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Synthesis and thermal properties of poly(urethane)s containing soft and flexible chain as the diols part

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Summary

α,ω-Diols with long carbon chains, $HO(CH_2)_{12}O(CH_2)_{12}OH$, $HO(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}OH$, and $HO(CH_2)_mOC_6H_4O(CH_2)_mOH$ (m =6, 12), reacted with diisocyanates to give the corresponding poly(urethane)s in 87-99% yields. Structure of the polyurethane was confirmed by ^1H and ^{13}C NMR spectroscopy. IR absorbance due to $\nu(C=O)$ vibration of the polymers obtained from hexamethylene diisocyanate was observed at lower wavenumber than that of the polymers from aromatic diisocyanates. Melting point of the poly(urethane)s decreased with increase in flexibility of the polymer chain.

Introduction

A number of papers have been published concerning poly(urethane)s containing both soft and hard segments since such poly(urethane)s were reported to show liquid crystalline and interesting thermal properties (1-8). Properties of the poly(urethane)s vary depending on the structure of the polymer backbone as well as the strength of their intermolecular NH•••O hydrogen bonding. For example, effects of the strength of the hydrogen bonding of poly(urethane)s on their physical properties have been investigated by using poly(urethane)s that contain polyether chain (C~100) or polymethylene chain (C2-C6) as a soft segment. IR and NMR spectroscopy, differential scanning calorimetry (DSC), and X-ray diffraction measurement (9-15) have been applied for the investigation.

We have recently reported synthesis of several new poly(urethane)s by polyaddition of 1,1'-methylenebis[4-isocyanatebenzene] and of 1,3-bis(isocyanatemethyl)benzene with long alkane α,ω-diols (*e.g.*, bis(12-hydroxy-1-dodecamethylene)ether, 1, 12-bis(13-hydroxy-1-oxadodecyl)dodecane, 1,4-bis(7-hydroxy-1-oxaheptyl)benzene, and 1,4-bis(13-hydroxy-1-oxadodecyl)benzene) and found that melting point (T_m) of the polymers varies depending on the structure (16). We have expanded the research and here report preparation and properties of series of poly(urethane)s having a long or moderate length of polymethylene chain (C12-C36) as a soft segment.

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Experimental

General Data, Materials and Measurement

All the manipulations were performed under nitrogen using standard Schlenk techniques. *N*-methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylformamide (DMF) were distilled by usual methods and stored under nitrogen. Bis(12-hydroxy-1-dodecamethylene)ether, 1,12-bis(13-hydroxy-1-oxadodecyl)dodecane, 1,4-bis(7-hydroxy-1-oxaheptyl)benzene (BHHB), and 1,4-bis(13-hydroxy-1-oxadodecyl)benzene (BHDB) were prepared according to the literature procedure (16) and other organic chemicals were purchased and used as received. IR and NMR spectra were recorded on a JASCO-IR 810 spectrophotometer and a JEOL EX-400 spectrometer, respectively. Elemental analyses were carried out by a Yanaco MT-5 CHN autocorder. GPC analyses were performed on a Toso HLC 8120 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a DMF solution of LiBr (0.02 M) as the eluent with a flow rate of 1.0 mL min^{-1} and with RI and UV detectors. DSC data were obtained on a Shimadzu DSC-50 thermal analyzer.

Polyaddition

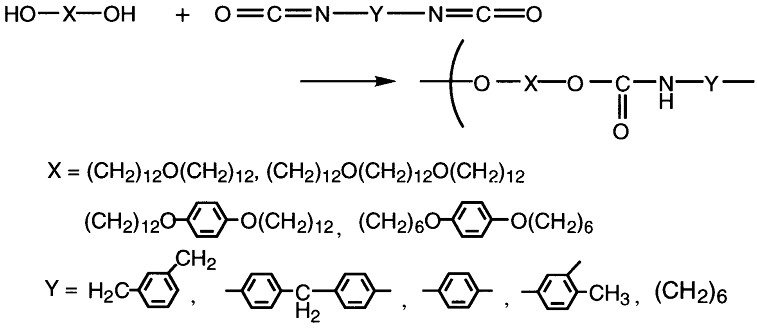
Typical procedure for the polyaddition is as follows. A Schlenk flask containing BHHB (311 mg, 1.0 mmol) and 1,4-benzenediisocyanate (160 mg, 1.0 mmol) was flashed with N_2 several times. After addition of NMP (2 cm^3), the mixture was heated at 100 °C for 20 h with stirring. The product was poured into MeOH (250 cm^3) to lead to separation of the polymer product as a colorless solid which was collected by filtration, washed with MeOH and dried in vacuo to give **11** (440 mg, 93%). IR (KBr, cm^{-1}): 3314, 3050, 2922, 2850, 1695, 1607, 1551, 1520, 1467, 1410, 1305, 1221, 1116, 1072, 834, 767, 720, 659. ^{1}H NMR (400 MHz in DMSO-d_6): δ 9.4 (s, NH), 7.3 (s, OC_6H_4O), 6.8 (s, NC_6H_4N), 4.3 (br, $CH_2O\mathit{H}$ of terminal group), 4.1 (s, $CH_2O(C{=}O)$), 3.9 (s, $C_6H_4OC\mathit{H_2}$), 3.4 (br, $C\mathit{H_2}OH$ of terminal group), 1.6 and 1.4 (s, $(CH_2)_4$). $^{13}C\{^1H\}$ NMR (100 MHz in DMSO-d_6): δ 153.6 (C=O), 152.5 (1,4-positions of OC_6H_4O), 133.9 (1,4-positions of NC_6H_4N), 118.7 (3,4-positions of NC_6H_4N), 115.4 (3,4-positions of OC_6H_4O), 67.7 ($CH_2OC_6H_4$), 63.9 ($CH_2O(C{=}O)$), 60.6 (CH_2OH), 32.4, 28.8, 28.7, 28.5, 25.4, 25.2, 25.1, 25.0. Anal Calcd. for $(C_{26}H_{34}N_2O_6)_n$: C = 66.36%, H = 7.28%, N = 5.95%. Found: C = 66.07%, H = 7.36%, N = 6.20%.

Polyaddition of other substrates were carried out analogously. Spectroscopic data of **1**, **4**, **5**, **9**, and **10** have been reported in ref. 16. Spectroscopic and analytical data of **2**: IR (KBr, cm^{-1}): 3316, 3050, 2922, 2850, 1701, 1607, 1551, 1520, 1467, 1410, 1305, 1221, 1116, 1072, 834, 767, 719, 659, 518. ^{1}H NMR (400 MHz in DMSO-d_6): δ 7.3 (s, C_6H_4), 4.0 (s, CH_2OCH_2), 1.3-1.6 (m, $(CH_2)_{11}$). Anal Calcd. for $(C_{32}H_{57}N_2O_5)_n$: C = 71.17%, H = 10.01%, N = 4.88%. Found: C = 69.84%, H = 9.95%, N = 5.56%. Spectroscopic and analytical data of **3**: IR (KBr, cm^{-1}): 3322, 2920, 2852, 1680, 1535, 1467, 1341, 1262, 1143, 1117, 1054, 778, 718, 635. ^{1}H NMR (400 MHz in $CDCl_3$): δ 4.7 (s, NH), 4.05 (s, $CH_2O(C{=}O)$), 3.65 ($C\mathit{H_2}OH$ of terminal group), 3.4 (t, CH_2OCH_2, J = 5 Hz), 3.15 (q, $C\mathit{H_2}NH$, *J*= 7 Hz), 1.5-1.6 and 1.3 (m, $(CH_2)_{10}$ and $(CH_2)_4$). Anal Calcd. for $(C_{32}H_{62}N_2O_5)_n$: C = 67.88%, H = 11.77%, N = 5.28%. Found: C = 67.34, H = 10.75%, N = 6.17%. Spectroscopic and analytical data of **6**: IR

(KBr, cm^{-1}): 3312, 3030, 2920, 2850, 1698, 1607, 1550, 1508, 1466, 1410, 1305, 1224, 1072, 820, 768, 719, 657, 518. ^{1}H NMR (400 MHz in DMSO-d_6): δ 7.2-7.3 (m, $CH_2C_6\mathit{H}_4CH_2$), 6.8 (s, OC_6H_4O), 5.0 (br, NH), 4.3 (s, $C_6H_4C\mathit{H}_2$ and $CH_2O\mathit{H}$ of terminal group), 4.1 (s, $CH_2O(C{=}O)$), 3.9 (s, $C_6H_4OC\mathit{H}_2$), 3.6 ($C\mathit{H}_2OH$ of terminal group), 1.4-1.7 (m, $(CH_2)_{10}$). Anal Calcd. for $(C_{38}H_{58}N_2O_6)_n$: C = 71.44%, H = 9.15%, N = 4.38%. Found: C = 71.16%, H = 9.25%, N = 4.66%. Spectroscopic and analytical data of **7**: IR (KBr, cm^{-1}): 3300, 3050, 2922, 2852, 1700, 1598, 1530, 1509, 1466, 1414, 1230, 1056, 1000, 876, 823, 768, 719, 522, 455. ^{1}H NMR (400 MHz in DMSO-d_6): δ 7.8 and 7.2 (s, NH), 6.4-7.1 (m, OC_6H_4O and C_6H_3), 4.1 (s, $CH_2O(C{=}O)$), 3.9 (s, $C_6H_4OC\mathit{H}_2$), 3.6 ($C\mathit{H}_2OH$ of terminal group), 2.1 (s, Me), 1.3-1.8 (m, $(CH_2)_{10}$). Anal Calcd. for $(C_{39}H_{60}N_2O_6)_n$: C = 71.74%, H = 9.26%, N = 4.29%. Found: C = 71.22%, H = 9.12%, N = 4.65%. Spectroscopic and analytical data of **8**: IR (KBr, cm^{-1}): 3322, 3052, 2918, 2852, 1685, 1535, 1511, 1475, 1396, 1342, 1262, 1236, 1141, 1052, 1039, 822, 771, 716, 642. Anal Calcd. for $(C_{38}H_{66}N_2O_6)_n$: C = 70.55%, H = 10.28%, N = 4.33%. Found: C = 70.06%, H = 10.56%, N =4.56%. Spectroscopic and analytical data of **12**: IR (KBr, cm^{-1}): 3278, 2936, 2858, 1699, 1599, 1533, 1506, 1228, 1065, 998, 821, 765, 516. ^{1}H NMR (400 MHz in DMSO-d_6): δ 9.5 and 8.7 (s, NH), 7.5 (s, 3-position of C_6H_3), 7.05 (ABq, 5,6-positions of C_6H_3, J = 8 and 43 Hz), 4.3 (br, $CH_2O\mathit{H}$ of terminal group), 4.05 (s, $CH_2O(C{=}O)$), 3.8 (s, $C_6H_4OC\mathit{H}_2$), 3.4 (br, $C\mathit{H}_2OH$ of terminal group), 2.1 (s, Me), 1.6 and 1.4 (s, $(CH_2)_4$). Anal Calcd. for $(C_{27}H_{36}N_2O_6)_n$: C = 66.92%, H = 7.49%, N = 5.78%. Found: C = 66.26%, H = 7.42%, N = 5.84%. Spectroscopic and analytical data of **13**: IR (KBr, cm^{-1}): 3326, 3050, 2938, 2862, 1685, 1534, 1538, 1476, 1261, 1234, 1140, 1111, 1013, 821, 771, 726, 636, 520. ^{1}H NMR (400 MHz in DMSO-d_6): 6.8 (s, OC_6H_4O), 4.0 (s, $CH_2O(C{=}O)$), 3.9 (s, $C_6H_4OC\mathit{H}_2$), 3.1 (br, $C\mathit{H}_2OH$ of terminal group), 1.2-1.8 (m, $(CH_2)_4$). Anal Calcd. for $(C_{26}H_{42}N_2O_6)_n$: C = 65.25%, H = 8.84%, N = 5.85%. Found: C = 64.64%, H = 8.76%, N = 6.23%.

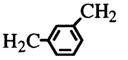
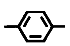
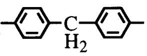
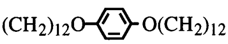
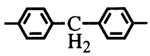
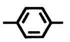
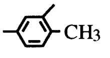
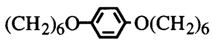
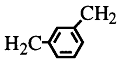
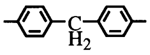
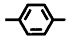
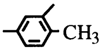
Results and Discussion

Polyaddition of long α,ω-diols with 1,4-benzenediisocyanate, 1-methyl-2,4-benzenediisocyanate, and hexamethylene diisocyanate gave the corresponding poly(urethane)s in high yields (Scheme).



Scheme 1 Polyaddition of diols with diisocyanates.

Table Polyaddition of α,ω-Diols (HO-X-OH) with Diisocyanate (OCN-Y-NCO) [a)]

	Substrates		Products					
Run	X	Y	Polymer	Yield(%)	$10^{-3}M_n$ [b]	$10^{-3}M_w$ [b]	T_m/°C	ν(C=O)/cm^{-1}
1	$(CH_2)_{12}O(CH_2)_{12}$		**1**	98	24.6	27.3	108	1695
2			**2**	92	2.8	3.1	160	1701
3		$(CH_2)_6$	**3**	99	2.8	2.9	122	1680
4	$(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}$		**4**	95	50.8	84.4	117	1701
5			**5**	98	76.5	107	138	1696
6			**6**	91	4.5	4.8	172	1698
7			**7**	93	4.1	6.4	90	1700
8		$(CH_2)_6$	**8**	90	7.3	7.4	133	1681
9			**9**	89	20.9	24.9	126	1695
10			**10**	97	42.4	59.9	150	1699
11			**11**	93	10.2	12.3	204	1695
12			**12**	87	22.4	34.9	93	1699
13		$(CH_2)_6$	**13**	93	5.9	6.1	147	1685

a) Run 1, 4, 5, 9, and 10 are the results taken from ref. 16. Reaction conditions: 100 °C, 20 h in 2 cm^3 of NMP (run 1-3, 6-9, and 11-13) or DMF (run 4, 5, and 10).

b) Obtained from GPC using DMF containing LiBr (0.02 M) as the eluent and polystyrene standards.

The results are summarized in Table together with previously reported polyaddition (run 1, 4, 5, 9, and 10).

Figure 1 depicts the ^1H and ^{13}C NMR spectra of polymer **11**. Peaks due to NH, $CH_2O(C=O)$, and $C_6H_4OCH_2$ hydrogens are observed at δ 9.4, 4.1, and 3.9, respectively. Hydrogens due to the CH_2OH terminal group show the small peaks at δ 4.3 and 3.4. M_n values of the polymers calculated from the relative peak intensity are smaller than those by GPC. The ^{13}C NMR spectrum of **11** shows a peak due to C=O group at δ 153.6 and that due to terminal CH_2OH group at δ 60.6.

IR absorbance due to ν(C=O) vibration of polymers **3**, **8**, and **13**, which are prepared from hexamethylene diisocyanate, is observed at a lower wavenumber (1680-1685 cm^{-1}) than that of polymers **1, 2, 4-7,** and **9-12** (1695-1701 cm^{-1}) which are derived from aromatic diisocyanates. The IR data indicate that the former polymers form

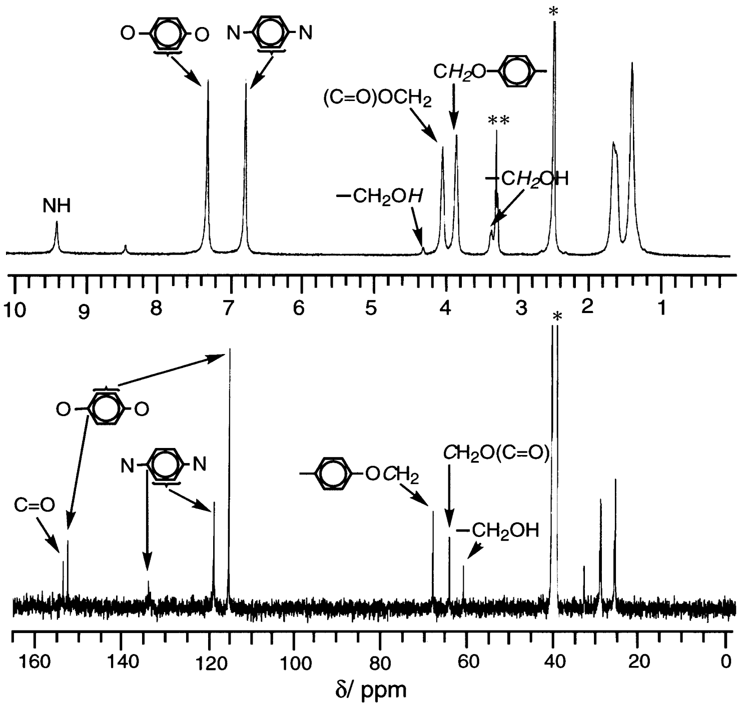


Figure 1 ^1H (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra of **11** in DMSO-d_6. Peak with an asterisk is due to the solvent and that with a double asterisk is due to H_2O contaminated in the solvent.

stronger hydrogen bond (NH···O) than the latter polymers, arising from higher acidity of the N-H group of the aliphatic poly(urethane) than the aromatic one.

GPC measurements show that molecular weights of the poly(urethane)s obtained in this work are strongly influenced by diisocyanates; polymers prepared from 1,4-benzenediisocyanate and 1, 1'-methylenebis[4-isocyanatebenzene] have high molecular weights in spite of the diol part, while those from hexamethylene diisocyanate have moderate molecular weights. The difference of molecular weight of the polymers may be ascribed to difference of reactivity between aromatic and aliphatic isocyanate groups. Solubility of the polymers depends on molecular weight rather than structure of the polymers. Polymers **3, 7,** and **9-13** are soluble in polar solvents such as DMF, DMSO, and NMP. High molecular weight polymers **1, 2,** and **4-6** are partially soluble in the solvents.

The poly(urethane)s obtained in this work start thermal decomposition around 300 °C as measured by thermogravimetry. T_m of the polymers measured by DSC decreased with increase in the length of the carbon chain of the diol part and with decrease in rigidity of the diisocyanate part as shown in Figure 2.

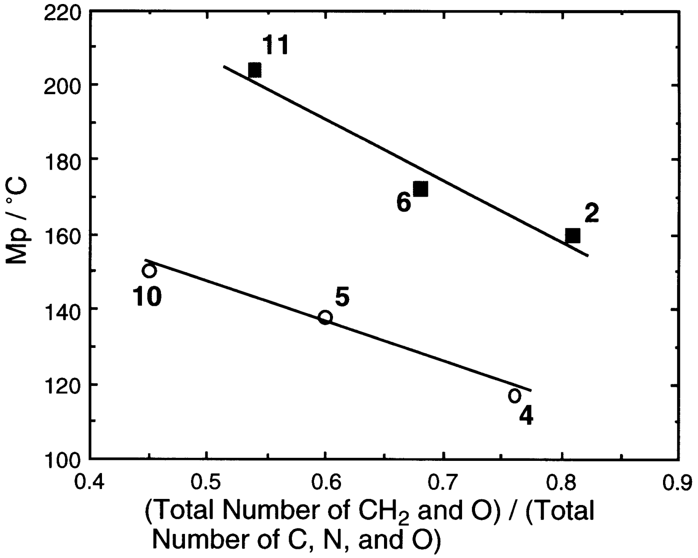


Figure 2 Plots of melting point of poly(urethane) of (a) 1,4-benzenediisocyanate and (b) 1,1'-methylenebis[4-isocyanatebenzene] as a function of fraction of the CH_2 and O units in all of C, N, and O atoms in the polymer.

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