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Preparation of α,ω-Diols of Long Carbon Chains and Their Use in Polyurethane Synthesis

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NaH promoted coupling reaction of $HO(CH_2)_{12}O$–TBDMS (**1**, TBDMS=$SiMe_2$(*t*-Bu)) and $Br(CH_2)_{12}O$–TBDMS (**2**) followed by deprotection of the organosilyl groups affords $HO(CH_2)_{12}O(CH_2)_{12}OH$ (**5**). 1,12-Dodecanediol reacts with an excess amount of **2** in the presence of NaH to give TBDMS–$O(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}O$–TBDMS (**6**) which is turned into $HO(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}OH$ (**7**) by removal of the protecting groups. Similar 1 : 2 condensation of hydroquinone with **2** and with $Br(CH_2)_6O$–TBDMS (**3**) leads to formation of the corresponding α,ω-diols, $HO(CH_2)_{12}OC_6H_4O(CH_2)_{12}OH$ (**9**) and $HO(CH_2)_6OC_6H_4O(CH_2)_6OH$ (**11**), respectively. The four new long α,ω-diols are isolated and characterized by means of IR and NMR spectroscopy as well as elemental analyses. Polyaddition reactions of **5**, **7**, **9**, and **11** to 1,3-bis(isocyanatomethyl)benzene and 1,1′-methylenebis[4-isocyanatobenzene] give the corresponding poly(urethane)s in high yields. The obtained polymers, which were characterized by IR and NMR spectroscopy, have molecular weights over 20000 as determined from gel permeation chromatography using polystyrene standards.

Low molecular weight poly(ethylene oxide) and poly(tetramethylene oxide) are utilized as building blocks of macromonomers,[1] liquid crystalline compounds,[2] polyrotaxanes,[3] polyurethane elastomers,[4] and block copolymers containing both hydrophilic and hydrophobic segments.[5] The polyether structure in the repeating units of aromatic poly(urethane)s renders the polymer chain soft and flexible and results in microphase separation of the polymer materials. The flexible short poly(ethylene oxide) chain serves as the thread of polyrotaxane with macrocylcic compounds.

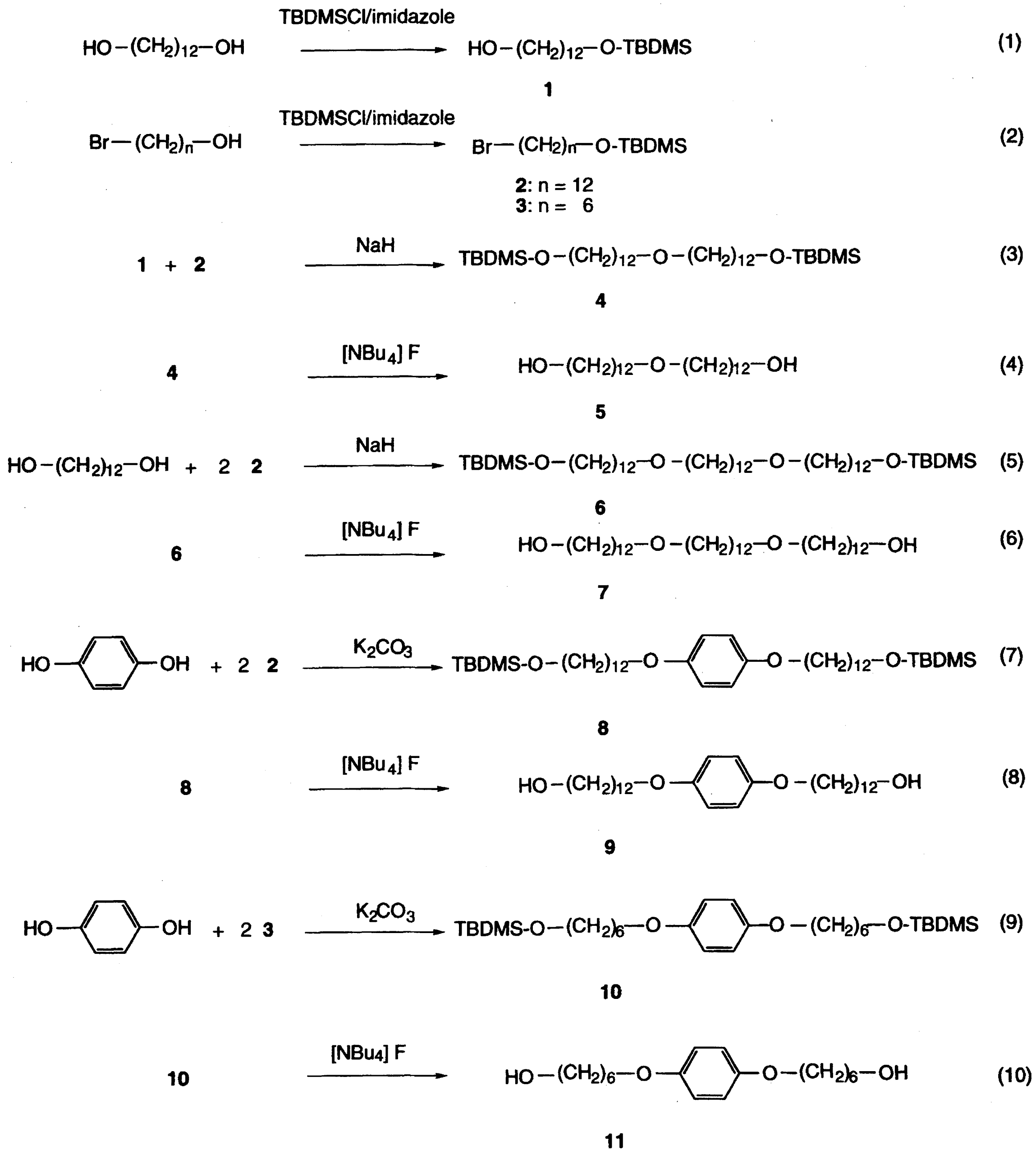
α,ω-Alkanediols with long carbon chains will also be useful as another type of building block for polymers with similar flexibility and with less hydrophilic nature. Recently we reported preparation of polybenzimidazoles having a $(CH_2)_{11}O(CH_2)_{11}$ unit in their main chains as well as preparation of their polyrotaxanes with cyclodextrines.[6]

Two terminal OH groups of the α,ω-diols would react with various bifunctional compounds such as diisocyanates and dicarboxyl chlorides to give poly(urethane)s and polyesters containing the flexible diol part. However, general and convenient preparation methodology of the long α,ω-diols has not been presented. Preparation of α,ω-diols has been achieved by using hemiacetal protected diol.[7] Our strategy for the synthesis of these molecules in the present study includes base-promoted coupling of CH_2Br and CH_2OH groups of diols and bromoalkanols whose OH groups are adequately protected in part with tertiary silyl group.[8] In this paper, we present preparation of four new long α,ω-diols based on the above idea, as well as their reactions with diisocyanates to give the corresponding poly(urethane)s.

Results and Discussion

The long α,ω-diols can be prepared by base promoted coupling reactions of α,ω-diols and $Br(CH_2)_nOTBDMS$ ($n=6$, 12; TBDMS=$SiMe_2$(*t*-Bu)) as summarized in Scheme 1. A reaction of $HO(CH_2)_{12}O$–TBDMS (**1**) and $Br(CH_2)_{12}O$–TBDMS (**2**) promoted by NaH followed by deprotection of the organosilyl group with $[NBu_4]F$ gives $HO(CH_2)_{12}O(CH_2)_{12}OH$ (**4**) as colorless crystals. A similar reaction of two terminal OH groups of 1,12-dodecanediol with **2** (Eq. 5) leads to the corresponding α,ω-diol, $HO(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}OH$ (**7**). Hydroquinone also serves as the starting materials of α,ω-diols $HO(CH_2)_{12}OC_6H_4O(CH_2)_{12}OH$ (**9**) and $HO(CH_2)_6OC_6H_4O(CH_2)_6OH$ (**11**).

The diols **5**, **7**, and **11** are soluble in $CHCl_3$, whereas **9** is practically insoluble in the solvent. All the diols are dissolved in polar solvents such as DMF, DMSO, and NMP (*N*-methyl-2-pyrrolidone) at 60 °C, while they are sparingly soluble in these solvents at room temperature. The above four α,ω-diols give the spectroscopic and analytical data which are consistent with the proposed structure. The ^{1}H NMR spectrum of **5** in $CDCl_3$ shows a triplet due to CH_2–O–CH_2 hydrogens at $\delta=3.37$ and a triplet due to α-CH_2 hydrogen of the OH group at $\delta=3.62$. The OH hydrogen signal is not observed, probably due to extreme broadening of the signal, although the presence of OH group is confirmed by the IR spectrum which shows the ν(OH) vibration at 3238 cm^{-1}. The other diols, **7**, **9**, and **11** also give the sufficient spectroscopic data to determine the structure. The ^{1}H NMR peak of CH_2 hydrogens bonded to OH group of **9** is observed as a doublet of triplet at room temperature. The splitting

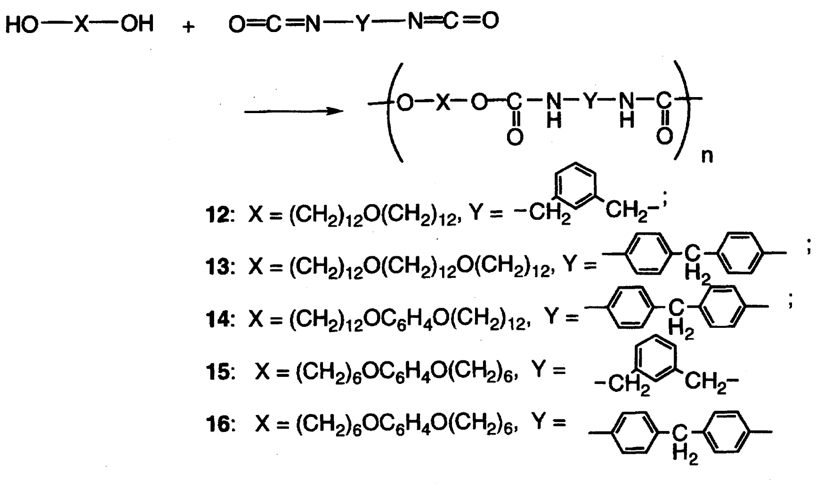


Scheme 1.

of the signal by coupling with OH hydrogen suggests that intermolecular exchanges of the OH hydrogens occur more slowly than in common primary alcohols.

Polyaddition of **5** to 1, 3-bis(isocyanatomethyl)benzene occurs at 100 °C to give the polyurethane [–O–$(CH_2)_{12}$–O–$(CH_2)_{12}$–O–CONH–$CH_2C_6H_4CH_2$–NHCO–$]_n$ (**12**). Similar reactions of **7**, **9**, and **11** with 1,3-bis(isocyanatomethyl)benzene and 1,1′-methylenebis[4-isocyanatobenzene] give the corresponding poly(urethane)s **13**—**16** as shown in Scheme 2. Table 1 summarizes yields and results of elemental analyses of the polymers. Polymers **15** and **16** are soluble in polar solvents such as DMF, DMSO, and NMP, while **12**—**14** are partially soluble in these solvents. $CHCl_3$ dissolves **12** well, but **13** and **16** sparingly. The poly(urethane)s obtained in this study show satisfactory IR and NMR data to support the polyurethane structure. The IR spectra of **12**—**16** contain bands characteristic for the NH–CO–O linkage at 3294—3318 cm^{-1} (ν(NH)), 1695—1701 cm^{-1} (ν(C=O)), and 1034—1119 cm^{-1} (ν(C–O)). Figure 1 shows the ^1H and ^{13}C NMR spectra of **16**, showing the signals which are consistent with the structure. The NHCOO group in the polymer shows the ^1H NMR peak due to the NH hydrogen at $\delta = 9.48$ and the ^{13}C NMR peak due to the carbonyl carbon at $\delta = 152.5$. The ^1H NMR spectrum shows not only the signals due to the main chain but terminal CH_2OH hydrogens at $\delta = 4.32$ and 3.39. The polymers with moderate to high molecular weights ($M_n = 21$—77×10^3 vs. polystyrene and 13—53×10^3 vs. poly(methyl methacrylate)) are obtained for all the combinations of the diols and diisocyanates examined.

The polymers show thermal decomposition above 300 °C



Scheme 2.

Table 1. Polyaddition of α,ω-Diol (HO–X–OH) to Diisocyanate (OCN–Y–NCO)[a]

Run	Substrates		Products						
					Analysis[b]			Molecular weight[c]	
	X	Y	Polymer	Yield(%)	C(%)	H(%)	N(%)	$10^{-3}M_n$	$10^{-3}M_w$
1	$(CH_2)_{12}O(CH_2)_{12}$	$CH_2C_6H_4CH_2$	**12**	98	69.80	9.33	5.85	24.6	27.3
					(71.04	10.17	4.87)		
2	$(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}$	$C_6H_4CH_2C_6H_4$	**13**	95	74.14	9.33	3.53	50.8	84.4
					(74.59	10.31	3.41		
3	$(CH_2)_{12}OC_6H_4O(CH_2)_{12}$	$C_6H_4CH_2C_6H_4$	**14**	98	73.57	8.65	4.12	76.5	107
					(74.14	8.85	3.84)	[53.4	80.6]
4	$(CH_2)_6OC_6H_4O(CH_2)_6$	$CH_2C_6H_4CH_2$	**15**	89	67.01	7.66	5.97	20.9	24.9
					(67.45	7.68	5.62)	[12.9	15.9]
5	$(CH_2)_6OC_6H_4O(CH_2)_6$	$C_6H_4CH_2C_6H_4$	**16**	97	69.96	7.38	5.22	42.4	59.9
					(70.69	7.19	5.00)	[28.4	42.5]

a) Reaction conditions: 100 °C, 20 h in 2 cm^3 of NMP (Runs 1 and 4) or DMF (Runs 2, 3, and 5). b) Calculated values are given in parentheses. c) Obtained from GPC using DMF containing LiBr (0.02 M) as the eluant and polystyrene standards. Molecular weights using PMMA standards are given in brackets. The data of **12**—**14** are for the soluble part of the polymers.

as measured by thermogravimetry. Figure 2 compares the DSC scan of the poly(urethane)s **12**—**16** which show a transition due to melting in the temperature range, 100—150 °C, whereas polyurethane prepared similarly from polyaddition of 1,4-bis(hydroxymethyl)benzene with 1,1′-methylenebis-[4-isocyanatobenzene] does not show the melting transition below 200 °C. The melting point obtained from the DSC decreases in the order, **16** (150 °C), **14** (138 °C), **15** (126 °C), **13** (117 °C), and **12** (108 °C). These results imply that introduction of a long polymethylene group in the structural unit of the aromatic polyurethanes renders the melting point of the polymer lower.

In summary, the present work has provided a convenient synthetic route for long α,ω-diols containing the CH_2OCH_2 linkage from repetition of intermolecular condensation of CH_2OH and CH_2Br groups and proper protection and deprotection of the OH groups. This simple preparation method will be able to be extended to synthesis of various new α,ω-diols with higher molecular weights by repetition of the synthetic process. α,ω-Diols obtained in the present work effectively couple with diisocyanates to give poly(urethane)s. Extension of this work will provide bases for better understanding of properties of poly(urethane)s depending on their building blocks.

Experimental

General Procedure, Materials, and Measurement. Most manipulations were carried out under nitrogen or argon using Schlenk technique. Solvents were dried in usual manners, distilled and stored under nitrogen atmosphere. Organic chemicals were obtained from commercial suppliers and used without further purification. NaH was obtained and used as a dispersion in mineral oil (55%). IR spectra were obtained on a JASCO-IR810 spectrophotometer. NMR spectra (^{1}H and ^{13}C) were recorded on JEOL EX-90 and EX-400 spectrometers. Elemental analyses were carried out by a Yanaco MT-5 CHN autocorder. GPC analyses were carried out by a Toso HPLC 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 analyses were performed on a Shimadzu DSC-50.

Preparation of $HO(CH_2)_{12}O$–TBDMS (1), $Br(CH_2)_{12}O$–TBDMS (2), and $Br(CH_2)_6O$–TBDMS (3). To a DMF (100 cm^3) solution of 1,12-dodecanediol (2.02 g, 10 mmol) and imidazole (817 mg, 12 mmol) was added a DMF (40 cm^3) solution of TBDMSCl (603 mg, 4 mmol) dropwise over a period of 17 h with stirring at room temperature. The resulting solution was quenched with NH_4Cl aq, and the product was extracted with ethyl acetate three

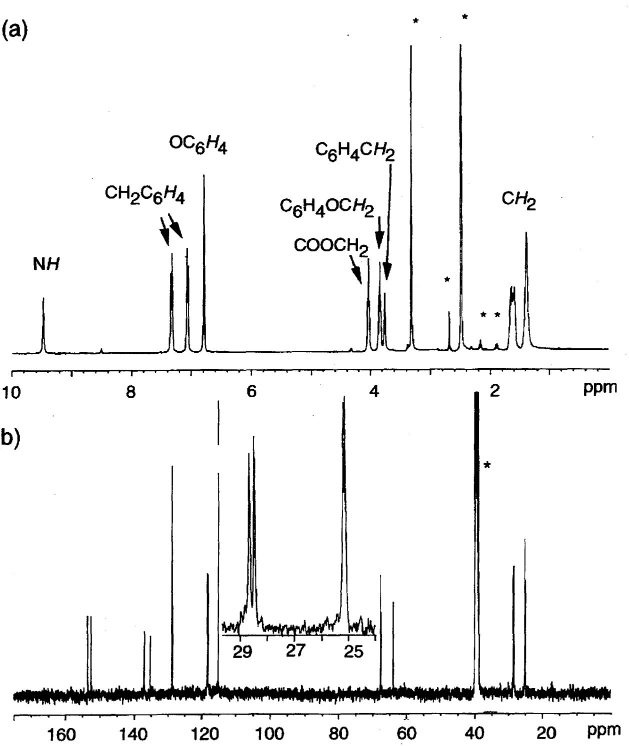


Fig. 1. (a) ^{1}H (400 MHz) and (b) ^{13}C{^{1}H} (100 MHz) NMR spectra of poly(urethane) **16** in DMSO-d_6. The ^{1}H NMR peaks with asterisks are due to the solvent ($\delta = 2.5$), and H_2O impurity in it ($\delta = 3.3$) and the residual NMP ($\delta = 1.9$, 2.2, and 2.7). The small peaks at $\delta = 4.32$ and 3.39 are assigned to OH and CH_2 hydrogens of the terminal CH_2OH group, respectively. The ^{13}C NMR peak with an asterisk is due to the solvent.

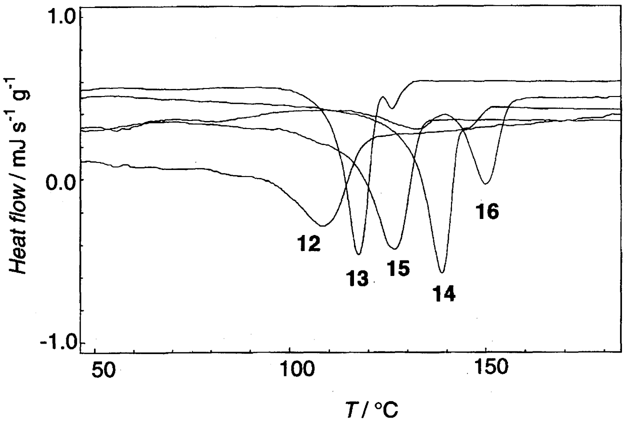


Fig. 2. DSC scan of **12**—**16** obtained at a heating rate of 10 °C min^{-1} under helium stream. Scan range is −100—200 °C.

times. The combined organic phase was washed with 1 M HCl aq (1 M = 1 mol dm^{-3}), $NaHCO_3$ aq and then with NaCl aq, and dried over Na_2SO_4. Recrystallization from a hexane–ethyl acetate mixture followed by column chromatography on silica gel (gradient from hexane to hexane–ethyl acetate mixture (5 : 1)) afforded HO-$(CH_2)_{12}$O–TBDMS as colorless crystals (766 mg, 61%). $R_f = 0.57$ ($CHCl_3$–MeOH, 10 : 1).

A similar reaction of $Br(CH_2)_{12}OH$ and of $Br(CH_2)_6OH$ with TBDMSCl and ensuing purification by column chromatography gave quantitative amounts of **2** and **3**, respectively. ^{1}H NMR of **2** (400 MHz in $CDCl_3$) $\delta = 0.03$ (s, 12H, $SiCH_3$), 0.87 (s, 18H, $C(CH_3)_3$), 1.25 (br, 14H, CH_2), 1.4—1.5 (m, 4H, CH_2), 1.84 (m, 2H, CH_2), 3.39 (t, 2H, $BrCH_2$, $J = 7$ Hz), 3.58 (t, 2H, CH_2OSi, $J = 7$ Hz). ^{13}C{^{1}H} NMR of **2** (100 MHz in $CDCl_3$) $\delta = -5.3$, 18.4, 25.8, 26.0, 28.2, 29.4, 29.5, 29.6, 32.9, 34.0, 63.3.

Preparation of $HO(CH_2)_{12}O(CH_2)_{12}OH$ (5). A mixture of NaH (203 mg, 4.7 mmol) and **1** (738 mg, 2.3 mmol) in THF (10 cm^3) was stirred for 1 h at room temperature. After cooling the mixture at 0 °C, **2** (885 mg, 2.3 mmol) was gradually added with stirring. The reaction was continued for 48 h at 40 °C. The resulting mixture was quenched by NH_4Cl aq at room temperature, and the organic product was extracted with Et_2O three times. The combined organic phase was washed with HCl aq (1 M), $NaHCO_3$ aq, and NaCl aq, and dried over $MgSO_4$. Column chromatography on silica gel ($CHCl_3$–hexane, 1 : 1) afforded TBDMS–$O(CH_2)_{12}O(CH_2)_{12}O$–TBDMS (**4**) as a colorless liquid (391 mg, 27%). ^{1}H NMR (400 MHz in $CDCl_3$) $\delta = 0.02$ (s, 12H, $SiCH_3$), 0.87 (s, 18H, $C(CH_3)_3$), 1.24 (br, 32H, CH_2), 1.4—1.6 (m, 8H, CH_2), 3.36 (t, 4H, CH_2OCH_2, $J = 7$ Hz), 3.57 (t, 4H, CH_2OSi, $J = 7$ Hz); ^{13}C{^{1}H} NMR (100 MHz in $CDCl_3$) $\delta = -5.2$, 18.4, 25.8, 26.0, 26.2, 28.5, 29.4, 29.45, 29.52, 29.62, 29.8, 32.9, 63.3, 67.0.

To a THF (10 cm^3) solution of **4** (370 mg, 0.60 mmol) was added $[NBu_4]F$ (0.8 cm^3 of 1.0 M THF solution, 0.80 mmol) at 0 °C. After stirring for 2.5 h at 30 °C reaction mixture was quenched by H_2O. The product was extracted with ethyl acetate three times and washed with 1 M HCl aq, $NaHCO_3$ aq, and NaCl aq, and dried over $MgSO_4$. Column chromatography ($CHCl_3$–MeOH, 1 : 10) afforded $HO(CH_2)_{12}O(CH_2)_{12}OH$ (**5**) as colorless crystals (136 mg, 58%). Found: C, 74.31: H, 13.20%. Calcd for $C_{24}H_{50}O_3$: C, 74.55; H, 13.03%. IR (cm^{-1} in KBr) 3238 (ν(OH)) and 1121 (ν(C–O)). ^{1}H NMR (400 MHz in $CDCl_3$) $\delta = 1.2$—1.4 (br, 4H, CH_2), 1.53 (m, 36H, CH_2), 3.37 (t, 4H, CH_2OCH_2, $J = 7$ Hz), 3.62 (t, 4H, CH_2OH, J(CH) = 7 Hz). ^{13}C{^{1}H} NMR (100 MHz in $CDCl_3$) $\delta = 25.7$, 26.2, 29.5, 29.6, 29.8, 32.8, 63.1, 71.0.

Preparation of $HO(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}OH$ (7). A mixture of NaH (800 mg, 20 mmol) and 1,12-dodecanediol (1.01 g, 5.0 mmol) in DMF (10 cm^3) was stirred for 1 h at 50 °C. After the mixture was cooled at room temperature, $Br(CH_2)_{12}O$–TBDMS (3.80 g, 10 mmol) was added and the resulting mixture was stirred for 17 h at 100 °C. The reaction mixture was quenched by NH_4Cl aq at room temperature. The organic product was extracted with Et_2O three times. The organic phase was washed with HCl aq (1 M), $NaHCO_3$ aq, and then with NaCl aq, and dried over Na_2SO_4. Three products, TBDMS–$O(CH_2)_{12}O(CH_2)_{12}O(CH_2)_{12}O$–TBDMS (**6**; 1.03 g, 26%; $R_f = 0.30$), $HO(CH_2)_{12}O(CH_2)_{12}O$–TBDMS (751 mg, 30%; $R_f = 0.36$), and $CH_2{=}CH(CH_2)_{10}O$–TBDMS (965 mg, 32%; $R_f = 0.70$) were isolated after separation by column chromatography on silica gel ($CHCl_3$–hexane, 1 : 1).

To a THF (2 cm^3) solution of **6** (925 mg, 1.2 mmol) was added $[NBu_4]F$ (1.4 cm^3 of 1.0 M THF solution; 1.4 mmol) at room temperature, and the mixture was stirred for 2.5 h at 30 °C. After quenching the mixture by water, the organic product was extracted with $CHCl_3$ three times and washed with 1 M HCl aq, $NaHCO_3$ aq, and NaCl aq and dried over $MgSO_4$ to give $HO(CH_2)_{12}O(CH_2)_{12}O$-$(CH_2)_{12}OH$ (**7**) as colorless crystals (324 mg, 49%). Found: C, 75.33; H, 13.28%. Cacld for $C_{36}H_{74}O_4$: C, 75.73; H, 13.06%. ^{1}H NMR (400 MHz in $CDCl_3$) $\delta = 1.2$—1.4 (br, 48H, CH_2), 1.56 (m, 12H, CH_2), 3.37 (t, 8H, CH_2OCH_2, $J = 7$ Hz), 3.5 (t, 4H, CH_2OH, $J = 7$ Hz). ^{13}C{^{1}H} NMR (100 MHz in $CDCl_3$) $\delta = 26.1$, 26.5, 29.7, 29.8, 29.9, 30.1, 33.1, 63.3, 71.3.

Preparation of $HO(CH_2)_{12}OC_6H_4O(CH_2)_{12}OH$ (9) and $HO(CH_2)_6OC_6H_4O(CH_2)_6OH$ (11). A mixture of hydroquinone (2.08 g, 19 mmol), **2**, (14.3 g, 38 mmol) and K_2CO_3 (5.50 g, 40 mmol) in MeCN (175 cm^3) was heated under reflux with stirring for 42 h. After addition of water the product was extracted with $CHCl_3$ three times. The organic phase was washed with $NaHCO_3$ aq and NaCl aq and dried over Na_2SO_4. Column chromatography on silica gel ($CHCl_3$–hexane, 1 : 1) afforded TBDMS–$O(CH_2)_{12}OC_6H_4O(CH_2)_{12}O$–TBDMS (**8**) as colorless crystals (10.3 g, 77%). Found: C, 70.98; H, 11.79%. Calcd for $C_{42}H_{82}O_4Si_2$: C, 71.32; H, 11.69%. ^1H NMR (400 NHz in $CDCl_3$) $\delta = 0.03$ (s, 12H, $SiCH_3$), 0.87 (s, 18H, $C(CH_3)_3$), 1.2—1.4 (br, 28H, CH_2), 1.47 (m, 8H, CH_2), 1.73 (m, 4H, CH_2), 3.57 (t, 4H, CH_2OH, $J = 7$ Hz), 3.86 (t, 4H, CH_2OPh, $J = 7$ Hz), 6.79 (s, 4H, C_6H_4).

To a THF (5 cm^3) solution of **8** (4.14 g, 5.9 mmol) was added $[NBu_4]F$ (7.0 cm^3 of 1.0 M THF solution; 7.0 mmol) at room temperature and the mixture was stirred for 3 h at 30 °C. After the mixture was quenched in water, the resulting solid was collected by filtration, washed with H_2O, Et_2O, and then with $CHCl_3$. Recrystallization from hot MeOH afforded $HO(CH_2)_{12}OC_6H_4O(CH_2)_{12}OH$ (**9**) as colorless crystals (2.56 g, 91%). Found: C, 74.79; H, 11.79%. Calcd for $C_{30}H_{54}O_4$: C, 75.26; H, 11.37%. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 1.23$ (m, 28H, CH_2), 1.3—1.4 (m, 8H, CH_2), 1.65 (m, 4H, CH_2), 3.35 (dt, 4H, CH_2OH, $J = 7$ Hz), 3.86 (t, 4H, CH_2OPh, $J = 7$ Hz), 4.29 (m, 2H, OH) 6.80 (s, 4H, C_6H_4). ^{13}C NMR data were not available due to **9**'s low solubility in common organic solvents.

A similar reaction using 1,6-hexanediol instead of the 1,12-dodecanediol and ensuing desilylation by $[NBu_4]$ F gave TBDMS–$O(CH_2)_6OC_6H_4O(CH_2)_6O$–TBDMS (**10**) and $HO(CH_2)_6OC_6H_4O(CH_2)_6OH$ (**11**), respectively, as colorless crystals.

10: Yield 51%; R_f 0.72 ($CHCl_3$/MeOH=1/1). Found: C, 65.91; H, 10.47%. Calcd for $C_{30}H_{58}O_4Si_2$: C, 66.86; H, 10.85%. ^1H NMR (400 MHz in $CDCl_3$) $\delta = 0.03$ (s, 12H, $SiCH_3$), 0.88 (s, 18H, $C(CH_3)_3$), 1.37—1.55 (m, 18H, CH_2), 1.74 (m, 4H, CH_2), 3.59 (t, 4H, CH_2OH, $J = 6$ Hz), 3.88 (t, 4H, CH_2OPh, $J = 6$ Hz), 6.79 (s, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR $\delta = -5.2$, 18.3, 25.6, 25.9, 29.4, 32.8, 63.2, 68.6, 115.4, 153.2.

11: Yield 100%; R_f 0.37 ($CHCl_3$/MeOH=10/1). Found: C, 69.91; H, 9.80%. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%. ^1H NMR (400 MHz in $CDCl_3$) $\delta = 1.40$—1.63 (m, 12H, CH_2), 1.75 (m, 4H, CH_2), 3.65 (t, 4H, CH_2OH, $J = 6$ Hz), 3.88 (t, 4H, CH_2OPh, $J = 6$ Hz), 6.79 (s, 4H, C_6H_4). $^{13}C\{^1H\}$ NMR $\delta = 25.5$, 25.9, 29.3, 32.7, 62.9, 68.5, 115.4, 153.2.

Polyaddition. Typical experimental procedure for the polyaddition is as follows. A Schlenk flask containing **5** (386 mg, 1.0 mmol) and 1,3-bis(isocyanatomethyl)benzene (188 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 **12** (563 mg, 98%). IR (KBr, cm^{-1}) 3310, 2920, 2850, 1700, 1221, 1119. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 1.2$—1.3 (br, CH_2), 1.6 (m, CH_2), 3.38 (t, CH_2OCH_2, 4H, $J = 7$ Hz), 4.07 (br, CH_2OCO, 4H, $J = 6$ Hz), 4.32 (br, CH_2NH, 4H), 5.20 (br, NH, 2H), 7.18 (br, C_6H_4, 4H).

Polyaddition of other substrates was carried out analogously. Spectroscopic data of **13**: IR (KBr, cm^{-1}) 3318, 2920, 2852, 1701, 1533, 1220, 1115, 1069. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 1.2$—1.4 (br, CH_2, 48H), 1.52—1.67 (m, CH_2, 12H), 3.39 (t, CH_2OCH_2, 8H, $J = 6$ Hz), 3.88 (s, $C_6H_4CH_2$, 2H), 4.13 (t, CH_2OCO, 4H, $J = 7$ Hz), 6.60 (br, NH, 2H), 7.09 and 7.28 (d, C_6H_4, 8H, $J = 9$ Hz). Spectroscopic data of **14**: IR (KBr, cm^{-1}): 3296, 2918, 2850, 1696, 1525, 1507, 1227, 1109, 1018. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 1.4$ (br, CH_2), 1.7 (br, CH_2), 3.88 (br, $CH_2OC_6H_4$, 4H), 4.07 (br, CH_2OCO, 4H), 4.32 (br, $CH_2C_6H_4$), 5.04, (s, NH, 2H), 6.79 (s, C_6H_4, 4H), 7.17 and 7.24 (br, C_6H_4, 4H). Spectroscopic data of **15**: IR (KBr, cm^{-1}) 3312, 2934, 2856, 1695, 1233, 1034. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 1.4$ (br, CH_2, 8H), 1.6 (br, CH_2, 4H), 1.7 (br, CH_2, 4H), 3.88 (br, $CH_2OC_6H_4$, 4H), 4.07 (br, CH_2OCO, 4H), 4.32 (br, $CH_2C_6H_4$, 4H), 5.04 (s, NH, 2H), 6.80 (s, C_6H_4, 4H), 7.17 and 7.24 (br, C_6H_4, 4H). Spectroscopic data of **16**: IR (KBr, cm^{-1}) 3294, 2936, 2862, 1699, 1532, 1508, 1226, 1069, 1017. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 1.4$ (br, CH_2, 8H), 1.6 (br, CH_2, 8H), 3.39 (m, CH_2OH), 3.75 (s, CH_2, 2H), 3.84 (br, $CH_2OC_6H_4$, 4H), 4.03 (br, CH_2OCO, 4H), 4.32 (t, OH, $J = 8$ Hz), 6.78 (s, C_6H_4, 4H), 7.06 and 7.33 (d, C_6H_4, 8H, $J = 8$ Hz), 9.48 (s, NH, 2H). $^{13}C\{^1H\}$ NMR (100 MHz in DMSO-d_6) $\delta = 25.1$ ($COOCH_2CH_2CH_2$), 25.2 ($C_6H_4OCH_2CH_2CH_2$), 28.5 ($COOCH_2CH_2$), 28.7 ($C_6H_4OCH_2CH_2$), 63.9 ($COOCH_2$), 67.7 ($C_6H_4OCH_2$), 115.2 (CH carbon of OC_6H_4), 118.2 ($C_6H_4CH_2$), 128.8 (CH carbon of NHC_6H_4), 135.3 (*ipso* carbon of $CH_2C_6H_4$), 137.1 (*ipso* carbon of NHC_6H_4), 152.5 (C=O), 153.6 (*ipso* carbon of OC_6H_4).

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