Synthesis of imide siloxane prepolymers using blocked isocyanates

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Imide siloxane prepolymers were synthesized from α,ω-anhydride-terminated poly(dimethylsiloxane)s and 4,4′-diphenylmethanediisocyanate. The isocyanate groups were blocked with imidazole or oxime to achieve imide formation by solvent-free condensation at 90°C. The products, which are on average triblock copolymers, were characterized by ^{1}H n.m.r., ^{13}C n.m.r. and i.r. spectroscopy.

(Keywords: imide siloxane prepolymer; poly(dimethylsiloxane); blocked isocyanate; condensation; synthesis; characterization)

Introduction

The incorporation of siloxanes is a well investigated method to improve the fracture and impact strength of highly crosslinked network polymers. The compatibility of the siloxane and the crosslinking resin is considered to be an important factor for developing the desired microphase separated morphology[1–3]. The goal of our work was to study the network formation and morphology of epoxy resins modified with imide siloxane prepolymers containing anhydride or isocyanate as reactive groups. The imide structure should result in an improved compatibility with epoxy resins. The predominant route to make poly(imide siloxane)s is the reaction of aminopropyl-terminated dimethylsiloxane oligomers with aromatic dianhydrides, which proceeds via a poly(amic acid) intermediate[4,5]. The synthetic approach described in this communication is the condensation of α,ω-anhydrido-propyl-terminated poly(dimethylsiloxane) and 4,4′-diphenylmethanediisocyanate (MDI) which proceeds with evolution of CO_2. To obtain imide formation, blocking of the isocyanate groups by reaction with imidazole or oxime is required.

Experimental

All manipulations were carried out under argon atmosphere. MDI (Bayer) and phenyl isocyanate were distilled under reduced pressure before use; imidazole (Aldrich), 2-butanone oxime (Aldrich), allylsuccinic anhydride (Wacker) and *N*,*N*-dimethylaminopyridine (DMAP) (Aldrich) were used without further purification. $H_2PtCl_6 \cdot 6H_2O$ (Merck), 0.01 M in tetrahydrofuran (THF), was used as hydrosilylation catalyst. $HSiMe_2O(Me_2SiO)_nSiMe_2H$ with $n=6$(HSi$_8$), was donated by Wacker. *N*,*N*-Dimethylacetamide (DMAC) was dried over molecular sieves (4 Å), and toluene and THF were dried over sodium metal and distilled before use. I.r. and n.m.r. spectra were run on a Bruker IFS 45 and a Bruker AC 300 spectrometer. D.s.c. measurements were performed with a Perkin-Elmer DSC 7 at a heating rate of 10°C min^{-1}.

Synthesis of the blocked isocyanates. The imidazole adduct of phenyl isocyanate and MDI (MDI-IM) was obtained by reacting the isocyanate with a stoichiometric amount of imidazole in THF at room temperature[6]. The oxime adduct of MDI (MDI-OX) was produced as described earlier[7].

Synthesis of the model compound N-*phenylsuccinimide.* Allylsuccinic anhydride (2.0 g, 0.02 mol), imidazole-blocked phenyl isocyanate (3.74 g, 0.02 mol) and DMAP (0.24 g, 0.002 mol) were placed in a 100 ml three-necked flask, equipped with a thermometer and a gas burette. The mixture was heated to 90°C within 5 min, and kept at this temperature until the amount of CO_2 evolved was constant. Cooling to room temperature resulted in a white precipitate which was recrystallized from ethanol to give colourless crystals (yield 2.52 g, 72%). M.p. 136–137°C. I.r. (KBr): ν(cm^{-1}) = 1780, 1740, 1710 (C=O), 1390, 1110, 770(δN–CO–N$_{\text{ring.}}$).

Synthesis of α,ω-bis(succinylanhydrido-n-propyl)hexadecylmethyloctasiloxane (SiAN). In a 500 ml three-necked flask, equipped with a reflux condenser, a dropping funnel and an argon inlet tube were placed HSi$_8$ (58 g, 0.1 mol) dissolved in 100 ml toluene, and $H_2PtCl_6 \cdot 6H_2O$ (256 mg, 2×10^{-5} mol). The mixture was heated to 90°C and a solution of allylsuccinic anhydride (28 g, 0.2 mol) was added very slowly while stirring. The progress of the reaction was followed by i.r. spectroscopy. After the complete disappearance of the Si-H band at 2120 cm^{-1}, the mixture was refluxed until platinum metal was formed. The black reaction mixture was purified by filtration over charcoal. The solvent was removed under reduced pressure to afford a pale yellow oil (yield 83.1 g, 97%). Viscosity: 150 mPa s. I.r. (film): ν (cm^{-1}) = 1860, 1780 (C=O), 1260, 800 (Si–CH$_3$), 1060 (Si–O). ^{1}H n.m.r. (CDCl$_3$): δ (ppm) = 0.06 (Si–CH$_3$), 0.55 (Si–C*H*$_2$–CH$_2$–CH$_2$–), 1.45 (Si–CH$_2$–C*H*$_2$–CH$_2$–), 1.65, 1.91 (Si–CH$_2$–CH$_2$–C*H*$_2$–), 3.09 (CH–C=O), 2.6, 3.05 (CH$_2$C=O). ^{13}C n.m.r. (CDCl$_3$): δ (ppm) = 0.13, 1.03, 1.15 (Si–CH$_3$), 17.71 (Si–*C*H$_2$–CH$_2$–CH$_2$–), 20.77 (Si–CH$_2$–*C*H$_2$–CH$_2$–), 34.02 (Si–CH$_2$–CH$_2$–*C*H$_2$–), 34.42 (*C*H$_2$–C=O), 40.39 (*C*H–C=O), 170.51 (CH$_2$–*C*=O), 173.93 (CH–*C*=O).

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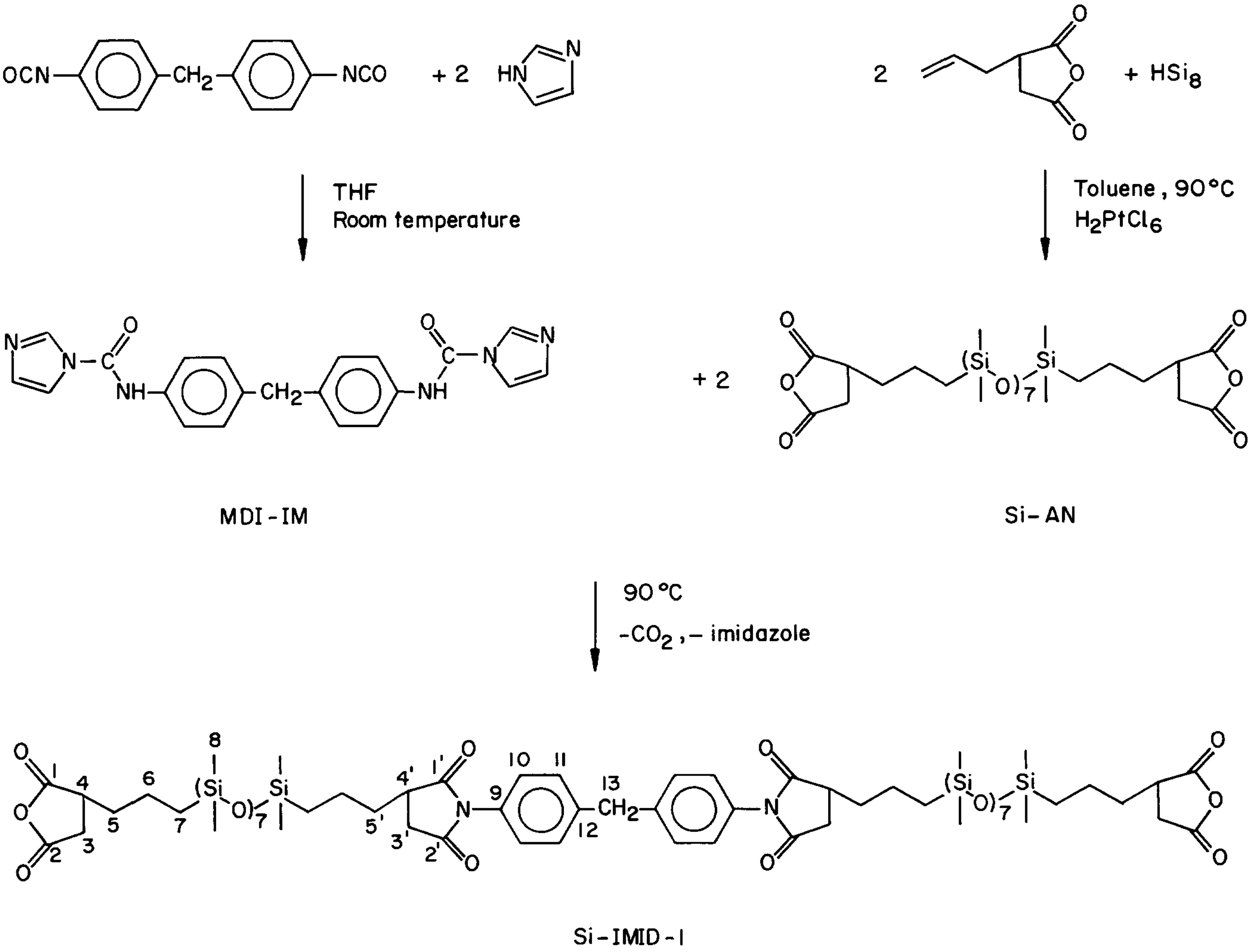
Synthesis of the imide siloxane Si-IMID-1. The reaction of SiAN with MDI-IM was carried out as described for *N*-phenylsuccinimide using 3.36 g (4 mmol) SiAN and 0.78 g (2 mmol) MDI-IM. The reaction mixture was kept at 90°C until the amount of CO_2 evolved was constant. The pale yellow oil was filtered off under pressure. Residual imidazole was removed by sublimation *in vacuo* at 90°C (yield 3 g, 84%). Viscosity: 3500 mPa s. I.r. (film): ν (cm^{-1}) = 1870, 1790 ($C{=}O_{anhydride}$), 1710 ($C{=}O_{imide}$), 1410 (δ $N{-}C{=}O_{ring}$), 1260, 800 ($Si{-}CH_3$), 1060 (Si–O). ^{13}C n.m.r. ($CDCl_3$): δ (ppm) = 179.94 (C1′), 176.59 (C2′), 173.52 (C1), 169.96 (C2), 34.91 (C3), 34.35 (C3), 34.20 (C5′), 33.97 (C5), 40.29 (C4′), 39.54 (C4), 20.65 (C6), 17.61 (C7), 0.03–1.04 (C8), 38.35 (C9), 27.34 (C10), 26.07 (C11).

Results and discussion

The condensation of diisocyanates and dianhydrides with evolution of CO_2 is a well known polyimide-forming reaction[8,9]. In most cases, aromatic isocyanates and aromatic anhydrides have been used as reactants for imide preparation. For aliphatic compounds, however, this reaction often does not work at moderate temperatures. Therefore, we examined as a first step the reaction of the aliphatic succinic anhydride with phenyl isocyanate in DMAC, which is a model for the reaction of the aliphatic anhydride groups of SiAN. No evolution of CO_2 from the reaction mixture could be observed up to 150°C and there was no evidence of imide formation in the i.r. spectrum. However, the i.r. signal at 1705 cm^{-1} indicated isocyanurate formation resulting from the trimerization of the isocyanate. It should be noted that CO_2 evolution starts at low temperatures (80°C) using phthalic anhydride instead of succinic anhydride to give *N*-phenylphthalimide in high yield[10].

In order to prevent trimerization we repeated the model reaction with succinic anhydride using imidazole-blocked phenyl isocyanate. Now CO_2 evolution was nearly quantitative at 90°C within a period of 2 h. The yield of *N*-phenylsuccinimide was 82%. The method to block the isocyanate with imidazole was recently proposed by Wenzel *et al.*[11] to obtain high molecular weight aromatic polyimides. The blocked isocyanate approach also provided the possibility of reacting MDI with two equivalents of SiAN as outlined in *Scheme 1*. At 90°C MDI-IM is soluble in SiAN and the amount of CO_2 corresponds to 90% imidization. The fact that imide formation occurred well below the deblocking temperature of the neat MDI-IM, which was determined by d.s.c. to be 185°C, indicated that a bimolecular reaction of the anhydride on the blocked isocyanate took place. *FT*i.r. spectra of the liquid Si-IMID-1 (cf. *Figure 1*) revealed the asymmetric carbonyl stretching band of the imide structure at 1710 cm^{-1} while the symmetric band was



Scheme 1

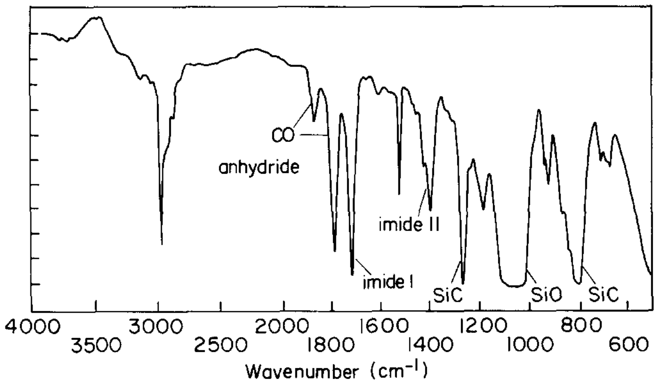


Figure 1 *FT*i.r. spectrum of Si-IMID-1

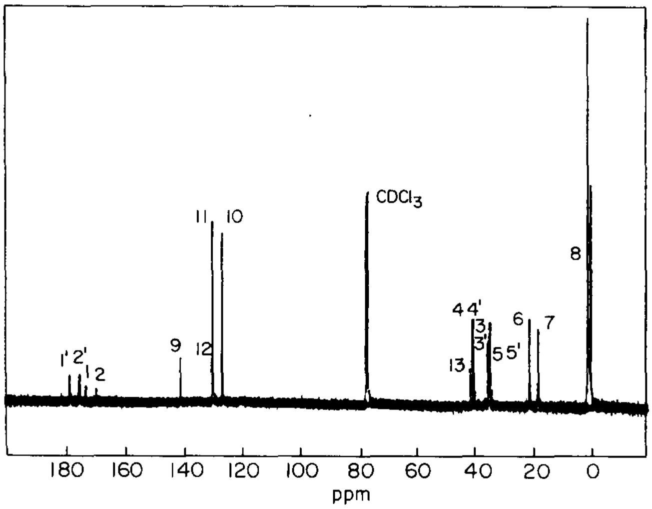


Figure 2 ^{13}C n.m.r. spectrum of Si-IMID-1

covered by the C=O band of the terminal anhydride groups. The ^{13}C n.m.r. (cf. *Figure 2*) showed new signals at 175 and 178 ppm assignable to the imide carbonyl groups. The signals at 170 and 173 ppm arise from the carbonyl groups of the anhydride. For the reaction of SiAN with two equivalents of MDI-IM a small amount of imidazole is required to make the reaction mixture homogenous at 90°C. The free imidazole was removed from the imide siloxane by sublimation without causing the isocyanate end groups to be unblocked. Another blocking agent investigated was 2-butanone oxime which can easily be removed by distillation. A 2:1 molar ratio of SiAN and MDI-OX was used to obtain Si-IMID-1. The imidization temperature was ~140°C which coincides with the deblocking temperature of MDI-OX measured by d.s.c. to be 143°C.

Conclusions

Imide siloxane prepolymers have been synthesized by condensation of anhydride-terminated siloxanes and blocked isocyanates. At present we are able to produce low molecular weight prepolymers which contain anhydride or blocked isocyanate as terminal groups. Blocking of the aromatic isocyanate with imidazole or oxime was shown to be necessary to afford imide formation with aliphatic anhydride units. The evaluation of the siloxane imides to modify epoxy resins is in progress.

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