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Synthesis of new triisocyanate curatives 2,2-bis(isocyanatomethyl)propyl isocyanate and 4-(isocyanatomethyl)-1,7-heptyl diisocyanate

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SUMMARY

Two triisocyanate crosslinking agents were synthesized. The 2,2-bis(isocyanatomethyl)-propyl isocyanate was synthesized from 2,2-bis(hydroxymethyl)propanol in three steps via the triazide and the triamine with an overall yield of 20% and >95% purity as determined by NMR. The 4-(isocyanatomethyl)-1,7-heptyl diisocyanate was synthesized from 1,3,5-pentanetricarboxylic acid in six steps with an overall yield of 23.5% and >98% purity as determined by NMR. This synthesis proceeded via the trimethyl ester, the triol, the tris(p-toluenesulfonate), the triazide and the triamine.

INTRODUCTION

A common binder system currently employed in solid propellants is a polyetherurethane-crosslinked network formed from low molecular weight hydroxy-terminated pre-polymers cured in the presence of catalysts and polyisocyanates. Problems associated with these polyetherurethane formulations include substandard mechanical properties, excessive crosslinking and high lot-to-lot variability.

Recent trends towards binder systems which use network polymers with higher molecular weight between crosslinks but with lower number of skeletal atoms require the binder network to operate at optimum efficiency. It was demonstrated that the mechanical properties of bimodal polyurethane networks could be improved by substituting a purely trifunctional isocyanate, 1,3,5-triisocyanatopentane, for the commonly used commercial polyfunctional isocyanate.[1] However, secondary hydroxy-terminated pre-polymers gave no network formation when 1,3,5-triisocyanatopentane was used.

Through a critical analysis of known crosslinking agents used in polyurethane network formation, we attempted to correlate curative structure with network mechanical properties. Common structural features of the most successful crosslinking agents included: 1) all primary isocyanates; 2) trifunctionality; and 3) biuret-free structure. Primary isocyanates give a complete cure with the primary- and secondary-hydroxy-terminated groups of the prepolymer. Trifunctional crosslinking agents provide a good network polymer with difunctional pre-polymers. Both of these features minimize the number of non-load-bearing chains or loops in the cured polymer and therefore result in good mechanical properties. Biuret structures create relatively rigid crosslink points in the binder because the resulting crosslink points can undergo intramolecular hydrogen bonding to form six-membered ring structures (fig.1). It is believed that this type of interaction may be responsible for some of the poor mechanical properties observed when these type of curatives are used.[1]

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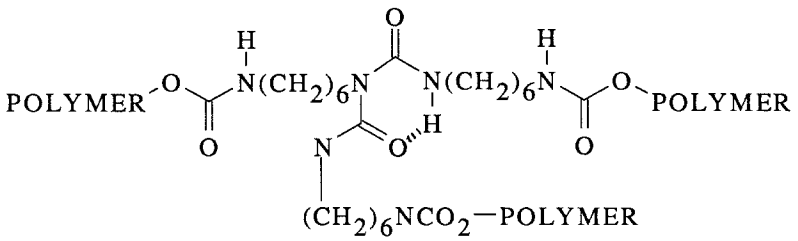
Figure 1. Intramolecular Hydrogen-Bonding of Biuret Structures

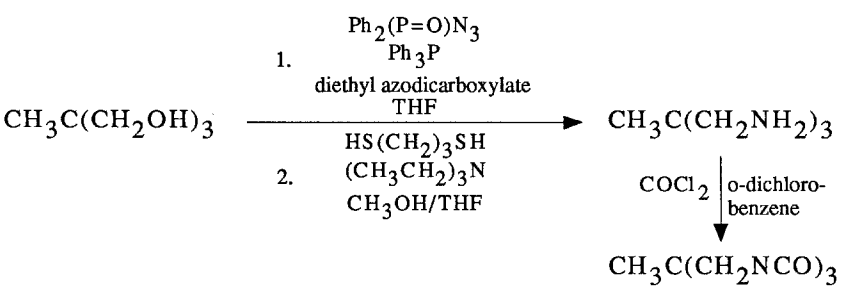


Combining these common structural features, we arrived at a general structure for the ideal isocyanate crosslinking agent: R-C[$(CH_2)_n$-NCO]$_3$, where $n \geq 2$ and R = H, alkyl, etc.[2] From this general structure, we targeted two new triisocyanates: 2,2-bis-(isocyanatomethyl)propyl isocyanate and 4-(isocyanatomethyl)-1,7-heptyl diisocyanate. This paper reports the high-purity syntheses of these triisocyanates.[3]

RESULTS AND DISCUSSION

The synthesis of the triisocyanate 2,2-bis(isocyanatomethyl)propyl isocyanate was performed in two steps (fig. 2). In the first step, the triol 2,2-bis(hydroxymethyl)propanol was converted to the triamine using a one-pot method which was developed by combining and modifying two previously reported methods: one involving the synthesis of azides from alcohols using diphenylphosphoryl azide[4] and the other involving the reduction of azides to amines using 1,3-propanedithiol.[5]

Figure 2. Synthesis of 2,2-Bis(isocyanatomethyl)propyl Isocyanate

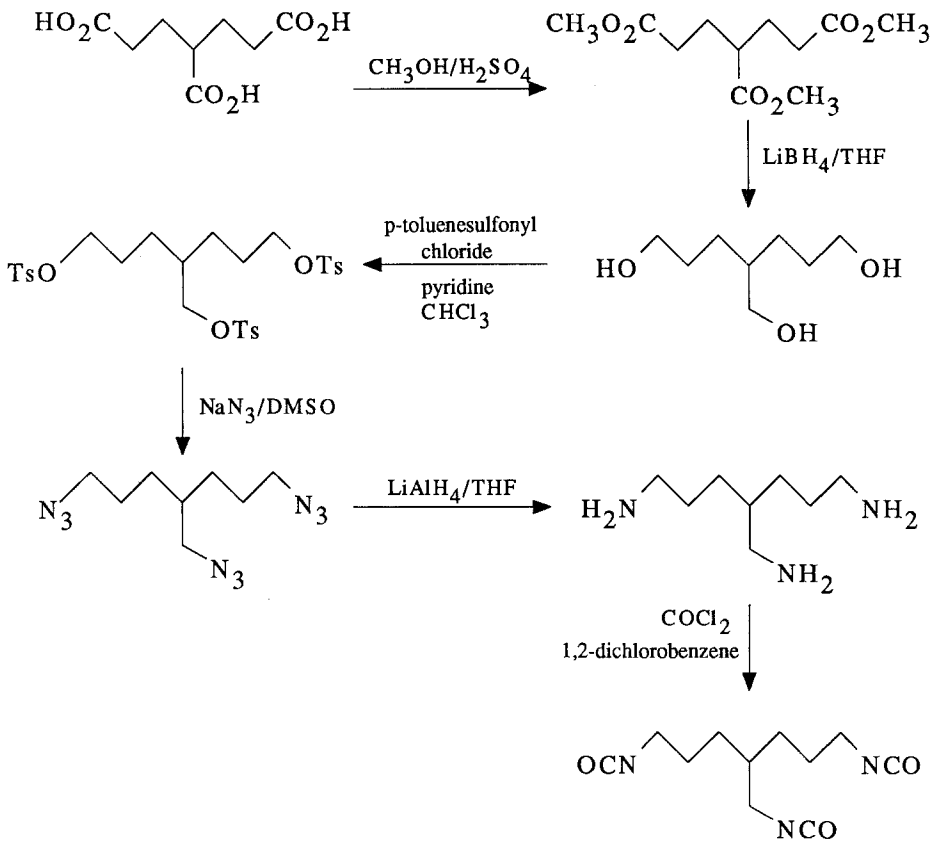


Thus, diphenylphosphoryl azide was added to a THF solution of 2,2-bis(hydroxymethyl)-propanol, triphenylphosphine and diethyl azodicarboxylate. Following a 5-hr. reflux, the triol appeared (by ^{1}H-NMR) fully converted to 2,2-bis(azidomethyl)propyl azide. Triethylamine, 1,3-propanedithiol and methanol were then added to the cooled reaction mixture and followed by a 30-hr. reflux to convert the triazide in situ to 2,2-bis(amino-methyl)propylamine in 87% yield.

In the second step, the triamine is converted to the desired triisocyanate via a traditional method of carbonylation of amines with phosgene. A solution of 2,2-bis(aminomethyl)-

propylamine in o-dichlorobenzene was added to a solution of phosgene in o-dichlorobenzene at 0°-78°C. Following reaction at 140°C for 16 hrs. and subsequent distillation, the 2,2-bis(isocyanatomethyl)propyl isocyanate was obtained in 23% yield. Overall yield for the synthesis was 20%. The triisocyanate was characterized by IR and ^{1}H-NMR which were consistent with the structure. Purity was determined by ^{1}H-NMR to be at least 95%.

Figure 3. Synthesis of 4-(Isocyanatomethyl)-1,7-heptyl Diisocyanate



The synthesis of 4-(isocyanatomethyl)-1,7-heptyl diisocyanate followed a six-step procedure starting from 1,3,5-pentanetricarboxylic acid (fig. 3). This tricarboxylic acid was esterified in 75% yield to the trimethyl ester with methanol and hydrochloric acid for 21 hrs. at reflux. The trimethyl ester in THF was then reduced with lithium borohydride to the 4-(hydroxy-methyl)-1,7-heptanediol in 98% yield (after chromatographic purification).[6] A solution of this triol in pyridine and chloroform was converted to the tris(p-toluenesulfonate) using p-toluenesulfonyl chloride; following chromatographic purification, the yield was 86%. The triazide was subsequently formed in 94% yield by reacting sodium azide with the triol in DMSO for 21 hrs. at room temperature. Reduction of the triazide in THF with lithium aluminum hydride for 4 hrs. at reflux gave the triamine, which was isolated and subsequently distilled to 76% yield. The final step employed a commonly used method for the conversion

of amines to isocyanates, phosgenation of the triamine in o-dichlorobenzene to the triisocyanate. This resulted in a 90% crude yield (by ^{1}H-NMR) and a 52% yield after distillation.

The intermediates and final product were characterized by ^{1}H-NMR, ^{13}C-NMR and IR. The spectra were consistent with the product structures. Purity of the 4-(isocyanatomethyl)-1,7-heptyl diisocyanate was determined to be at least 98% based on ^{1}H- and ^{13}C-NMR. Overall yield of this triisocyanate synthesis was 23.5%.

EXPERIMENTAL

SYNTHESIS OF 2,2-BIS(ISOCYANATOMETHYL)PROPYL ISOCYANATE

Synthesis of 2,2-Bis(aminomethyl)propylamine: A solution of diphenylphosphoryl azide (560 µL, 0.715 g, 2.6 mmol) in anhydrous tetrahydrofuran (THF) (2.0 mL) was added dropwise to a solution of 2,2-bis(hydroxymethyl)propanol (0.10 g, 0.83 mmol), triphenylphosphine (0.69 g, 2.6 mmole) and diethyl azodicarboxylate (412 µL, 0.453 g, 2.60 mmol) in anhydrous THF (70.0 mL) at 22°C under N_2. The reaction was warmed to reflux for 5 hrs. ^{1}H-NMR analysis indicated that the triol (at 3.73 ppm, -C$\underline{H}_2$OH) had been completely converted to the triazide (at 3.66 ppm, -C$\underline{H}_2N_3$). After cooling the mixture to 25°C, anhydrous methanol (100 mL), triethylamine (1.73 mL, 1.26 g, 12.5 mmole) and 1,3-propanedithiol (1.25 mL, 1.35 g, 12.5 mmole) were added. The mixture was heated to reflux (65°C) for 30 hrs., then cooled to room temperature. Solvent was removed in vacuo. Ethyl acetate was added and the organic phase was washed with 3.5% aq. HCl (10.0 mL). The aqueous phase was collected, made basic, and extracted with $CHCl_3$. Solvent was removed in vacuo to give 2,2-bis(aminomethyl)propylamine (0.084 g, 87%). ^{1}H-NMR spectral data was consistent with literature.[7]

Synthesis of 2,2-Bis(isocyanatomethyl)propyl Isocyanate: A solution of 2,2-bis(amino-methyl)propylamine (1.8 g, 15.4 mmol) in anhydrous o-dichlorobenzene (25 mL) was added dropwise via syringe to a solution of phosgene in o-dichlorobenzene (1000 mL) at 0°C (prepared by condensing phosgene into the o-dichlorobenzene using a -78°C trap for 2 hrs.). Phosgene was continuously fed in throughout the remainder of the reaction. Mechanical stirring was used along with a -78°C trap. The reaction was heated to 140°C; at 110°C, vigorous gas evolution was observed. After heating 16 hrs. at 140°C, the clear solution was cooled and N_2 bubbled in for 2 hrs. to purge excess phosgene. Solvent was removed in vacuo to give a tan oil. The crude oil was distilled in vacuo to give 2,2-bis(isocyanatomethyl)propyl isocyanate (0.67 g, 23%).

^{1}H-NMR ($CDCl_3$, 90 MHz, ppm): δ 3.3 (s, 6H, -C$\underline{H}_2$-NCO), 1.0 (s, 3H, C$\underline{H}_3$-).
IR (film, cm^{-1}): 2900 w, 2275 s.

SYNTHESIS OF 4-ISOCYANATOMETHYL-1,7-HEPTYL DIISOCYANATE

Synthesis of Trimethyl 1,3,5-Pentanetricarboxylate: Sulfuric acid (5 mL) was added to a solution of 1,3,5-pentanetricarboxylic acid (50 g, 0.245 mol) in anhydrous methanol (1000 mL). The solution was warmed to reflux for 21 hrs., after which it was cooled. Solvent was

removed in vacuo to give a yellow oil to which was added diethyl ether (300 mL) and water (300 mL). The aqueous phase was neutralized with 10% aq. NaOH (15 mL) and extracted with diethyl ether (3 x 100 mL). The organic phases were combined and washed with 10% aq. $NaHCO_3$ (100 mL), H_2O (100 mL), saturated aq. NaCl (100 mL), and dried over anhydrous $MgSO_4$. The solution was filtered and the solvent removed in vacuo to give a clear oil which was distilled (0.9 mm Hg, 130°C) to yield trimethyl 1,3,5-pentane-tricarboxylate (43.4 g, 75%).

^{1}H-NMR ($CDCl_3$, 90 MHz, ppm): δ 3.6 (s, 9H, -CH($CO_2C\underline{H}_3$)$_3$), 2.4 (m, 5H, -$C\underline{H}_2CO_2CH_3$ and -$C\underline{H}CO_2CH_3$), 1.8 (m, 4H, -$C\underline{H}_2CHC\underline{H}_2$-).
^{13}C-NMR (CD_3OD, 22.5 MHz, ppm): δ 176.8, 174.8, 52.1, 45.0, 32.3, 28.1.
IR (film, cm^{-1}): 2954 m, 1736 s.

Synthesis of 4-(Hydroxymethyl)-1,7-heptanediol: Lithium borohydride (6.6 g, 0.3 mol) was added over a 30 min. period via a solids addition funnel to a solution of trimethyl 1,3,5-pentanetricarboxylate (33.1 g, 134 mol) in THF (500 mL, freshly distilled from Na/K benzophenone) at 0°C. Following the addition, the reaction refluxed for 3 hrs., after which it was transferred to a 4 L beaker, quenched with a solution of H_2O/THF (60 mL/100 mL) while cooling over a 1 hr. period, then stirred at 25°C for 2 hrs. Solvent was then removed to give a clear oil (25 g) which was chromatographed (SiO_2 230/400 mesh:compound ratio, 30:1; ethyl acetate/methanol, 20:3; R_f = 0.30) to give 4-(hydroxymethyl)-1,7-heptanediol (21.3 g, 98%).

^{1}H-NMR (D_2O, 90 MHz, ppm): δ 3.2 (m, 6H, -C($C\underline{H}_2OH$)$_3$), 1.1 (m, 9H, $HOCH_2C\underline{H}_2C\underline{H}_2C\underline{H}(CH_2OH)C\underline{H}_2C\underline{H}_2CH_2OH$).
^{13}C-NMR (CD_3OD/D_2O, 22.5 MHz, ppm): δ 64.3, 62.2, 39.1, 28.7, 26.4.
IR (film, cm^{-1}): 3334 s, 2935 m.

Synthesis of 4-(Hydroxymethyl)-1,7-heptanediol, Tris(p-toluenesulfonate): Pyridine (101.7 mL, 99.9 g) was added to a solution of 4-(hydroxymethyl)-1,7-heptanediol (34 g, 0.21 mol) in anhydrous $CHCl_3$ (600 mL, stored over sieves) under N_2. The solution was cooled to 0°C and p-toluenesulfonyl chloride (180 g, 0.945 mol) was added in portions via a solids addition funnel. The reaction was stirred for 4 hrs., then poured into a mixture of diethyl ether/H_2O (1500 mL/400 mL). The diethyl ether phase was washed with 2N aq. HCl (3 x 300 mL), 5% aq. $NaHCO_3$ (300 mL), H_2O (500 mL), saturated aq. NaCl (300 mL) and dried over $MgSO_4$. After filtering, solvent was removed and the resulting oil deposited on silica gel (150 g). Chromatography (SiO_2 230/400 mesh:adsorbed-compound ratio, 20:1; ethyl acetate/ hexane) gave the tris(p-toluenesulfonate) of 4-(hydroxymethyl)-1,7-heptanediol (113 g, 86%).

^{1}H-NMR ($CDCl_3$, 90 MHz, ppm): δ 7.8 (d, 8 Hz, 6H, aromatic), 7.35 (d, 8 Hz, 6 H, aromatic), 3.9 (m, 6H, -$C\underline{H}_2$-OTs), 2.3 (s, 9H, -C($C\underline{H}_3$)$_3$), 1.3 (m, 9H, $TsOCH_2C\underline{H}_2C\underline{H}_2C\underline{H}(CH_2OTs)C\underline{H}_2C\underline{H}_2CH_2OTs$).
^{13}C-NMR ($CDCl_3$, 22.5 MHz, ppm): δ 144.9, 144.8, 132.8, 132.5, 129.8, 127.7, 71.4, 70.0, 36.6, 26.4, 25.8, 21.5.
IR (film, cm^{-1}): 1356 s, 1189 s.

Synthesis of 4-(Azidomethyl)-1,7-heptyl Diazide: Sodium azide (54.4 g, 0.84 mol) was added to a solution of the tris(p-toluenesulfonate) of 4-(hydroxymethyl)-1,7-heptanediol (113 g, 0.18 mol) in anhydrous dimethyl sulfoxide (1 L) under N_2 at ambient temperature. The reaction was stirred for 21 hrs. and then was poured into a mixture of diethyl ether/water (2 L/1.5 L). The ether phase was separated and washed with H_2O (3 x 600 mL), saturated aq. NaCl (300 mL) and dried over $MgSO_4$. The solvent was removed to give 4-(azidomethyl)-1,7-heptyl diazide (40 g, 94%).

^{1}H-NMR ($CDCl_3$, 90 MHz, ppm): δ 3.3 (m, 6H, -C($C\underline{H}_2N_3)_3$), 1.5 (m, 9H, $N_3CH_2C\underline{H}_2C\underline{H}_2C\underline{H}(CH_2N_3)C\underline{H}_2C\underline{H}_2CH_2N_3$).
^{13}C-NMR ($CDCl_3$, 22.5 MHz, ppm): δ 54.6, 51.4, 37.5, 28.7, 25.9.
IR (film, cm^{-1}): 2098 s.

Synthesis of 4-(Aminomethyl)-1,7-heptyldiamine: A solution of 4-(azidomethyl)-1,4-heptyl diazide (8.4 g, 35.4 mmol) in THF (100 mL) was added dropwise to a suspension of $LiAlH_4$ (5.7 g, 150 mmol) in anhydrous THF (250 mL). The reaction was heated at reflux for 4 hrs., after which it was cooled with an ice bath and worked up by addition of H_2O (5.7 mL), 10% aq. NaOH (8.5 mL), and H_2O (12.8 mL). The mixture was then filtered and the precipitate extracted 24 hrs. in a soxhlett extractor using the THF from the workup as the extraction solvent. The solvent was then stripped to give an oil which was azeotropically dried (benzene, Dean-Stark trap) for 24 hrs. The benzene was removed and the oil distilled (Kugelrohr, 135°C, 60 mm) to give 4-(aminomethyl)-1,4-heptyldiamine (4.3 g, 76%). (TLC: R_f = 0.15, 3:1:1 methanol:dichloromethane:n-butylamine).

^{1}H-NMR ($CDCl_3$, 90 MHz, ppm): δ 2.7 (s, 6H, -C($C\underline{H}_2NH_2)_3$), 1.4 (m, 15H, $N\underline{H}_2CH_2C\underline{H}_2C\underline{H}_2C\underline{H}(CH_2N\underline{H}_2)C\underline{H}_2C\underline{H}_2CH_2N\underline{H}_2$).
^{13}C-NMR ($CDCl_3$, 22.5 MHz, ppm): δ 44.8, 42.3, 30.6, 28.4.
IR (film, cm^{-1}): 3360 br, 2926 s.

Synthesis of 4-(Isocyanatomethyl)-1,7-heptyl Diisocyanate: A solution of phosgene (about 100 g) in anhydrous o-dichlorobenzene (800 mL) was prepared by bubbling phosgene into o-dichlorobenzene for 1 hr. using a -40°C condensor. A solution of 4-(aminomethyl)-1,7-heptyldiamine (2.0 g, 112.6 mmol) in anhydrous o-dichlorobenzene (20 mL) was added via syringe to the above phosgene solution. The reaction, under N_2, was slowly warmed to 160°C over about 4 hrs. Upon clearing, the reaction was allowed to cool to ambient temperature and the low temperature condensor replaced by an "air condensor." Nitrogen was used to purge phosgene from the reaction for 2 hrs. The solvent was removed and the resulting oil (2.7 g, 90%) was purified by distillation (Kugelrohr, 165°C, 0.03 mm) to give 4-(isocyanatomethyl)-1,7-heptyl diisocyanate (1.54 g, 52%).

^{1}H-NMR ($CDCl_3$, 90 MHz, ppm): δ 3.3 (m, 6H, -C($C\underline{H}_2NCO)_3$), 1.5 (m, 9H, $(NCO)CH_2C\underline{H}_2C\underline{H}_2C\underline{H}(CH_2NCO)C\underline{H}_2C\underline{H}_2CH_2(NCO)$).
^{13}C-NMR ($CDCl_3$, 22.5 MHz, ppm): δ 121.9, 45.7, 42.9, 38.2, 28.4, 28.2.
IR (film, cm^{-1}): 2272 s, 2950 s.

ACKNOWLEDGMENTS

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