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Synthesis of Poly(*N*-acylurethane)s, a New Class of Polyurethanes

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ABSTRACT: The preparation of novel polyurethanes, poly(*N*-acylurethane)s, by polyaddition of bis(*N*-acyl isocyanate)s with diols under mild conditions is described. Bis(*N*-acyl isocyanate)s (**1a–c**) were derived from the reaction of the corresponding diamides with oxalyl chloride in good yields. The polyaddition of **1** with aliphatic and aromatic diols (**2** and **3**) was performed at room temperature in dimethylacetamide without catalyst to quantitatively afford the corresponding poly(*N*-acylurethane)s (**4** and **5**, respectively). The high reactivity of the *N*-acyl isocyanate group compared to the unsubstituted isocyanate was demonstrated by the fact that bis(*N*-acyl isocyanate)s readily form a polymer with 2-*n*-dodecyl-1,3-propanediol while *m*-phenylene diisocyanate does not form a polymer under the same conditions. Poly(*N*-acylurethane) with a polymeric diol segment was prepared similarly using hydroxy-terminated poly(tetrahydrofuran). Solubility, molecular weight, glass transition temperature (T_g), and 10% weight loss temperature (T_d) of the polymers were evaluated.

Introduction

Isocyanates with electron-accepting groups on the nitrogen atoms are much more reactive than the corresponding unsubstituted isocyanates. For example, *N*-acyl isocyanates readily react with various nucleophiles such as alcohols and phenols under mild conditions and without any catalyst to afford the corresponding adducts.[1-3] This is in contrast to the reactivity of isocyanates, which usually require some catalyst such as tertiary amine and/or tin compounds.[4] Further, *N*-acyl isocyanates such as trichloroacetyl isocyanate react with ethyl vinyl ether[5] and cyclopentanone[6] to afford the corresponding adducts. While a variety of polyurethanes are synthesized by polyaddition of diols to bifunctional isocyanates,[7,8] no poly(acylurethane) has been prepared so far. In addition to the above-mentioned synthetic advantage, the properties of these novel poly(acylurethane)s are also interesting. For example, each structural modification of poly(acylurethane) by exchange of the diol segments is expected, since acylurethanes are able to swiftly undergo transesterification with alcohols.[9] Thus, poly(*N*-acylurethane)s can be regarded as belonging to the interesting reactive group. This paper discloses the first synthesis of poly(acylurethane)s by polyaddition of diols to bis(*N*-acyl isocyanate)s in the absence of catalyst and under mild conditions.

Experimental Section

Measurements. IR, ^{1}H NMR, ^{13}C NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were performed using a JASCO FT/IR-5300, a JEOL JNM-EX90 (^{1}H NMR: 90 MHz; ^{13}C NMR: 22.5 MHz), a JEOL JNM-GX-500 (^{13}C NMR: 125 MHz), a SEIKO DSC220C (heating rate: 10 K/min under nitrogen), and a SEIKO TG/DTA220 (heating rate: 10 K/min under nitrogen), respectively.

Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh Co. HLC-8020 equipped with polystyrene gel columns (TSKgel G5000HXL, TSKgel G4000-HXL, and TSKgel G2500HXL), using dimethylformamide as solvent at a flow rate of 1.0 mL/min, polystyrene calibration, and ultraviolet (UV) detectors.

Materials. Dimethylacetamide (DMAc), tetrahydrofuran (THF), and 2-*n*-butyl-1,3-propanediol were purified by distillation after removal of water according to common methods. 2,2-Dimethyl-1,3-propanediol, 2-*n*-octyl-1,3-propanediol, 2-*n*-dodecyl-1,3-propanediol, 4,4′-dihydroxydiphenyl ether, Bisphenol A, and 4,4′-dihydroxybiphenyl were purified by recrystallization from ethanol. Catechol was purified by recrystallization from benzene.

Synthesis of Monomers. Isophthaloyl Diisocyanate (1a).[10] Isophthalamide (5.4 g, 33 mmoL), oxalyl chloride (25 g, 197 mmoL), and dry carbon tetrachloride (30 mL) were placed in a 100-mL round-bottom flask equipped with a reflux condenser carrying a calcium chloride tube. The mixture was refluxed for 30 h and then evaporated under reduced pressure, and the residue was distilled to give the title compound. Yield 6.4 g (96%). Bp 121–122 °C (0.3 mmHg) [lit.[10] bp 126 °C (2 mmHg)]. ^{13}C NMR ($CDCl_3$): δ 164.2, 136.1, 132.5, 132.3, 132.0, 129.6. IR ($CDCl_3$): 2338, 2232, 1705, 1404, 1177, 1163, 1028, 976 cm^{-1}.

Since **1a** was very reactive toward moisture, elemental analysis data were not compatible with the formula. For this reason the elemental analysis was carried out using the corresponding methanol adduct derived by direct reaction with methanol. The methanol adduct was synthesized as follows. **1a** (50 mg, 0.23 mmol) and excess methanol (0.5 mL) were mixed in a drybox at room temperature. After 1 min, the solvent was evaporated and the residue was dried under reduced pressure. The adduct was pure enough not to require further purification. Yield 64.8 mg (100%). Mp (dec) 196 °C. ^{1}H NMR (DMSO-d_6): δ 10.74 (bs, 2H), 8.20–7.35 (m, 4H), 3.67 (s, 6H). IR (KBr): 3416, 3231, 1771, 1678, 1524, 1202, 1011, 783, 718 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.20; H, 4.45; N, 10.08.

Terephthaloyl Diisocyanate (1b).[10,11] The title compound was obtained from terephthalamide (5.4 g, 33 mmol) and oxalyl chloride (25 g, 197 mmoL) in a manner similar to that used for the isophthaloyl diisocyanate synthesis. Yield 4.8 g (68%). Bp 110–111 °C (0.3 mmHg) [lit.[10] bp 158 °C (3 mmHg)]. ^{13}C NMR ($CDCl_3$): δ 164.4, 136.3, 131.9, 130.7. IR ($CDCl_3$): 2338, 2263, 1703, 1408, 1225, 972 cm^{-1}. The methanol adduct (64.8 mg) was obtained from **1b** (50 mg, 0.23 mmol) and methanol (0.5 mL) similarly to the case of isophthaloyl diisocyanate. Yield 100%. Mp (dec) 222 °C [lit.[11] mp 247–248 °C]. ^{1}H NMR (DMSO-d_6): δ 10.99 (bs, 2H), 7.87 (s, 4H), 3.70 (s, 6H). IR (KBr): 3451, 3240, 1771, 1680, 1526, 1202, 1007, 843, 785, 727 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.40; H, 4.26; N, 10.13.

5-*tert*-Butylisophthaloyl Diisocyanate (1c). Anhydrous ferric chloride (1.0 g, 6.2 mmol) was slowly added to a mixture of *m*-xylene (53.1 g, 0.5 mol) and *tert*-butyl chloride (46.3 g, 0.5 mol). *tert*-Butyl chloride (9.3 g, 0.1 mol) was added to the mixture as the evolution of hydrogen chloride ceased. The resulting mixture was stirred for 1 h at room temperature, refluxed for 30 min, cooled to room temperature, and washed with saturated sodium hydrogen carbonate and sodium chloride solutions. The

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organic layer that separated was dried with calcium chloride and evaporated to give 1-*tert*-butyl-3,5-dimethylbenzene (58.9 g, 0.36 mol, yield 72%) as a colorless liquid.

Potassium permanganate (190 g, 1.2 mol) was slowly added to a boiling mixture of the product (40.6 g, 0.25 mol), pyridine (250 mL), and water (500 mL). The mixture was stirred for 12 h at room temperature. The manganese(IV) oxide formed was removed by filtration and washed with hot water (200 mL). The combined filtrates were concentrated under reduced pressure to ca. 150 mL, to which hydrochloric acid (6 M, 50 mL) was added at 0 °C. 5-*tert*-Butyl-1,3-benzenedicarboxylic acid (41.4 g, 0.19 mol, yield 76%) precipitated (white powder) and was collected by filtration and dried under reduced pressure.

A mixture of the dicarboxylic acid (25.0 g, 0.11 mol), thionyl chloride (90 mL), and a drop of dimethylformamide was refluxed for 6 h. The resulting mixture was distilled under reduced pressure to give 5-*tert*-butyl-1,3-benzenedicarbonyl dichloride (22.7 g, 0.09 mol, yield 82%). The dichloride (20.0 g, 0.08 mol) was added to 28% ammonia water (150 mL) at 0 °C. 5-*tert*-Butylbenzene-1,3-dicarboxamide precipitated and was collected by filtration and washed with water three times. The product was dried at 80 °C under reduced pressure (15.6 g, 0.07 mol, yield 92%).

The title compound was obtained from 5-*tert*-butylbenzene-1,3-dicarboxamide (4.6 g, 21 mmol) and oxalyl chloride (16 g, 125 mmoL) in a manner similar to that used for the synthesis of isophthaloyl diisocyanate. Yield 4.8 g (84%). Bp 140–141 °C (0.75 mmHg). ^{1}H NMR ($CDCl_3$): δ 8.56–8.52 (m, 1H), 8.36–8.33 (m, 2H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.6, 153.6, 133.2, 132.2, 131.9, 130.0. IR ($CDCl_3$): 2971, 2338, 2240, 1701, 1404, 1233, 1167, 723, 714 cm^{-1}. Methanol adduct of **1c**: Yield 100%. Mp (dec) 150–151 °C. ^{1}H NMR ($CDCl_3$): δ 10.99 (bs, 2H), 8.22–7.97 (m, 3H), 3.75 (s, 6H), 1.39 (s, 9H). IR (KBr): 3416, 2959, 1763, 1690, 1618, 1520, 1200, 1053, 1030, 779 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.99; N, 8.37. Found: C, 56.96; H, 5.89; N, 8.21.

Polyaddition Reaction of Bis(*N*-acyl isocyanate)s. A Typical Procedure for the Synthesis of 4d (Table 1). **1a** (108 mg, 0.5 mmoL), 2-*n*-dodecyl-1,3-propanediol (**2d**) (122 mg, 0.5 mmoL), and dry dimethylacetamide (DMAc, 0.25 mL) were placed at 0 °C in a 20-mL round-bottom three-neck flask equipped with an argon inlet tube. The mixture was kept at 0 °C for 10 min and at room temperature for 170 min under an argon atmosphere. The mixture was diluted with DMAc (1 mL) and poured into ether (30 mL). The precipitated poly(acylurethane) (**4d**) was collected by filtration and dried at 80 °C under reduced pressure. Yield 214 mg (93%, white powder). ^{1}H NMR (DMSO-d_6): δ 11.00 (bs, 2H), 8.50–7.40 (m, 4H), 4.20 (bs, 4H), 2.10 (bs, 1H), 1.20 (bs, 22H), 1.00 (bs, 3H). IR (KBr): 3353, 2926, 2855, 1774, 1699, 1508, 1289, 1179, 1022, 772 cm^{-1}. $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) = 20700 (1.65).

Spectral Data of Other Poly(acylurethane)s (4a–c, 4e–g, 5a–d). (**4a**) ^{1}H NMR (DMSO-d_6): δ 11.04 (s, 2H), 8.50–7.50 (m, 4H), 4.01 (s, 4H), 0.99 (bs, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 165.1, 151.7, 133.6, 132.0, 128.5, 128.1, 69.9, 34.9, 21.1. IR (KBr): 3422, 2967, 1769, 1707, 1622, 1510, 1194, 1017, 774, 720 cm^{-1}.

(**4b**) ^{1}H NMR (DMSO-d_6): δ 10.87 (s, 2H), 8.45–7.48 (m, 4H), 4.21 (d, J = 5.5 Hz, 4H), 2.0 (bs, 1H), 1.37 (bs, 6H), 0.88 (bs, 3H). IR (KBr): 3285, 2960, 1767, 1709, 1626, 1514, 1287, 1186, 1019, 774, 720 cm^{-1}.

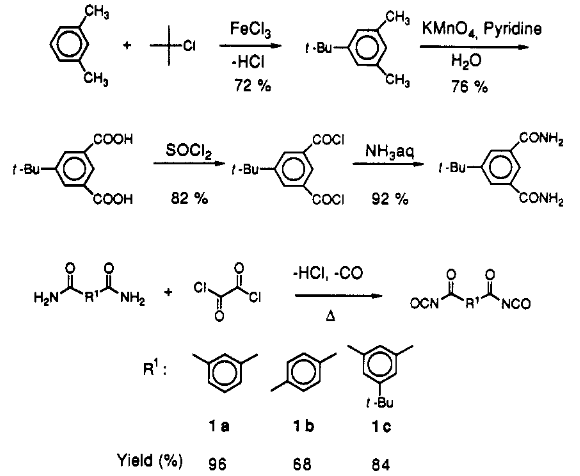
(**4c**) ^{1}H NMR (DMSO-d_6): δ 10.87 (s, 2H), 9.50–7.48 (m, 4H), 4.21 (d, J = 5.5 Hz, 4H), 2.00 (bs, 1H), 1.25 (bs, 14H), 0.82 (bs, 3H). IR (KBr): 3289, 2928, 2857, 1767, 1711, 1626, 1514, 1287, 1186, 1020, 774, 720 cm^{-1}.

(**4e**) ^{1}H NMR (DMSO-d_6): δ 11.06 (bs, 2H), 7.95 (s, 4H), 4.04 (s, 4H), 1.02 (s, 6H). IR (KBr): 3414, 2965, 1780, 1710, 1618, 1526, 1179, 1005, 774 cm^{-1}.

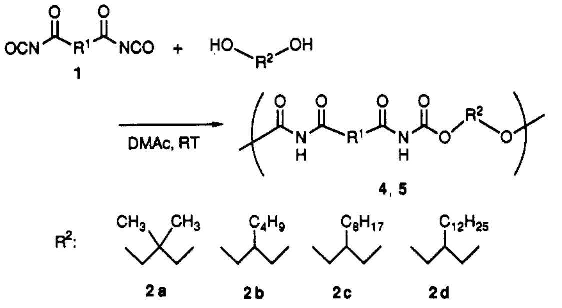
(**4f**) ^{1}H NMR (DMSO-d_6): δ 10.93 (bs, 2H), 7.93 (s, 4H), 4.22 (d, J = 5.4 Hz, 4H), 2.00 (bs, 1H), 1.23 (bs, 22H), 0.84 (bs, 3H). IR (KBr): 3416, 2926, 2855, 1765, 1709, 1620, 1528, 1495, 1287, 1184, 1005, 866, 774, 716 cm^{-1}.

(**4g**) ^{1}H NMR (DMSO-d_6): δ 10.89 (s, 2H), 8.18 (s, 1H), 8.05 (s, 2H), 4.07 (s, 4H), 1.34 (s, 9H), 1.03 (s, 6H). IR (KBr): 3414, 2967, 1767, 1707, 1620, 1512, 1279, 1186, 1042, 777 cm^{-1}.

Scheme 1



Scheme 2



(**5a**) ^{1}H NMR (DMSO-d_6): δ 11.48 (s, 2H), 8.45–7.89 (m, 3H), 7.45–6.74 (m, 8H), 1.40 (s, 9H). IR (KBr): 3412, 2963, 1786, 1665, 1618, 1489, 1165, 995, 847, 764 cm^{-1}.

(**5b**) ^{1}H NMR (DMSO-d_6): δ 11.44 (s, 2H), 8.50–8.00 (m, 3H), 7.45–6.55 (m, 8H), 1.62 (s, 6H), 1.39 (s, 9H). IR (KBr): 3297, 2967, 1780, 1671, 1615, 1497, 1169, 1017, 833, 766, 693 cm^{-1}.

(**5c**) IR (KBr): 3416, 2965, 1788, 1661, 1617, 1493, 1385, 1240, 1192, 748, 635 cm^{-1}.

(**5d**) IR (KBr): 3237, 2963, 1796, 1663, 1615, 1520, 1489, 1387, 1262, 1163, 993 cm^{-1}.

Polyaddition Reaction of Diisocyanate 8. A mixture of *m*-phenylene diisocyanate (**8**) (80 mg, 0.5 mmol), 2-*n*-dodecyl-1,3-propanediol (**2d**) (122 mg, 0.5 mmol), and dry DMAc (0.25 mL) was placed at room temperature in a 20-mL round-bottom three-neck flask equipped with an argon inlet tube. The mixture was stirred for 3 h, diluted with DMAc (1 mL), and precipitated with ether (30 mL). No ether-insoluble polymer was obtained.

Results and Discussion

Aromatic bis(*N*-acyl isocyanate)s (**1a**,**b**) were prepared by the reaction of the corresponding commercially available diamides with oxalyl chloride. 5-*tert*-Butylbenzene-1,3-dicarboxamide, which was synthesized from *m*-xylene via several steps, was used for the synthesis of *tert*-butyl-substituted isophthaloyl diisocyanate (**1c**) according to Scheme 1.

Reaction of an equimolar mixture of isophthaloyl diisocyanate (**1a**) with 2-*n*-dodecyl-1,3-propanediol (**2d**) in DMAc was carried out at room temperature for 3 h under an argon atmosphere to give an ether-insoluble polymer (white powder, $\bar{M}_n$ = 20700, $\bar{M}_w/\bar{M}_n$ = 1.65) in 94% yield (Scheme 2). The structure of this polymer was determined as poly(acylurethane) by its IR and NMR spectra. Similarly, several poly(acylurethane)s (**4a–c**, **e–g**) were prepared using bis(*N*-acyl isocyanate)s and aliphatic diols in quantitative yields (Table 1). Typical IR and ^{1}H NMR spectra of the polymer (**4d**) are shown in Figure 1. In the ^{1}H NMR spectrum, the signal of the NH proton (a)

Table 1. Polyaddition of Alkanediols to Bis(*N*-acyl isocyanate)s[a]

polymer	bis(*N*-acyl isocyanate)	diol	concn (M)	yield[b] (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	T_g (°C)	T_d[d] (°C)
4a	**1a**	**2a**	1	99	12 000	1.26	66	232
4b	**1a**	**2b**	1	99	12 400	1.35	64	234
4c	**1a**	**2c**	1	89	11 700	1.41	65	230
4d	**1a**	**2d**	4	94	20 700	1.65	112	238
4e	**1b**	**2a**	1	99	13 200	1.32	102	239
4f	**1b**	**2d**	1	79	12 300	1.45	75	259
4g	**1c**	**2a**	4	93	17 600	1.49	144	260

[a] The reaction was carried out for 10 min at 0 °C and for 170 min at room temperature. [b] Yield of ether-insoluble polymer. [c] Estimated by GPC (eluent: DMF, PSt standards). [d] 10% weight loss temperature in N_2.

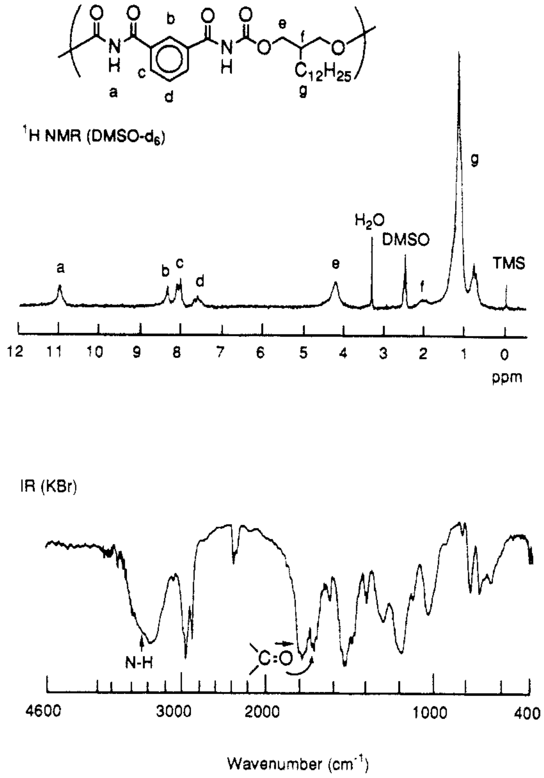
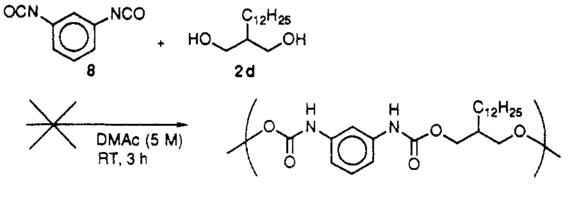


Figure 1. ¹H NMR spectrum (top) and IR spectrum (bottom) of poly(acylurethane) **4d**.

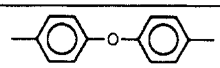
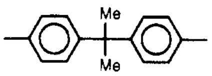
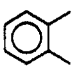
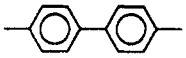
Scheme 3



was observed at very low magnetic field (11.00 ppm), probably because of the electron-withdrawing character of the *N*-acyl group. Signals of the aromatic protons (b–d) were found around 8 ppm, and those of the methylene protons adjacent to the oxygen atom (e) appeared around 4.2 ppm. The IR spectrum (Figure 1) displays two carbonyl absorptions of the acyl and carbamate groups at 1699 and 1773 cm⁻¹, respectively, besides a broad N–H absorption at 3200 cm⁻¹. A few poly(acylurethane)s having different diol segments were similarly prepared (Scheme 2).

To demonstrate the enhanced reactivity of the *N*-acyl isocyanate group, a polyaddition of *m*-phenylene diisocyanate (**8**) with 2-*n*-dodecyl-1,3-propanediol (**2d**) was carried out under the same conditions (Scheme 3) and compared to the above polyaddition. No ether-insoluble polymer was obtained by this polyaddition. This result clearly reveals that the reactivity of *N*-acyl-substituted isocyanate is much higher than the reactivity of the unsubstituted isocyanate.

Table 2. Polyaddition of Diphenols to Bis(*N*-acyl isocyanate) 1c[a]

polymer	diphenol	yield[b] (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$	T_d[d] (°C)
5a	 **3a**	96	4300	1.04	209
5b	 **3b**	98	4500	1.05	214
5c	 **3c**	88[e]			174
5d	 **3d**	94[e]			205

[a] The reaction was carried out for 10 min at 0 °C and for 170 min at room temperature. Polymerization concentration was 4 M. [b] Yield of ether-insoluble polymer. [c] Estimated by GPC (eluent: DMF, PSt standards). [d] 10% weight loss temperature in N_2. [e] Polymer was precipiated during polymerization and was insoluble in solvents such as DMF and DMAc.

Poly(acylurethane)s derived from **1b** and diol (**2a** and **2b**) were soluble in polar solvents such as DMAc and dimethyl sulfoxide (DMSO) but insoluble in less polar solvents such as tetrahydrofuran (THF) and dichloromethane. However, the solubility was considerably improved by using diols **2c** and **2d** with longer alkyl chains, and eventually the obtained poly(acylurethane)s were soluble in THF and dichloromethane. Further, poly(acylurethane)s derived from **1c** were soluble in various solvents such as THF and dichloromethane. The T_g of **4d** was higher than that of **4a–c** derived from **1a**, probably because the $\bar{M}_n$ of **4d** was higher than that of **4a–c**. The T_g of **4g** (144 °C) was higher than those of **4a–f** (64–112 °C). These results seem to be due to the rotation of the polymer main chain, which is more restricted in **4g** than the other polymers due to the bulky *tert*-butyl and dimethyl groups.

When diphenols (**3a–d**) were reacted with **1c** in the absence of catalyst, the corresponding aromatic poly(acylurethane)s (**5a–d**) were obtained in 88–98% yields.

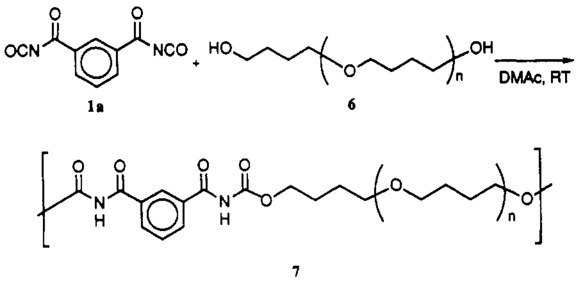
While the polyaddition of **1c** to rigid diphenols (**3c**,**d**) resulted in a precipitation of the corresponding poly(acylurethane)s which were insoluble in ordinary organic solvents during polymerization, **3a** and **3b** gave poly(acylurethane)s soluble in DMAc and THF (Table 2). However, their $\bar{M}_n$'s estimated by GPC were considerable lower than those derived from the aliphatic diols (Table 1). Presumably this results from partial decomposition of the polymers (**5**) with some anionic species in the GPC

Table 3. Effect of Solvent on Physical Properties of Poly(*N*-acylurethane)s

polymer	solvent	time (h)	yield[a] (%)	η_{inh}[b] (dL/g)	T_g (°C)
5a	DMAc	3	96	0.12	72
5a′	THF	1	99	0.16	157
5b	DMAc	3	98	0.10	113
5b′	THF	1	95	0.18	134
4g	DMAc	3	93	0.11	144

[a] Ether-insoluble polymer. [b] Measured in DMAc (0.5 g/dL, 30 °C).

Scheme 4



solvent DMF, because they are more sensitive toward anionics than polymers **4**. In fact, the inherent viscosities of poly(acylurethane)s **4g**, **5a**, and **5b** were almost the same (η_{inh} = 0.11, 0.12, and 0.10 dL/g, respectively) (Table 3).

In addition, when the polyadditions of **1c** to **3a** or **3b** were carried out in THF for 1 h, the inherent viscosities of the obtained polymers (**5a′** and **5b′**, η_{inh} = 0.16 and 0.18 dL/g, respectively) were higher than those of the polymers (**5a** and **5b**) obtained by reaction in DMAc for 3 h. A similar trend can be seen in the glass transition temperatures (T_g's) and the 10% weight loss temperatures (T_d's) of 4 and 5, as shown in Table 3. That is, the T_g's and T_d's of **5a′** and **5b′** are higher than those of **5a** and **5b**. Consequently, it is reasonable that the $\bar{M}_n$'s of **5a**, **5b**, **5a′**, and **5b′** are equally as high as those of **4**, suggesting that THF is a good solvent for this type of polyaddition giving polymers with an aryl–*N*-acylurethane bond. The T_d's of **4** and **5** are almost identical, suggesting that the initial thermal decomposition of poly(acylurethane)s occurs at the acylurethane C–O bond.

Poly(*N*-acylurethane) with a polymeric diol segment was similarly prepared in 80% yield using poly(tetrahydrofuran) (**6**, $\bar{M}_n$ = 750, $\bar{M}_w/\bar{M}_n$ = 2.35). The polymer obtained was identified as the corresponding poly(acylurethane) (**7**) by ^{1}H NMR and IR spectra. The $\bar{M}_n$ was 23 100 ($\bar{M}_w/\bar{M}_n$ = 1.56). **7** was soluble in ordinary organic solvents such as dichloromethane, tetrahydrofuran and dimethylformamide.

In summary, this paper reports the first synthesis of poly(acylurethane)s by polyaddition of diols and diphenols to bis(*N*-acyl isocyanate)s. The synthesis is characterized by mild conditions, high yields, and the absence of catalyst. The obtained poly(*N*-acylurethane)s can be regarded as reactive polymers because they have activated urethane bonds which might be responsible for the instability of poly(aromatic *N*-acylurethane)s in DMF as mentioned above. Further studies on poly(*N*-acylurethane)s, especially on the polymer reaction related to the reactive urethane bond, are under way.

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