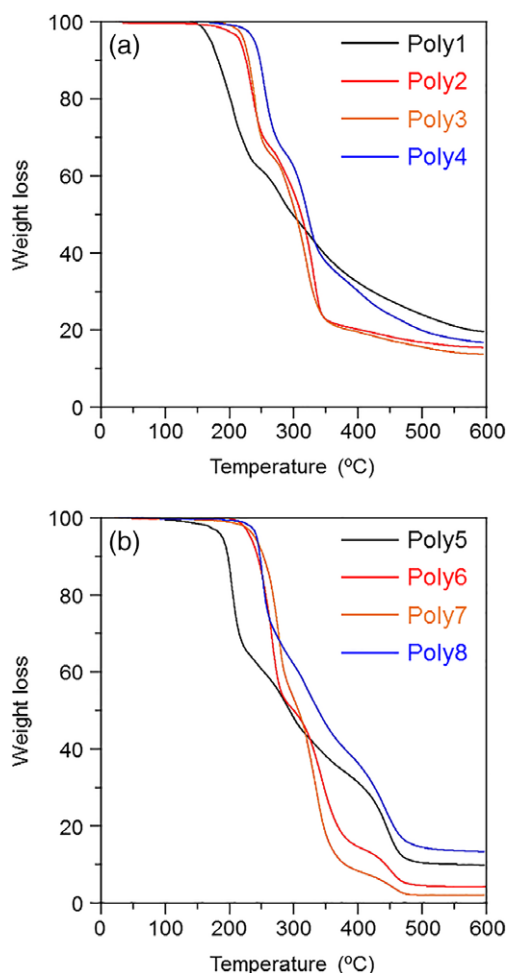
FIGURE 1 TGA profiles for series of poly(urethane)s: (a) MDI-based one, (b) HDI-based one using **diol-1**, **diol-2**, **diol-3**, and **diol-4**. [Color figure can be viewed at wileyonlinelibrary.com]

condition. In the case of HDI, the prepared poly(urethane)s has more linear character, therefore, poly(urethane) chains have stronger interaction of hydrogen bonding (urethane unit) than the case of MDI, resulting in lower solubility comparing with MDI containing poly(urethane)s. The solubility of each poly(urethane)s was evaluated in organic solvents (conc.: 2 mg mL^{-1}). HDI-based poly(urethane): **Poly5**, **Poly6**, **Poly7**, and **Poly8** are soluble in a high polar solvent including DMF and DMSO, but partially soluble in CHCl$_3$, THF, and acetone. On the other hand, MDI-based poly(urethane): **Poly1**, **Poly2**, **Poly3**, and **Poly4** have high solubility in common organic solvents except for hexane.

Supporting Information Figure S2 illustrates the ^{1}H NMR spectra of the obtained eight poly(urethane)s, indicating that the diisocyanates and vicinal diols unit were successfully incorporated in the polymer structure. The protons of —NH— corresponding to urethane linkage was clearly observed in 9.5–10 ppm for MDI-based poly(urethane) and 7.0–8.0 ppm for HDI-based poly(urethane)s, respectively. Also, other characteristic peaks are totally compatible. As shown in spectra of the Supporting Information Figure S2b, f, the peak of 8.0 ppm for **Poly2** and

Poly6, assigned to the —NH— proton of amide moiety represents the clear evidence that there was no any side reaction between diisocyanates and —NH— group of **diol-2** monomer during the polymerization. FTIR spectra of the poly(urethane)s was compared with their diol monomers in the Supporting Information Figure S3, in the following absorption peaks, the —OH and carbonyl groups of diol monomers were identified at around 3300 cm^{-1}, 1700 cm^{-1}, respectively. The monitored peaks around 1520 cm^{-1} for all polymers were assigned to N—H bonding of urethane repeating units. Additionally, the stretching vibrations of urethane carbonyl groups around 1690–1720 cm^{-1} were observed.

Thermal and Mechanical Properties of Poly(Urethane)S

Thermal stability of resultant poly(urethane)s was evaluated by thermal gravimetric analysis (TGA) under an nitrogen (N$_2$) atmosphere in the temperature range from 30 °C to 600 °C, and the scans are shown in Figure 1. Among the initial decomposition temperatures considering the 5% weight loss (T_{d5}), **Poly1** and **Poly5**, observed at 171 °C and 188 °C, respectively, exhibited the lowest thermal stability, because of decomposition of *tert*-butyl ester. Although, those of **Poly4** and **Poly8** was observed at 240 °C and 242 °C, respectively, that are highest thermal stability attributing to the incorporation of a rigid *N*-substituted succinimide structure on the polymer backbone. Moreover, the T_{d5} values of HDI-based poly(urethane)s were slightly high compared to those of MDI-based poly(urethane)s, because the intermolecular hydrogen bonding of MDI-based poly(urethane)s was relatively weak due to the bulkiness of methylenediphenyl moiety.
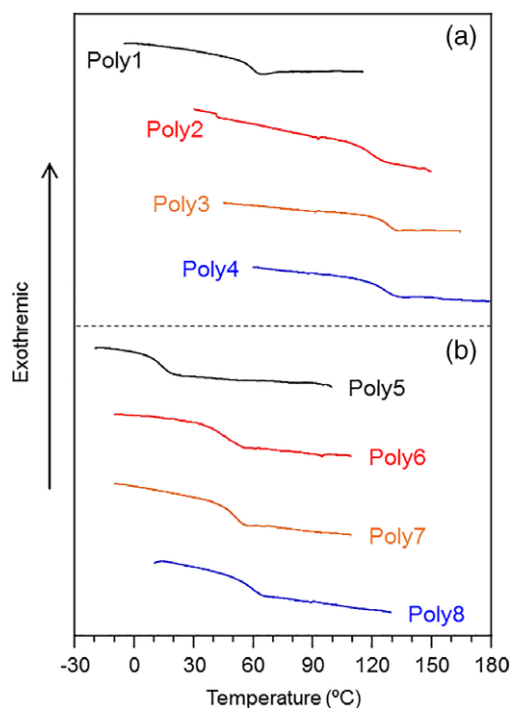

FIGURE 2 DSC profiles for series of MDI- based and HDI-based poly(urethane)s using **diol-1**, **diol-2**, **diol-3**, and **diol-4**. [Color figure can be viewed at wileyonlinelibrary.com]
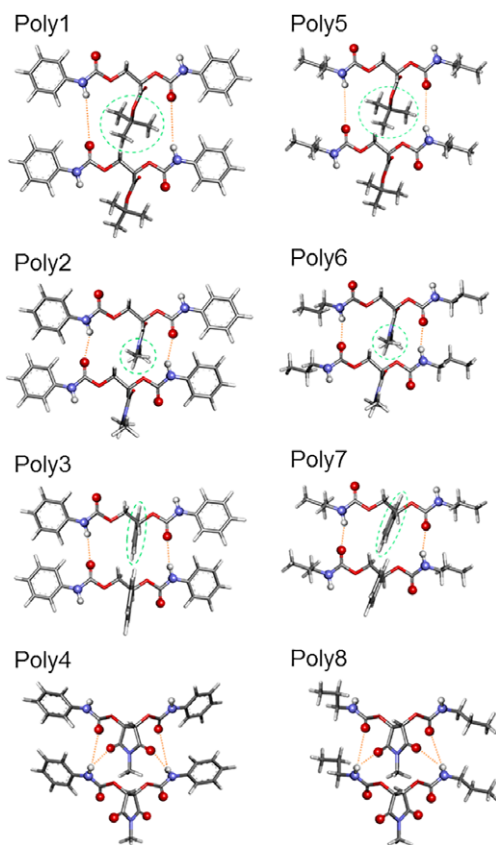
FIGURE 3 Specious models of intermolecular hydrogen bonding on urethane moiety based on **Poly1-8**. [Color figure can be viewed at wileyonlinelibrary.com]

DSC was also performed in the range of −30 to 180 °C (Fig. 2). As well as the behavior of T_{d5}, **Poly1** and **Poly5** exhibited the lowest glass-transition temperature (T_g), observed at 62.1 °C and 15.0 °C, respectively. The T_g of these poly(urethane)s depends on the behavior of intermolecular hydrogen bonding based on the bulkiness of diol unit (Fig. 3). Actually, the poly(urethane)s having a bulky *tert*-butyl ester moiety, that is, **Poly1** and **Poly5**, exhibited lower T_g value than those of a less bulkiness such as isopropylamide and phenyl moieties, that is, **Poly2**, **Poly3**, **Poly6**, and **Poly7**. On the other hand, T_g of **Poly4** and **Poly8** was the highest value, observed at 129.6 °C and 60.9 °C, respectively, because these poly(urethane)s formed significantly strong hydrogen bonding between two hydrogen atom of urethane moiety and four oxygen atoms of urethane and succinimide moieties (Fig. 3). Moreover, the T_g values of HDI-based poly(urethane)s were fairly low compared to those of MDI-based poly(urethane)s due to the flexibility of hexamethylene moiety on the polymer backbone.

To investigate the mechanical property, the solution of these poly(urethane)s in THF was cast on PTFE Petri dish, followed by drying at room temperature to fabricate thin film. Thin film, **diol-2**, **diol-4**-based poly(urethane) provides too brittle to pick it up Petri dish. Other films, the case of **diol-1** and **diol-3**-based poly(urethane), are flexible enough to evaluate its mechanical property by the tensile test using dumbbell-shaped test pieces.
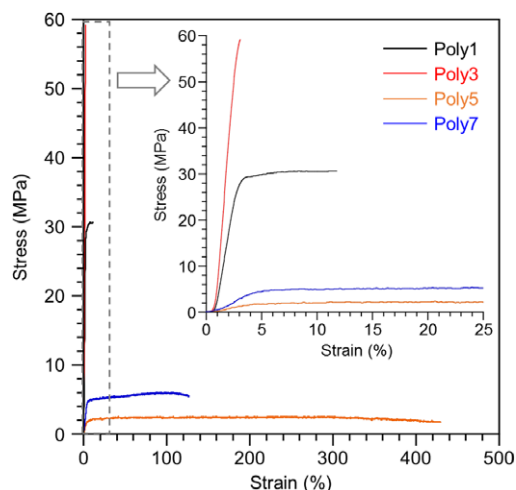
FIGURE 4 Stress–strain curves of **Poly1**, **Poly3**, **Poly5**, and **Poly7** films. [Color figure can be viewed at wileyonlinelibrary.com]
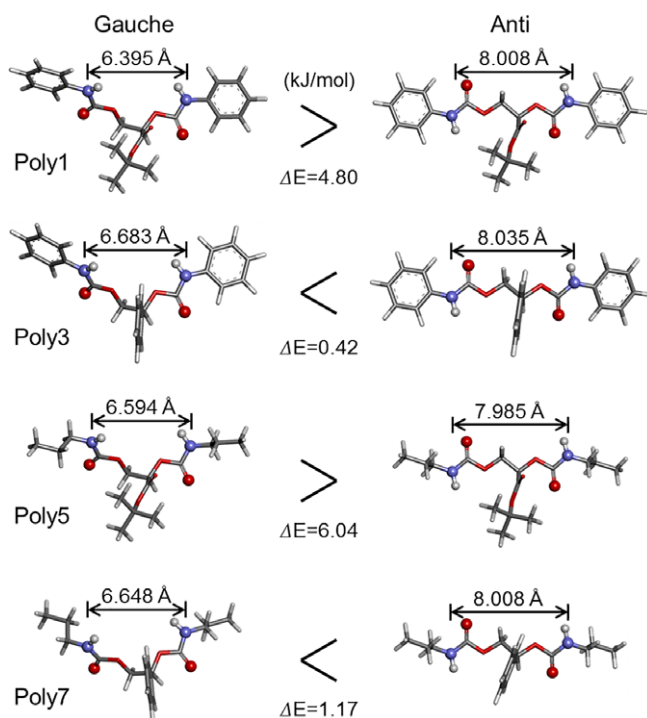
As shown in Figure 4 and Table 2, MDI-based poly(urethane) shows stiff films due to the presence of a rigid aromatic structure, whereas tensile properties are observed in case of HDI with flexible alkyl chain. We compared the side chain effect of diol between **diol-1** and **diol-3** on their mechanical properties. The incorporation of t*ert*-butyl ester moiety has a tendency to be lower Young's modulus than the case when **diol-3** was used because the steric hindrance of *tert*-butyl moiety makes the intermolecular hydrogen bonding of urethane moiety disordered.

Moreover, we evaluated the geometrical structure for model compounds of **diol-1** and **diol-3**-based poly(urethane)s using density functional theory (DFT) calculation (Fig. 5 and Supporting Information Table S1). Generally, ethylene glycol has two types of conformers due to anti and gauche conformations.[12] In the case of **diol-1**-based poly(urethane)s, the geometry optimized energy of gauche conformation of the **diol-1** unit was a lower value than that of anti conformation (Supporting Information Table S1). These estimated values mean that the gauche conformation of the **diol-1** unit is suitable conformer compared to anti conformation on the polymer backbone (Fig. 5, Poly1 and Poly5). In contrast, the geometry optimized energy of **diol-3**-based poly(urethane)s predicted that the anticonformation of the **diol-3** unit was more stable than gauche conformation on the

TABLE 2 Mechanical Properties of Poly(urethane) Films by a Tensile Test

Sample	Stress-at-break	Elongation-at-break	Young's modulus[a]
	(MPa)	(%)	(MPa)
Poly1	30.6 ± 1.17	11.8 ± 0.89	1367 ± 194.5
Poly3	59.1 ± 1.43	3.09 ± 0.21	2929 ± 140.7
Poly5	1.69 ± 0.05	430 ± 7.13	50.06 ± 8.034
Poly7	5.43 ± 0.58	127 ± 2.54	121.4 ± 54.30

[a] Estimated from the initial rising slope of stress–strain curve.

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FIGURE 5 Geometrical structure for model compounds of **diol-1** and **diol-3**-based poly(urethane) calculated using DFT with B3LYP/6-31G* method. [Color figure can be viewed at wileyonlinelibrary.com]

polymer backbone (Fig. 5, Poly3 and Poly7). Herein, the distance between two nitrogen atoms on the urethane moiety incorporating gauche conformation of the **diol-1** unit was shorter than that of anticonformation (Fig. 5, Poly1 and Poly5). Assuming that the main chains of **Poly1** and **Poly5** are stretched by tensile behavior accompanied with conformational isomerization of the diol unit from gauche to anti conformations, the tensile elongation is predicted to increase compared to that of **Poly3** and **Poly7**. Therefore, these results of computational evaluation suggest that the tensile elongation of **Poly1** and **Poly5** increases due to the weak hydrogen bonding disordered by bulky substituent and the main chain stretched by Gauche anticonformational isomerization.

CONCLUSIONS

Herein, we report a new type of poly(urethane)s by the polyaddition of the diisocyanate and the vicinal diol derivatives, possessing structural similarity to commercial vinyl monomers such as acrylate, acrylamide, styrene, and N-substituted maleimide. The dihydroxylation reactions of tert-butyl acrylate and N-Isopropyl acrylamide in the presence of a commercially available quaternary ammonium salt, TEBAC, and $KMnO_4$ give **diol-1** and **diol-2** in higher yield. The preparation of **diol-3** and **diol-4** was achieved in quantitative yields by the hydrolysis of styrene oxide with water, and the refluxing of L-tartaric acid and octylamine in p-xylene, respectively. The MDI and HDI were chosen as a model diisocyanate compound to perform the polyaddition reaction with these diol compounds. On the basis of an optimized condition of polymerization, the eight types of poly(urethane)s were successfully prepared in high molecular weight. In the key point of the study, we demonstrated the chemical structure of the used vicinal diol plays an important role in the thermal and mechanical properties on the resultant poly(urethane)s. The use of diols described in this study are readily prepared from commercially available compound and are capable to extend the synthesis of many different types of diols through dihydroxylation of vinyl monomers (acrylate, acrylamide, styrene and N-substituted maleimide derivatives) bearing a specific function, leading to the synthesis of a wide range of new types of poly(urethane)s.

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