

Communication

N-Heterocyclic carbene-catalyzed dehydration of α,ω -disilanol oligomers

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Received 18 December 2007; received in revised form 5 February 2008; accepted 5 February 2008

Available online 15 February 2008

Abstract

An efficient polycondensation reaction of α,ω -dihydroxy oligodimethylsiloxanes, catalyzed by *N*-heterocyclic carbenes (NHC), is developed for the first time. Surprisingly, in this polymerization, the moisture sensitive NHC catalyze the dehydration of disilanol oligomers, and remains intact. This result demonstrates the compatibility of NHCs with the intervention of H₂O in catalytic reactions.

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Keywords: *N*-Heterocyclic carbenes; Silicones; Organocatalyst; Polycondensation

1. Introduction

In a context where environment-benign processes are more than ever advocated, the removal of metallic contaminants and their replacement by non-toxic catalysts in some key polymerizations is becoming a major scientific and industrial issue that needs to be addressed. For instance, applications of polymers in fields like microelectronics or living systems should often be free of any metal residues. One of the most promising solutions for this issue should be the utilization of organic molecules as catalysts, namely organocatalysts which have recently become a highly active research domain [1]. Among them, *N*-heterocyclic carbenes (NHCs) [2] have been well recognized as a powerful tool for organic chemists as highly reactive organocatalysts [1a,1b,3].

In contrast, NHC catalysts have only been involved in a few polymerization reactions [4], such as polymerization of isocyanates [5], ring-opening polymerization (ROP) of cyclic esters [6], and cyclic siloxanes [7]. Recently we have also

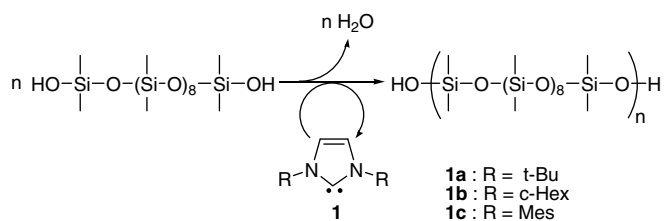
reported that NHCs are efficient catalysts for the ROP of cyclotetrasiloxane (D₄), which is one of the rare examples of the transformation of non-carbonyl compounds catalyzed by NHCs [8]. It is obvious that, in order to expand the scope of NHC applications, new types of catalytic activities should be developed.

We herein report a surprising novel catalytic activity of air-sensitive NHCs in dehydration reactions of disilanol oligomers (polycondensation) which is one of the most important processes for the production of silicone polymers [9].

α,ω -Dihydroxy oligodimethylsiloxanes [HO(SiMe₂O)₁₀-H] were heated at 80 °C, in a closed schlenk tube (50 mL), in the presence of a catalytic amount of isolated NHCs **1a–c** (2500 ppm) [10]. The polymerization reaction by polycondensation was evident because of the increasing viscosity of the reaction mixture and the formation of H₂O which is immiscible with the silicone polymer (see Scheme 1).

The analysis of the resulting polymer by ¹H NMR spectroscopy shows a simple statistical singlet signal at 0.29 ppm (typical for silicone polymers) compared to the highly complicated signal pattern for the much shorter starting α,ω -disilanol oligomers.

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Scheme 1. Polycondensation of α,ω -hydroxy oligodimethylsiloxane catalyzed by NHCs.

Size exclusion chromatography (SEC) analyses show high molecular weights with polydispersities similar to those obtained by ROP of D_4 catalyzed by NHCs [8]. The quantity of NHC catalyst affects the molecular weight of the resulting silicone polymers. Loading a smaller quantity

Table 1
Polycondensation of α,ω -dihydroxy oligodimethylsiloxane catalyzed by NHCs (**1a–c**)

[Cat.] (ppm)	NHC catalyst								
	1a			1b			1c		
	Mn ^a	Ip ^b	Yield ^c	Mn ^a	Ip ^b	Yield ^c	Mn ^a	Ip ^b	Yield ^c
10000	70	1.9	86	48	1.9	90	49	1.6	91
5000	75	1.8	87	62	1.7	89	50	1.8	94
2500	137	1.9	89	67	1.7	91	63	1.6	91
2500 ^d	294	1.7	91						

80 °C, 16 h in a closed schlenk tube (50 mL).

^a 10³.

^b Polydispersity index.

^c Yields (%) were calculated from the proportion of integrations [disilanol/cyclic polysiloxane (D_4, D_3)/silicone polymer] obtained by SEC.

^d Polymerization under a flow of argon.

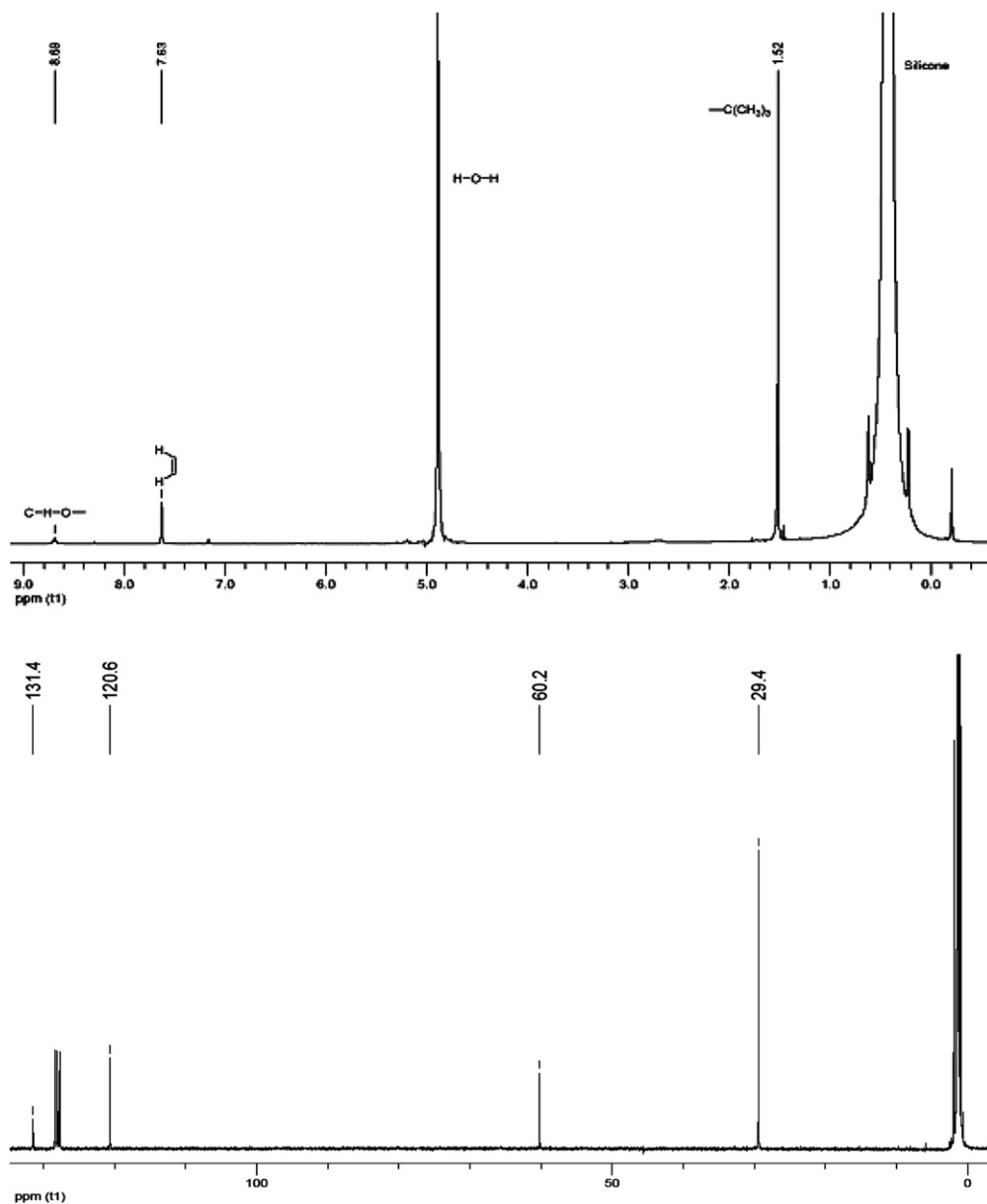


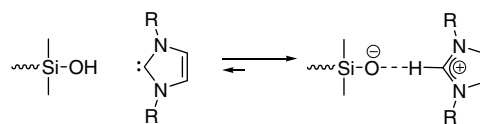
Fig. 1. ^1H and ^{13}C NMR of NHC **1a** after the polycondensation reaction.

of catalyst leads to longer polymers in all cases. The evacuation of the H₂O produced was found to be particularly important in regulating the molecular weights of the resulting polymers. Indeed, increasing molecular weights of the resulting silicone polymers were observed when the polymerization was carried out in a larger Schlenk tube (95 mL, $M_n = 175 \times 10^3$) or in an open reactor under argon ($M_n = 294 \times 10^3$). These results suggest that the NHCs also catalyze depolymerisation reactions in the presence of H₂O. Moreover, the decrease of molecular weights with larger quantities of NHC could be explained by preferential depolymerization reactions. Concerning the polydispersity index of the resulting silicone polymers, a narrower molecular weight distribution ($I_p = 1.6$ – 1.9) compared to that of the starting material α,ω -dihydroxy oligodimethylsiloxanes ($I_p = 2.1$) was observed. A similar phenomenon was reported by He et al. using an organotin compound as catalyst [11], which was explained by the dependence of functional reactivity on chain length (see Table 1).

The best results were obtained using the most basic *N,N'*-di-*tert*-butylimidazol-2-ylidene (**1a**) [12]. The catalytic performance of **1a** was surprisingly high, even in the closed system. In the best case, one molecule of NHC can remove about 400 molecules of H₂O. The high catalytic activity of **1a** suggests that the carbene behaves as a base in the polycondensation of dihydroxysiloxanes. In fact, the interaction of NHCs with relatively acidic proton has already been reported [7,13]. Therefore, the polycondensation reaction proceeds with the NHC bearing very bulky mesityl groups (**1c**) which is completely inactive for the ROP of cyclosiloxanes [8], suggesting that the role of the NHC catalyst is different in each case (ROP/polycondensation). Indeed, we already proposed that the reactive species in the ROP of cyclosiloxanes were formed by the nucleophilic attack of NHCs on the silicon atom to open the ring, which explains the inactivity of the very bulky NHC **1c**.

The ¹³C NMR spectrum of the silicone polymer obtained by polycondensation using NHC **1a** (5%), as catalyst, shows a strong interaction between the carbenic carbon atom and the hydroxyl group at the chain terminal, as indicated by a high field chemical shift (131 ppm) compare to that of the free carbene (211 ppm). This interaction was confirmed by ¹H NMR spectroscopy, which revealed a broad signal at 8.7 ppm corresponding to the silanol proton. Of particular interest, no traces of any hydrolyzed product of the NHC catalyst **1a** were detected by NMR analysis (see Fig. 1).

The high resistance and efficient catalytic activity of NHCs in polycondensation reactions can partially be explained by the strong hydrophobic character of silicone polymers [14,15], which efficiently eliminate the generated H₂O to allow the reaction to proceed and to protect the NHC catalyst. In a similar way, Kobayashi et al. recently reported the Lewis acid catalyzed condensation reactions between carboxylic acids and alcohols in a hydrophobic micelle system [16]. The surprising resistance of NHCs in this system might also be explained by the weak interaction



Scheme 2. Interaction NHC–silanol.

between the NHC and silicone polymers or silanol functions. In fact, we recently demonstrate the remarkable resistant character of NHCs in silicon polymers due to the weak carbene–silicon interaction (see Scheme 2) [17].

As already mentioned, after the first polymerization, no degradation of the *N*-heterocyclic carbene can be detected. Therefore, the NHC catalyst remains active, which is confirmed by the consumption of successively added disilanol monomers (yield = 94%). Smaller molecular weights of the corresponding silicone polymers [18] were obtained, probably due to the increasing quantity of H₂O after the second polymerization. The deactivation of NHC catalyst was successfully achieved by simply heating the polymer at 160 °C for 1 h.

2. Conclusion

In conclusion, we successfully achieved an efficient catalytic polycondensation reaction of α,ω -disilanol oligomers to provide silicone polymers without any metal contamination, using a “moisture sensitive” *N*-heterocyclic carbene catalyst. This process is important not only in industry, but also from a fundamental point of view. The discovery of the compatibility of NHCs with the presence of H₂O could be the breakthrough to expand the scope of NHC organocatalysts for new catalytic reactions.

3. Experimental details

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. α,ω -Dihydroxy oligodimethylsiloxanes [HO(SiMe₂O)₁₀H] were obtained from BLUESTAR-Silicone and used without any purification. Dry, oxygen-free solvents were employed. ¹H, ¹³C, NMR spectra were recorded on Bruker Avances 300 spectrometers. ¹H, ¹³C NMR chemical shift were reported in ppm relative to Me₄Si as external standard or referenced to residual solvent proton resonance. Coupling constants are given in Hz. The NHCs (**1a**–**1c**) were synthesized and purified before use by the methods previously described [10a,19].

The degree of conversion and molecular weight distributions were obtained from size exclusion chromatography (SEC) using a HP 1050 Series instrument. The instrument was fitted with two Waters styragel HR GPC columns (7.8 × 300 mm, HR4 and HR4E) heated to 40 °C. Toluene was used as the eluent. Sample detection was performed at 35 °C by a Waters 410 differential refractometer. A calibration was made by using a set of narrow molecular

weight distribution polystyrene from Polymer Laboratories.

4. Polycondensation of α,ω -dihydroxyoligodimethylsiloxanes

To α,ω -dihydroxy oligodimethylsiloxanes [HO(SiMe₂O)₁₀H, 3.00 mL, 3.31 mmol] was added a THF solution of NHC (**1a–c**) [C = 0.104 mol/L, (2500 ppm, 79.5 μ L, 8.3 μ mol), (5000 ppm, 159 μ L, 16.5 μ mol), (10⁴ ppm, 318 μ L, 33.1 μ mol)] in a schlenk tube (50 mL). The Schlenk tube was closed and then the mixture was heated at 80 °C for 16 h. The resulting silicon polymers were analysed without purification.

Acknowledgements

We are grateful to the CNRS and Bluestar Silicones for financial support of this work.

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