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Siloxanes with aliphatic isocyanate groups

A tetrafunctional cross-linking agent

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Summary

Tetramethylcylcotetrasiloxane (D4H) was hydrosilylated with α,α'-dimethyl meta-isopropenyl benzyl isocyanate (m-TMI). The reaction with this commercially available and inexpensive isocyanate produces in 100% yield a well characterized tetrafunctional siloxane-based aliphatic isocyanate useful as a cross-linking agent and as a precursor for star polymers. The silylation reaction can also be carried out with other siloxanes containing SiH groups such as 1,1,3,3-tetramethyldisiloxane yielding siloxanes with terminal isocyanate groups.

Introduction

In our studies on the ring opening polymerization of cyclotetrasiloxanes with large substituents leading to comb-like and functionalized polysiloxanes (1,2) it was noticed that very few siloxanes with isocyanate groups were available (3). It occurred to us that the hydrosilylation of tetramethylcylcotetrasiloxane (D4H) with an unsaturated isocyanate could lead to a tetrafunctional isocyanate. Such a compound could serve as an effective cross-linking agent and as a precursor for star polymers or starburst dendrimers (4). A further incentive was the fact that few if any well characterized and inexpensive tetrafunctional isocyanates are commercially available. Also, most multifunctional or pluriisocyanates have functionalities that frequently deviate from their idealized tri- or tetrafunctional structures (5-7).

This paper reports the hydrosilylation of D4H with the commercially available and inexpensive isocyanate m-TMI (α,α'-dimethyl meta-isopropenyl benzyl isocyanate). The reaction, with 100% yield, produces a well characterized tetrafunctional aliphatic isocyanate (Figure 1) which can undergo a variety of reactions.

Experimental

The isocyanate m-TMI (American Cyanamid) (8) was vacuum distilled under a slow flow of nitrogen. The fraction boiling at 127-128°C/12.7 mm Hg was collected for the hydrosilylation reaction. D4H (Petrarch) was used without further purification.

In a typical reaction, 10 g (0.0395 moles) of D4H was mixed with 50 g (0.2488 moles) of freshly distilled m-TMI in a three neck flask. To the clear solution was added 0.3 ml of a 3% solution of platinum divinyltetramethyldisiloxane in xylene (Petrarch) and the mixture heated under nitrogen at 40°C. The reaction was continued until no SiH absorption could be detected in the ^1H NMR spectrum. The total reaction time was 30-40 hrs. In the latter stages of the reaction a small quantity of fresh catalyst was added to complete the conversion. Excess TMI was removed under high vacuum at about 120°C. The product, a slightly colored viscous liquid (the color is caused by residual platinum catalyst) was analyzed by IR, NMR, GPC and elemental analysis. ^1H NMR ($CDCl_3$) δ -0.09 (Si-CH_3,s,3); 0.93 (Si-CH_2, d,2); 1.30 (CH-CH_3,d,3); 1.69 (C-CH_3,s,6); 2.95 (CH,m,1); 7.10 (arom CH,s,1); 7.30 (arom CH,m,3). ^{13}C NMR ($CDCl_3$), δ, 1.51 ($SiCH_3$); 25.55 (CH_3); 27.22 (Si-CH_2); 33.10 (C-CH_3); 35.35 (CH); 60.77 (C-N); 121.82,

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122.75, 125.30, 128.53 (arom C); 123.27 (C=O). Anal. Calc., C 64.33; H 7.33; N 5.35. Found, C 64.02; H 7.34; N 5.30.

Results and Discussion

The absence of a Si-H absorption in the ^1H NMR spectrum of tetra[2-methyl-2{3-(1-isocyanato-1-methylethyl)phenyl}ethyl]tetramethyl cylcotetrasiloxane, abbreviated as D4TMI, suggests complete substitution of the hydrogen in D4H by m-TMI. This is confirmed by the results of elemental analysis and by GPC. The gel permeation chromatogram (Figure 2) depicts only one sharp peak with a very small shoulder on the higher molecular weight side. The latter may result from the reaction of m-TMI with D5H, a likely impurity in D4H which is claimed to have a purity of 95% (3). The ^{13}C NMR spectrum (Figure 1) only shows the expected carbon absorptions. From all observations, it appears that the conversion to the tetrafunctional aliphatic isocyanate D4TMI is quantitative.

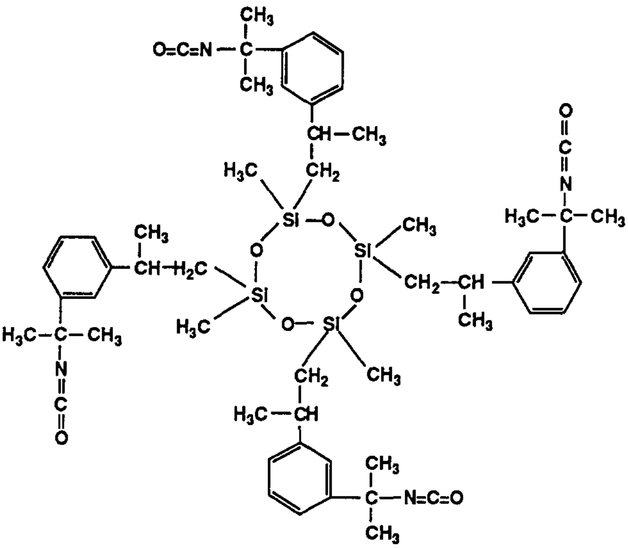

Figure 1. D4TMI

D4TMI is soluble in most organic solvents and can be used as a precursor for star polymers or starburst dendrimers, or as a cross-linking agent. The reaction with a series of monomethyl polyethylene glycol ethers of the general formula $CH_3(OCH_2CH_2)_nOH$ (n=3,7,12) in the presence of a small amount of tetramethylethylene diamine as catalyst proceeds smoothly and quantitatively in a few hours. The urethane product is water soluble for n=7 and 12. This compound can also be polymerized in the presence of D4 or other cyclosiloxanes to yield polysiloxanes with polyethylene oxide sidechains. Other products can be obtained by reacting D4TMI with reagents containing functional groups reactive with aliphatic isocyanate. For example, diethanol amine rapidly reacts with D4TMI via its amine group to yield a product with eight hydroxyl groups. Such reactions could lead to interesting starburst polymers (4). D4TMI can also be used as a cross-

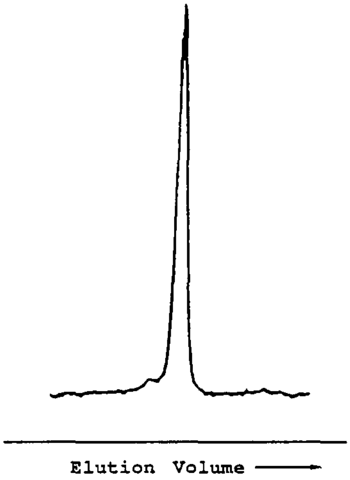

Figure 2. Gel permeation chromatogram of D4TMI

linking agent. Reactions with polyethylene glycols and diamines produce network polymers with urethane and urea linkages. Their properties are being evaluated.

The hydrosilylation reaction using m-TMI is also effective with other siloxanes containing the Si-H function. For example, 1,1,3,3-tetramethyldisiloxane, $HSi(CH_3)_2OSi(CH_3)_2H$ can be quantitatively converted into the diisocyanate by reaction with a slight excess of m-TMI. A small amount of toluene is used to make the mixture homogeneous. The diisocyanate can then be reacted with a dialcohol or diamine to yield linear polyurethanes or polyureas. The reaction of m-TMI with copolymers of D4 and D4H produces polysiloxanes with reactive isocyanate groups. We are also exploring the ring opening polymerization of D4TMI as a means towards obtaining polysiloxanes with isocyanate substituents.

Conclusions

The unsaturated aliphatic isocyanate m-TMI is an effective hydrosilylating agent. With D4H it produces in 100% yield a tetrafunctional isocyanate useful as a cross-linking agent and precursor for star polymers. Other siloxanes with SiH groups also react quantitatively with m-TMI.

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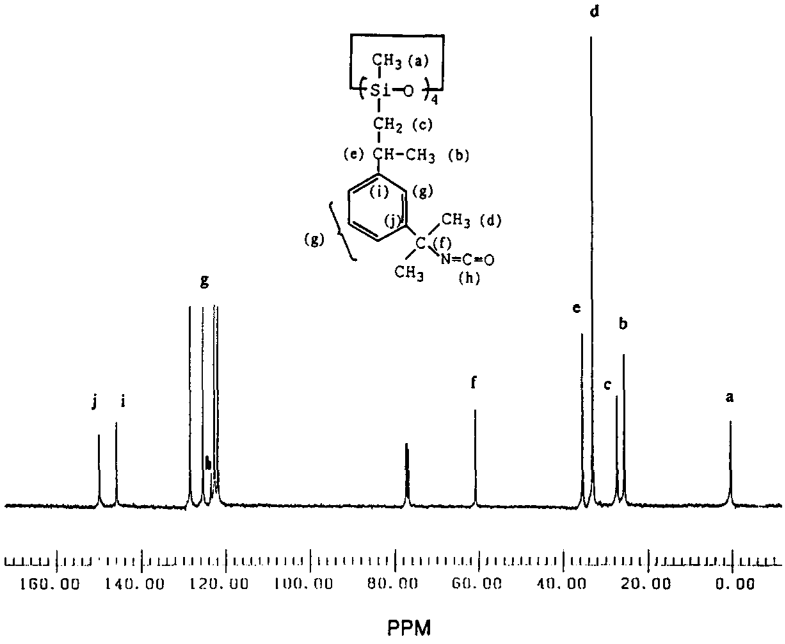

Figure 3. ^{13}C NMR spectrum of D4TMI

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