Novel Adhesives Based on Poly(isocyanates)

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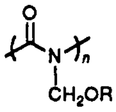
ABSTRACT: The preparation and characterization of four poly(alkoxymethyl isocyanates): poly(propoxymethyl), poly(butoxymethyl), poly[(hexyloxy)methyl], and poly[(benzyloxy)methyl] are described. The monomers were prepared by Curtius rearrangement of the alkoxyacetyl azides. The acyl azides were not isolated but were prepared from the acyl chlorides in cyclohexane/water mixtures. The acyl halides were derived from the (alkoxymethyl)acetic acids, which in turn were prepared from metal alkoxides and chloroacetate. The butoxymethyl and (hexyloxy)methyl derivatives are adhesives. Complete adhesive properties characterization was not performed but the material was found to have stronger adhesive than cohesive properties. The adhesives are stable to moisture and acid but unstable toward base.

Introduction

Alkyl isocyanates serve as excellent electrophiles for the formation of carbamates and ureas but tend to trimerize to cyanuric acid derivatives on standing or upon acid catalysis. At low temperature, straight-chain isocyanates polymerize readily in the presence of nucleophiles to produce very high molecular weight poly(isocyanates) 2.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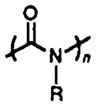
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The poly(alkyl isocyanates) are fascinating "1-nylons",[1] where some members of the family exhibit liquid-crystalline behavior.[1c,d] Polymers with very high intrinsic viscosities (15.7 dL/g, R = *n*-butyl)[1b] and molecular weights (2 × 10^7) have been reported.[1a] These polymers are prepared by the anionic polymerization of *N*-alkyl isocyanates.[1] More recently, their unusual chiral properties[2a] (induced helical excess) and use in ethylene oxide pendant ionic conducting polymers[2b] are being investigated. The chemistry and synthesis of poly(alkyl isocyanates) has been reviewed,[1a] and a complete literature search revealed that the polymers of composition 1 were not previously prepared. Polymers 2 (R = C_4H_9, C_6H_{13}) are also lyotropic liquid crystals in chloroform solution,[1c,d] implying that they could be processed into highly aligned fibers from these media. In fact, 2 (R = C_6H_{13}) was recently processed into crystalline filaments.[3] On the other hand, 1 (R = C_4H_9), where the number of links in the side chain is the same as in 2 (R = C_6H_{13}) but one methylene unit has been replaced by an ether oxygen, is an adhesive (gum) at room temperature. Lowering the T_g in polymers by introducing ethyleneoxy groups in the backbone is a common occurrence (e.g., PEGs, PPO) but such a dramatic change in physical properties (2, R = C_6H_{13}, T_g = ?[1c,4], T_m ~155 °C;[1c] 2, R = C_4H_9, "T_g = ?";[1c] 1, R = C_6H_{13}, T_g = −19 °C; 1, R = C_4H_9, T_g = −8.1 °C) by single substitution in the side chain is apparently unprecedented. The adhesive properties are remarkable; the polymer adheres equally well to stainless steel as it does to glass, paper, and wood. The resulting joint is flexible and tough.

In this article, we report the preparation of some alkoxymethyl isocyanate monomers and the characterization of the corresponding macromolecules produced by low-temperature cyanide ion polymerization.

Scheme I[a]

$$ClCH_2COONa \xrightarrow{i} ROCH_2COOH \xrightarrow{ii} ROCH_2COCl \xrightarrow{iii} ROCH_2CON_3 \xrightarrow{iv} ROCH_2NCO$$

[a] Reagents and conditions: i, $RO^{(-)}/ROH$; ii, $SOCl_2$; iii, NaN_3; iv, cyclohexane/Δ.

Results and Discussion

Monomer Synthesis. The monomer preparation is outlined in Scheme I. The alkoxyacetic acids [$ROCH_2COOH$ (R = alkyl or benzyl)] were obtained in ≥80% yield from the reaction of the corresponding alcohol, sodium or potassium metal, and the sodium salt of chloroacetic acid. To prepare the corresponding acid chlorides in nearly quantitative yield, these acids were allowed to react with thionyl chloride. The acid chlorides were converted to acid azides by reaction with sodium azide. The latter was not isolated and isocyanates were produced after the Curtius rearrangement reaction in ca. 70% yield, based on acid chloride.

All monomers could be purified by distillation under reduced pressure and their properties are summarized in Table I.

Polymerization Reaction. The best yields and highest molecular weights were obtained when solvents, reagents, and glassware were scrupulously cleaned and dried. Of all catalysts examined, a very dilute solution of sodium cyanide in DMF was the most effective. Molecular weights (M_n) in the range 38 000–1 020 000, depending on monomer, were obtained.

The polymerization reaction has been treated as an anionic process,[1] implying that, before quench, the reaction mixture should consist of living polymers. We were not able to show that this was the case.[5] For example, the thermal properties of acid-quenched or acetyl chloride quenched polymers were identical. The properties of polymers 1 with R = $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2(CH_2)_3CH_3$, and CH_2Ph are collected in Table II. In contrast to poly(hexyl isocyanate) (M_n ~ 10^6), which has an intrinsic viscosity of ~16 dL/g, poly(butoxymethyl isocyanate) (1; R = C_4H_9, M_n ~ 10^6 has an intrinsic viscosity of only ~1.6 dL/g. The weight-average molecular weights for poly[(hexyloxy)methyl isocyanate] and poly[(benzyloxy)methyl isocyanate] were obtained from light scattering and were 1.16 × 10^6 and 6.7 × 10^4,

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Table I
Physical Properties of Monomers

monomer	bp, °C (Torr)	IR, cm^{-1}	^{1}H NMR, ppm	MS, m/e
propoxymethyl isocyanate	132–133(760)	2965–2880, 2230, 1465, 1380, 1125, 1080, 840	4.78 (s), 3.53 (t), 1.63 (q), 0.95 (t)	43, 56, 72, 86
butoxymethyl isocyanate	32–33 (5)	2950–2860, 2230, 1465, 1375, 1115, 1080, 840	4.80 (s), 3.59 (t), 1.54 (m), 0.92 (t)	43, 56, 71, 86
(hexyloxy)methyl isocyanate	45–46 (5)	2950–2860, 2230, 1465, 1380, 1120, 1090, 840	4.77 (s), 3.55 (t), 1.35 (m), 0.88 (t)	43, 56, 69, 71, 84, 86
(benzyloxy)methyl isocyanate	88–90 (5)	3080–2880, 2240, 1500, 1455, 1365, 1280, 1250, 1210, 1115, 1080, 1030, 900, 845, 740, 700	7.80 (s), 4.70 (s), 4.53 (s)	43, 51, 56, 65, 77, 79, 91, 105, 120

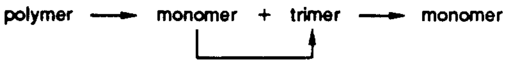
Table II
Physical Properties of Polymers

polymer	η_{int},[a] dL/g	IR, cm^{-1}	NMR,[a] ppm		elemental anal.		M_n[b] (×10^4)	M_w[c] (×10^5)
			^{13}C	^{1}H	calcd	obsd		
poly(propoxymethyl isocyanate)	0.74	2970–2880, 1740, 1465, 1380, 1265, 1230, 1100, 1050, 675	156.1 (s), 77.9 (s), 71.4 (s), 23.2 (s), 10.7 (s)	5.49 (s), 3.55 (s), 1.55 (d), 0.90 (t)	C 52.17 H 7.88 N 12.17	52.22 7.86 12.42	10	
poly(butoxymethyl isocyanate)[d]	1.59	2960–2880, 1740, 1465, 1380, 1265, 1220, 1100, 1055, 675	157.8 (s), 79.3 (s), 71.1 (s), 33.8 (s), 21.9 (s), 15.7 (s)	5.55 (s), 3.67 (s), 1.60 (d), 1.43 (d), 0.95 (t)	C 55.77 H 8.58 N 10.84	55.85 8.59 11.37	102	
poly((hexyloxy)methyl isocyanate)[e]	1.42	2960–2860, 1740, 1465, 1380, 1270, 1230, 1110, 1050	155.5 (s), 69.6 (s), 31.7 (s), 29.6 (s), 25.8 (s), 22.6 (s), 14.0 (s)	5.19 (s), 3.49 (t), 1.51 (s), 1.28 (m), 0.88 (t)	C 61.12 H 9.62 N 8.91	60.34 9.57 9.02	74	11.6
poly((benzyloxy)methyl isocyanate)	0.72	3170–2860, 1740, 1460, 1370, 1260, 1225, 1075, 740, 700	156.6 (s), 138.8 (s), 128.4 (t), 78.1 (s), 72.2 (s)	7.20 (t), 5.36 (s), 4.50 (s)	C 66.23 H 5.56 N 8.58	66.20 5.53 8.71	3.8	0.67

[a] PPMIC and PBMIC in toluene, PHMIC in CHCl$_3$, and PBZMIC in THF. [b] Peak molecular weight relative to polystyrene standard. [c] Weight-average molecular weight from light scattering. [d] T_g = −8.1 °C. [e] T_g = −19 °C.

respectively; the calculated polydispersities (M_w/M_n) for these polymers were 1.56 and 1.76, respectively. In addition, a logarithmic plot of the root mean square radius vs molecular weight for poly[(hexyloxy)methyl isocyanate] had a slope of 0.46, indicating that the solution conformation for this helical polymer is very likely coillike. This is in contrast to the known stiff helical solution conformations for poly(alkyl isocyanates).[6]

The polymers are colorless, adhesive semisolids that are soluble in most common organic solvents but not the lower alcohols. The tackiness is not due to moisture. A sample treated with thionyl chloride at room temperature and then isolated in Schlenk apparatus under strict moisture exclusion showed the same physical behavior; in fact, the adhesion was qualitatively improved. They can be purified by "reprecipitation" from toluene with MeOH. The reprecipitated material is very difficult to remove from the glass vessel because it adheres tenaciously.[7] As determined by thermal gravimetric analysis (see Figure 1), the polymers are thermally stable to ~170 (R = propyl) and ~215 °C (R = hexyl), where they precipitously degrade. Most of the decomposition is due to unzipping and formation of trimers.[8] The plateau in the decomposition, which is most pronounced for the (benzyloxy)methyl case, corresponds to the thermal decomposition profile of the trimer (cyanurate). Therefore, the thermal decomposition seems to follow the course



Qualitative tests (prying two wood or two glass surfaces apart) showed that the material fails in the bulk but not at the interface, indicating that the adhesive forces between polymer and substrate are stronger than the cohesive forces between polymer chains. The bond between glued parts is stable to water and acids but catastrophically unstable toward aqueous and nonaqueous (triethylamine) base; presumably due to base-initiated depolymerization in the latter medium.

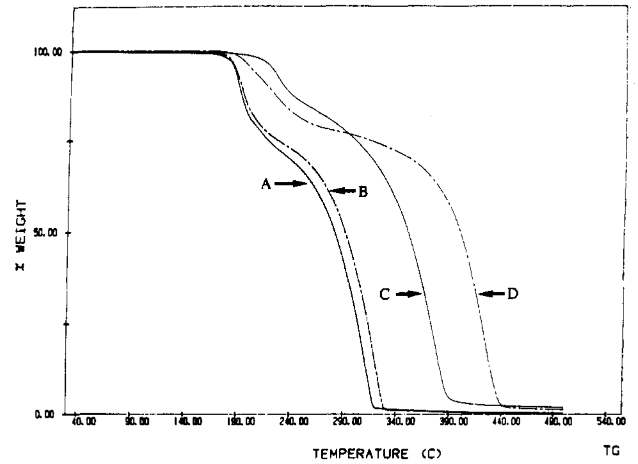


Figure 1. Thermal gravimetric analysis of poly(alkoxymethyl isocyanates) under nitrogen; heating rate, 40 °C/min. Curve A, propoxymethyl; curve B, butoxymethyl; curve C, (hexyloxy)methyl; curve D, benzyloxymethyl.

Experimental Section

Physical Measurements. Elemental analyses for the polymers were done at UC Berkeley. Dilute solution viscosities were determined at ambient temperature with Cannon-Ubbelohde glass viscometers. Tetrahydrofuran (THF) or toluene, distilled freshly over the sodium metal, was used as solvent. IR spectra were taken with a Perkin-Elmer Model 1330 spectrophotometer as samples on KBr disks for the monomers and neat cast film for the polymers and are reported in ν (cm^{-1}). ^{1}H NMR (60 MHz) spectra for monomers were taken in either $CDCl_3$ or CCl_4 solutions on a Varian Model EM-360L NMR spectrometer. ^{13}C or ^1H NMR (500 MHz) spectra for polymers were taken in either C_6D_6 or THF-d_8 solutions on a General Electric Model GE-500 spectrometer. All samples were internally calibrated with tetramethylsilane (TMS) and are reported in δ. Thermal analyses were carried out on Perkin-Elmer DSC-4 (differential scanning calorimetry) and TGS-2 (thermogravimetric analysis) systems (ca. 5 mg for DSC and ca. 10 mg for TGA, 40 °C/min heating rate and N_2 atmosphere). DSC and TGA data at 20 °C/min heating rate were indistinguishable from those at 40 °C/min heating rate. A Varian HPLC Model 5000 liquid chromatograph with TSK-Gel column was used to obtain approximate molecular weights relative to a standard polymer, polystyrene. Light scattering experiments were done on a multiangle laser photometer, Model DAWN F (Wyatt Technology Corp.). THF (HPLC grade) was used as eluent and also as solvent for the polymers.

Monomer Synthesis. (Hexyloxy)methyl Isocyanate as a Typical Procedure Using Potassium Alkoxide. Potassium metal (14 g, 0.36 mol) was dissolved in 300 g (2.9 mol) of hexyl alcohol. To this solution was added slowly 37.6 g (0.32 mol) of sodium chloroacetate. The mixture was refluxed overnight and cooled down to room temperature; the precipitated white products, sodium chloride and sodium (hexyloxy)acetate, were dissolved by adding water (400 mL) to the reaction mixture. The unreacted (excess) hexyl alcohol was removed from the solution by extraction with ether (3 × 250 mL). The aqueous layer, evaporated to a convenient bulk, was treated with a stoichiometric amount of 40% sulfuric acid. The liberated pale organic layer was then extracted with ether (3 × 250 mL), dried (anhydrous Na_2SO_4), and evaporated to obtain (hexyloxy)acetic acid as an almost colorless liquid (48 g, 94% yield): IR (neat) 3580–2220 (vs, br), 1730 (s), 1640 (m), 1440 (m), 1130 (m), 1050 (w), 900 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03 (br), 4.11 (s, 2 H), 3.55 (t, 2 H), 1.62 (m, 2 H), 1.25–1.40 (m, 6 H), 0.89 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 174.4, 71.8, 67.4, 31.4, 29.1, 25.3, 22.3, 13.74 ppm.

The (hexyloxy)acetic acid was mixed in a round-bottom flask with an excess of thionyl chloride under a nitrogen atmosphere. A rigorous reaction occurred with HCl gas evolution. The mixture was stirred at room temperature for 2 h and refluxed for 2 h more. A distillation unit was then attached to the flask and excess thionyl chloride distilled off under ambient pressure. The slightly colored crude (hexyloxy)acetyl chloride (extremely unpleasant/pungent odor) was then fractionally distilled on a Vigreux column to yield the pure acetyl chloride as a colorless liquid: bp 89–90 °C (3.75 mmHg); 47.9 g, 84% yield; IR (neat) 2920 (vs), 1875 (sh, m), 1815 (vs), 1470 (w), 1425 (w), 1355 (vw), 1275 (w), 1150 (s), 1020 (w), 940 (s), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.4 (s, 2 H), 3.57 (t, 2 H), 1.60 (m, 2 H), 1.25–1.40 (m, 6 H), 0.89 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 171.7, 75.97, 72.15, 31.35, 29.24, 25.3, 22.4, 13.73 ppm. This compound was converted to the acyl azide by the procedure outlined for the butoxymethyl case, below.

Butoxymethyl Isocyanate as a Typical Procedure Using Sodium Alkoxide. Sodium metal (8 g, 0.35 mmol) was dissolved in 75 g (1 mol) of butyl alcohol. To this solution was added slowly 36 g (0.31 mol) of sodium chloroacetate. A vigorous reaction occurred and the white products, sodium chloride and sodium butoxyacetate, precipitated. After being refluxed further for 2 h, the solution was cooled to room temperature and 50–100 mL of water was added to dissolve all the solid material. The unreacted (excess) butyl alcohol was removed from the solution by extraction with ether. The aqueous layer, evaporated to a convenient bulk, was treated with a stoichiometric amount of 25% sulfuric acid or concentrated sulfuric acid. Then, the yellowish organic layer was extracted with ether and fractionally distilled to obtain butoxyacetic acid (yield 80%, bp 44–46 °C (5 mmHg).

The butoxyacetic acid was mixed in a round-bottom flask with an excess of thionyl chloride under a nitrogen atmosphere and stirred at 40–45 °C for 3 h. The mixture was often allowed to stand overnight at room temperature and the excess thionyl chloride was removed by gentle heating under vacuum. This reaction yielded a nearly quantitative amount of butoxyacetyl chloride. The material was used without further purification in the next step.

To convert the acid chloride to the acid azide (**caution: azides are unpredictably explosive; the quantities described for this procedure should be scaled down if this preparation is to be done for the first time**), 3 mol of sodium azide was dissolved in 300 mL of water, and the solution was cooled by using an ice–water bath. To this solution was added 300 mL of cyclohexane and the temperature of the mixture was kept at ~5 °C then a solution of 1 mol of acid chloride in 300 mL of acetone was added slowly through an addition funnel. After the mixture was stirred for an additional 1 h, the solution was cooled and transferred to a separatory funnel, and the organic layer, containing the acid azide, was separated from the aqueous solution. The organic part was mixed with another 300 mL of cyclohexane and heated between 65 and 70 °C for at least 1 h until gas evolution subsided. After cooling, the solvents were evaporated followed by fractional distillation under vacuum to produce the butoxymethyl isocyanate, which was a clear colorless liquid (yield 55%, bp 65 °C (1 mmHg)). Additional characterization data are given in Table I.

All the monomers, which were obtained by the same method, were kept in a refrigerator until used.

Polymerization. Before the polymerization reaction, all the glassware was flame-dried and kept under a dry nitrogen atmosphere. Also, the solvents, mainly toluene and dimethylformamide (DMF), were dried and distilled freshly. In addition, DMF was stirred under vacuum to remove the dimethylamine produced during the distillation until no effervescence was noted. These solvents were kept in sealed bottles over 4A molecular sieves.

The sodium cyanide solution (catalyst) was prepared by dissolving dried NaCN powder in DMF (ca. 0.35% NaCN by weight) and stored under nitrogen gas until used.

In a three-neck round-bottom flask, equipped with a mechanical stirrer and nitrogen gas flow system and drying tube, 20 mL of DMF was injected with a hypodermic syringe and cooled to −55 °C (above the freezing point of the DMF). Then, 5 mL of the monomer was added and the reaction mixture was stirred until the temperature of the solution had stabilized. The catalyst solution was added drop by drop until gel particles appeared or the reaction mixture became viscous; then the reaction mixture was stirred further for $^1/_3$–$^1/_2$ h. The polymerization was terminated by adding a small amount of acetyl chloride (ca. 5 mL). The polymer was precipitated with 50–100 mL of precooled methanol and filtered through a fritted-glass filter. These polymers were often reprecipitated from toluene solution and dried under vacuum. Additional characterization data are given in Table I.

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References and Notes

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(4) Our sample showed *two* changes in slope (T_g? ~+5° and ~−10°) as a function of temperature in the DSC (Mettler TA3000).

(5) Professor M. M. Green (private communication, 1989) has made similar observations regarding the absence of "living" character.

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(7) The only way to transfer a sample is to redissolve it, transfer to a vial for storage, and evaporate the solvent.

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Registry No. $H(CH_2)_6OCH_2NCO$, 63578-98-3; $ClCH_2CO_2H\cdot Na$, 3926-62-3; $H(CH_2)_6OCH_2CO_2H\cdot Na$, 72170-34-4; $H(CH_2)_6OCH_2COCl$, 63579-01-1; $H(CH_2)_6OCH_2CO_2H$, 57931-25-6; $BuOCH_2NCO$, 15768-66-8; $BuOCH_2CO_2H\cdot Na$, 56637-93-5; $BuOCH_2CO_2H$, 2516-93-0; $H(CH_2)_3OCH_2NCO$, 15768-64-6; $PhCH_2OCH_2NCO$, 19810-32-3; $H(CH_2)_3OCH_2NCO$, 132622-59-4; $BuOCH_2NCO$ (homopolymer), 132622-60-7; $H(CH_2)_6OCH_2NCO$ (homopolymer), 132622-61-8; $PhCH_2OCH_2NCO$ (homopolymer), 132622-62-9; sodium azide, 26628-22-8.