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Aminoalkyl functionalized siloxanes

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Abstract: Polydimethylsiloxanes bearing aminoalkyl groups as terminal or side chain moieties have found a broad application as polymer modifiers, fabric conditioners, release agents, personal care products and hydrophobizing agents. Methods of aminosiloxane synthesis as well as established and future applications of these silicone materials are reviewed.

Keywords: aminosiloxanes, organosilicon synthesis, hydroxysiloxanes, aminoalkylalkoxysilanes, condensation, hydrosilylation, ring-opening.

Siloksany funkcjonalizowane grupami aminoalkilowymi

Streszczenie: Przedstawiono metody syntezy funkcjonalizowanych silikonów — aminoalkilosiloksanów — polimerów i oligomerów o szerokim spektrum zastosowań w budownictwie, przemyśle włókienniczym i kosmetycznym. Opisano procesy kondensacji, hydrosililowania oraz polimeryzacji z otwarciem pierścienia, a także metody otrzymywania małocząsteczkowych siloksanów wykorzystywanych jako modyfikatory polimerów (poliamidów, poliuretanów i epoksydów). Omówiono również tradycyjne i potencjalne zastosowania tych amfifilowych materiałów.

Słowa kluczowe: aminosiloksany, synteza krzemoorganiczna, hydroksysiloksany, aminoalkilosiloksany, kondensacja, hydrosililowanie, otwarcie pierścienia.

Polyorganosiloxanes (silicones) — polymers having an inorganic main chain, made of alternating silicon and oxygen atoms, with organic substituents at silicon atoms are one of the most important and intensively studied classes of organometallic polymers. Much of the growth of the area of organosilicon chemistry, in general, originates from wide field of application of polyorganosiloxanes and the necessity to optimize their synthesis and properties. Certain features of the siloxane (Si-O-Si) bond, such as low barrier of rotation around Si-O axis (~2.5 kJ/mol) and low barrier of linearization (~1.3 kJ/mol), account for the unique flexibility of polyorganosiloxane chain [1, 2]. These polymers exhibit also high thermal stability and electrical resistance, due to the strength of siloxane bond of their inorganic main chain. The presence of alkyl substituents at silicon atom is responsible for hydrophobicity and exceptionally low surface free energy of polyorganosiloxanes [3]. However, polyorganosiloxanes can exhibit also hydrophilic or amphiphilic properties when some of alkyl substituents at silicone atoms are replaced with polar groups such as aminoalkyl or polyethers.

Polysiloxanes bearing aminoalkyl moieties are often referred to as amino silicone fluids or aminosilicones. This important class of functionalized organosilicon polymers has a wide range of applications [4—6]. Due to

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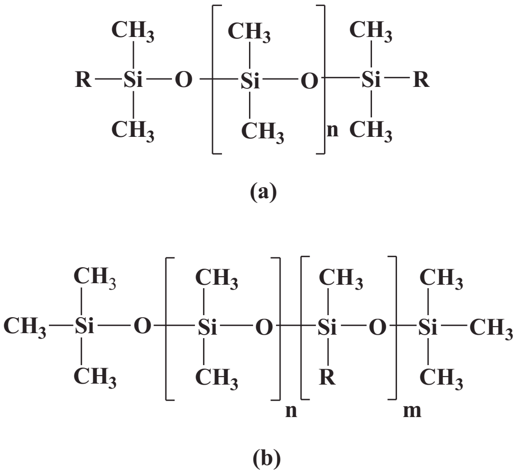


Scheme A

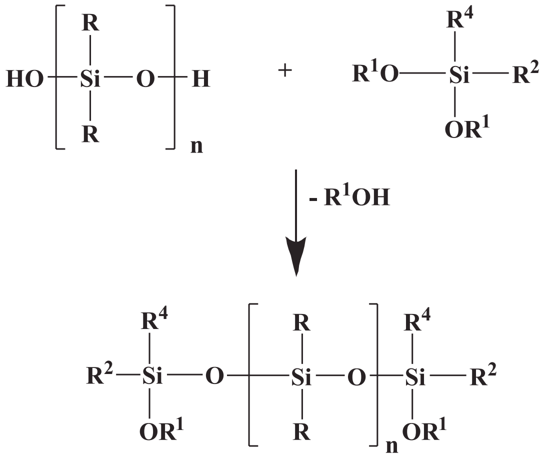
their unique amphipilic properties, excellent spreadability and ability to form aqueous micro-emulsions, aminosiloxanes have been used in cosmetic products and textile applications for decades [6—13]. The amino-functional silicones are also applied in some other areas such as treatment and modification of metal [14] and mineral surfaces [15]. The aminoalkyl groups can be either attached to the terminal silicon atoms of the linear polydimethylsiloxane chain or introduced as the pendant groups randomly distributed within the siloxane backbone (Scheme A). The properties of amino-polysiloxanes are well controlled by the structure of aminoalkyl moieties, their concentration and average molecular weight of the polymer.

LINEAR SYSTEMS — SYNTHETIC METHODS

As a result of a wide range of industrial applications of aminoalkylsiloxanes, the majority of synthetic methodologies have been disclosed in patents. Although many currently practiced industrial processes have been developed relatively long time ago, there is still a strong interest in the search for novel, more efficient and practical synthetic pathways to amino-functional polysiloxanes. This review concentrates on the most important, current development in this area.

Condensation of α,ω-dihydroxypolyorganosiloxanes (siloxanediols) with aminoalkyl-alkoxysilanes

Preparation of aminofunctional polyorganosiloxanes by a condensation of hydroxyl-terminated polyorganosiloxanes with aminoalkylalkoxysilanes was one of the first methods described in the literature. Patent literature [16—18] disclose the process of condensation of linear α,ω-dihydroxypolyorganosiloxanes ($HO\text{-}[SiR_2O]_nH$) of molecular weight from 4000 to 6800, where R denotes Me or Me, Ph, with phenyl radicals content Ph below 10 mol % with trialkoxysilanes [$R^2Si(OR^1)_3$], where R^1 is an alkyl radical with 1—4 carbon atoms, but most often the ethyl one. A wide range of aminoalkyl groups R^2 is patented. They include: $H_2N\text{-}(CH_2)_{1-6}$- or $H_2N\text{-}(CH_2)_xR^3\text{-}(CH_2)_y$, where R^3 represents -NH- lub -NH-CH_2CH_2-NH-, -O-, -S-, and x is equal or larger than 2, and y is equal or larger than 3 (Scheme B).

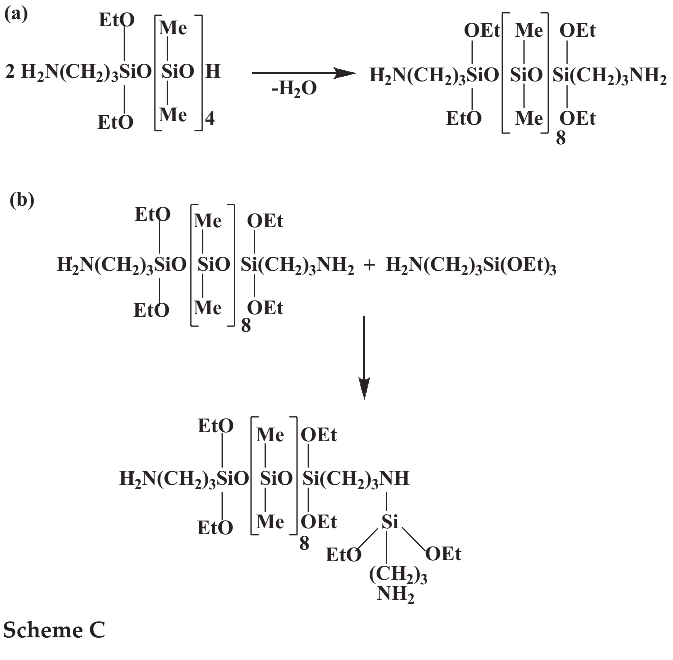


(a) R = Me or Me and Ph (Ph less then 10 % Me); R^1 = Me, Et; $R^2 = H_2N\text{-}(CH_2)_{1-6}$-, $H_2N\text{-}(CH_2)_xR^3\text{-}(CH_2)_y$-, R^3 = -NH-, -NH$(CH_2)_2$-, -O-, -S-; x = 1-2, y = 1-3, $R^4 = OR^1$

(b) Me, n = 55-90 [16, 18] or R = Me; R^1= -OMe, -OEt; $R^2 = \text{-}(CH_2)_3NHR^3$; R^3 = H, -$(CH_2)_2NH_2$; R^4 = Me, -OMe, -OEt; n = 4, 6, 7, 10 [19].

Scheme B

The typical process of condensation of siloxane diols with aminopropyltriethoxysilane [$H_2N(CH_2)_3Si(OEt)_3$] is carried out at relatively high temperature (180 °C), without any solvent. The byproduct of the condensation process, ethanol, is removed by distillation. The linear polysiloxane with terminal aminopropyldiethoxy groups can be obtained with high yield when a molar ratio of the siloxanediol to alkoxysilane is 1:2 [18]. If dihydroxypolysilo-



Scheme C

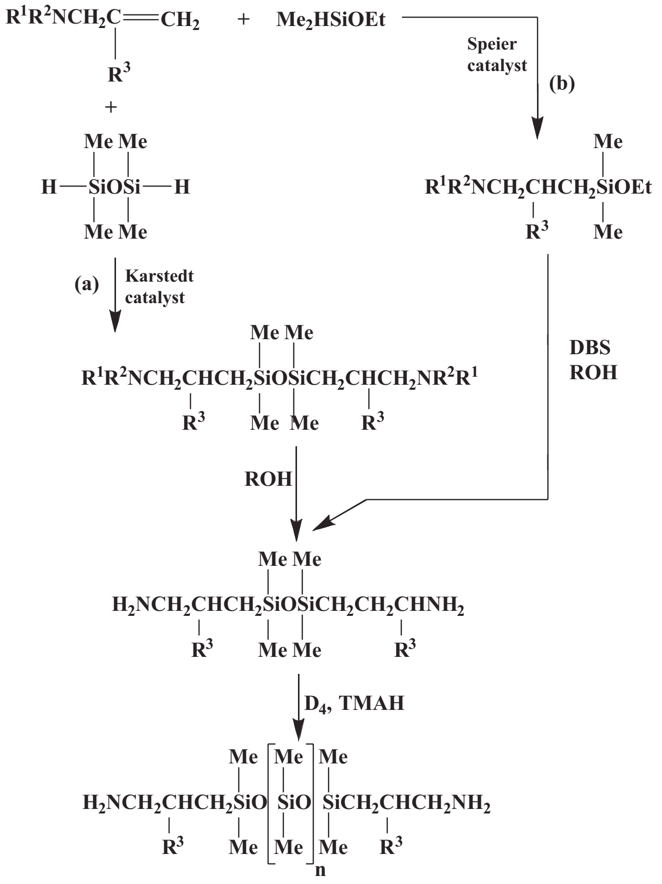
xane was used in excess to aminopropyltriethoxysilane (the molar ratio was 1:1.33) an increase of molecular weight of the aminofunctional siloxane was observed [16], as a result of partial homo-condensation of siloxanediol moieties (Scheme C, a).

The elevated temperature can, in such reactions, lead to additional side condensation of already substituted aminopropyl groups with alkoxy substituents generating the silyl substituted secondary amine structures and further on, generating branched or even crosslinked products. The first step of these coupling processes is shown schematically in Scheme C, b.

More systematic, kinetic studies of formic acid catalyzed condensation of the well-defined siloxane diols with aminoalkyl di- and trialkoxysilanes was recently published [19] (Scheme B, b). A selection of the well-defined siloxane diols allowed determining the effect of siloxane chain length on the rate of this process, eliminating a complication related to polydispersity [20] of siloxane diols, typically used in syntheses carried out on technical scale [21]. Indeed, it was determined that the length of siloxane chain affects reactivity of the respective diols and the observed rate constants of the condensation with aminopropyl(methyl)(diethoxy)silane increase as follows: 1.0 (HD_4OH) : 5.0 (HD_6OH) : 7.6 (HD_7OH) : 9.3 ($HD_{10}OH$). It can be ascribed to the higher basicity of hydroxyl oxygen atom the longer the siloxane chain is, as a result of stronger multicenter π-bonding between oxygen and silicon atoms in the chain as well as the intra-molecular hydrogen bonding of SiOH with siloxane units [19]. The condensation was proven to be of the second order in the respect to substrates, to a high degree of conversion, meaning that a reactivity of Si-OH group is not affected by substitution of aminoalkyl moiety at the other terminal silicon atom. The HCOOH catalyzed reaction is a very fast process and its activation energy is in the range of 20 kJ/mol [19].

Hydrosilylation of allylamine derivatives

Currently, there appears to be a growing interest in preparation of the simplest linear aminoalkyl siloxanes (Scheme A, a), where n = 0, which are used as modifiers of organic polymers. Thus, a three step process was developed, involving *e.g.* hydrosilylation of *N*,*N*-bis(trimethylsilyl)allylamine with dimethylethoxysilane in the presence of Speier's catalyst (H_2PtCl_6), followed by desilylation, hydrolysis and the final condensation, leading to 1,3-bis(3-aminopropyl)-tetramethyldisiloxane with yield ranging from 80 to 86 % [22]. The same product was obtained by a direct hydrosilylation of allylamine, protected by one trimethylsilyl group, with tetramethyldisiloxane, using Karstedt's catalyst (complex of platinum(0) with tetramethyldivinyldisiloxane) [23], eliminating the hydrolysis of alkoxysiloxane-allylamine addition product and further condensation step, presented in [22] (Scheme D). Hydrosilylation based method has been described in detail for the preparation of 1,3-bis[(*N*-ethyl)amino(2-methyl)propyl]tetramethyldisiloxane {$O[SiMe_2CH(CH_3)CH_2NHCH_2CH_3]_2$} by addition of tetramethyldisiloxane to *N*-ethyl-2-methylallylamine [24]. The obtained aminoalkyl-substituted tetramethyldisiloxanes were further applied as the end-stoppers to prepare low and high molecular weight α,ω-bis(aminoalkyl)polysiloxanes *via* insertion of octamethylcyclotetrasiloxane (D_4) in the presence of tetramethylammonium hydroxide [23, 24]. A reverse approach to synthesis of α,ω-bis(aminoalkyl)polysiloxanes, from the hydrogen terminated ones, by hydrosilylation of *t*-butyloxycarbonyl protected allylamine has been also described [25].



R = H, Me, Et; R^1 = Me_3Si, Et_3Si, Et; R^2= Me_3Si, H; R^3 = H, Me; n = 10—700
DBS = dodecylbenzenesulfonic acid
D_4 = octamethylcyclotetrasiloxane
TMAH = tetramethylammonium siloxanolate

Scheme D

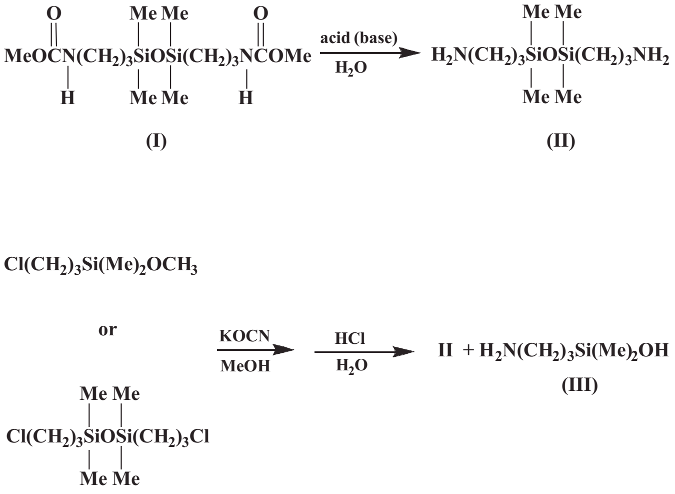
The environment, health and safety (EHS) concerns related to allylamine such as its toxicity, high volatility, and low flash point as well as multi-step process involving N-protection of amine, amine deprotection and the final hydrolysis strongly restricts the large scale applications of the hydrosilylation based method.

Thus, hydrosilylation method is mainly used to synthesize well defined siloxanes, such as 1,3-bis[(*N*-ethyl)amino(2-methyl)propyl]tetramethyldisiloxane.

However, an apparently effective synthesis was described for the reaction of unprotected allylamine with polydimethylsiloxanes, having terminal hydrogen atoms, in the presence of Karstedt's catalyst in xylene (or cyclic vinyl siloxanes) [18].

Carbamato-silanes and -siloxanes

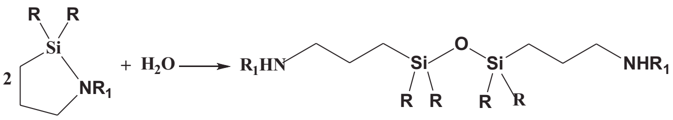
Recent US patent application [17] discloses a highly effective synthesis of bis(aminoalkyl)disiloxanes from corresponding carbamates. This process is based on earlier reported transformations devoted to a development of novel negative photoresist materials based on the light sensitive strong base precursors [26]. Similar approaches were applied to synthesis of aminoalkyl-functionalized siloxane nanocages [27] and silicas [28, 29] *via* thermolysis or acid hydrolysis of carbamates. Nevertheless, these rather distant and a sort of out of field material science contributions triggered the development of an efficient pathway to bis(aminoalkyl)disiloxanes allowing to avoid disadvantages of the hydrosilylation based synthetic approach. Although the patent literature [17] claims several carbamate derivatives of silanes and disiloxanes as substrates, the simplest and most efficient process involves acid or base catalyzed hydrolysis of bis(methylcarbamatopropyl)tetramethyldisiloxane [Formula (I)]. This potentially a one pot process, involving an *in situ* generation of carbamate derivatives, made from 3-chloropropyl group bearing alkoxysilanes or disiloxanes and potassium cyanate, yields the corresponding 3-aminopropyl derivatives of disiloxane (II) (Scheme E).



Scheme E

AMINOALKYLSILOXANES *VIA* RING-OPENING OF CYCLIC PRECURSOR

Another type of a process that avoids problems created by the described above hydrosilylation pathway and leads to pure bis(3-aminopropylsiloxanes) involves the use of cyclic 1-aza-2-silacyclopentanes. The ring opening hydrolysis of such derivatives (Scheme F) leads exclusively to the formation of 3-aminopropyl isomers [30, 31], which are difficult to obtain by the hydrosilylation as a mixture of the Markovnikov and anti-Markovnikov addition products is generated [31]. The hydrolysis of 1-aza-2-silacyclopentane and a subsequent condensation of formed silanols yields exclusively bis(3-aminopropyl)disiloxane. Longer polysiloxanes bearing the aminopropyl end groups can be obtained by equilibration of 1-aza-2-silacyclopentanes with linear organopolysiloxanes having terminal SiOH functional groups, in the presence of tetramethylammonium hydroxide (TMAH) [32].



R= alkyl, aryl, alkoxy radicals; R_1= alkyl, aryl, trimethylsilyl radicals

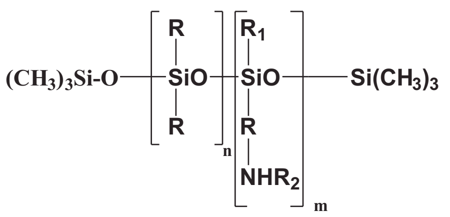
Scheme F

Each of the methods leading to linear alkylamine terminated siloxanes has, from the synthetic point of view, some positive but also negative features. Condensation is a simple one step process but generates siloxanes of a different chain length as on an industrial scale a mixture of linear hydroxyl-terminated siloxanes is used. Hydrosilylation may be used to produce well defined siloxanes once *e.g.* tetramethyldisiloxane is used as an adduct across unsaturated amines, however it brings in complications due to a lengthy three step process involving blocking and de-blocking of the amine group and may lead to undesired isomer mixture. Finally, the use of carbamates or aza-silacyclopentanes offers clean and selective reactions but these systems require an additional step of their synthesis.

SYNTHESIS OF POLYSILOXANES WITH PENDANT AMINOALKYL GROUPS

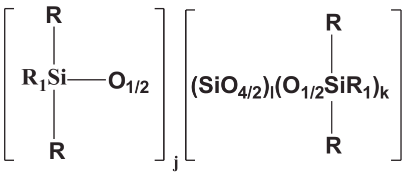
Polysiloxanes with pendant aminoalkyl groups (Scheme G, a) are mainly used as release agents (oils) and active components of microemulsions, used in personal care products [33]. They are also used to produce amino-functionalized so called MQ resins by co-hydrolysis and condensation processes (Scheme G, b) [34, 35]. Synthesis of water soluble amino- and alkyl-functional siloxanes resins by acid catalyzed co-hydrolysis and condensation of aminopropyltriethoxysilanes and isobutyltrimethoxysilane in aqueous system has been recently described. In this case hydrolysis involves transient formation of corresponding silanols which further undergo condensation, leading to a mixture of branched and cyclic aminoalkyl siloxane resin [36].

(a)



R = alkyl or arylalkyl radicals of 1-18 carbon atoms,
R_1= alkyl or arylalkyl radicals of 1-18 carbon atoms,
or polyorganosiloxane chain having 1-100 diorganosiloxy units
R_2= hydrogen, alkyl or arylalkyl radicals of 1-18 carbon atoms
n = 50-200 and m = 1-5

(b)

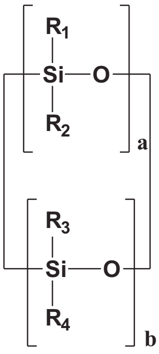


For a preferred resin j=2, k=0, l=1 and $R=R_2=CH_3$

Scheme G

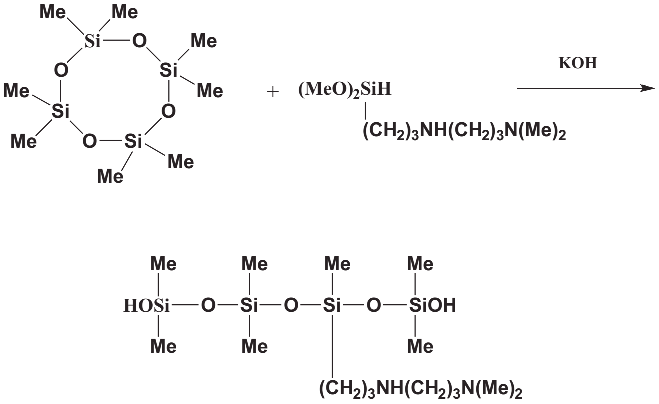
A direct hydrosilylation of poly(methylhydrogensiloxane) {$Me_3SiO[(Me)(H)SiO]_{40}SiMe_3$} and blocked amine *i.e.* 2-propylideneallylamine — ($Me_2C=NCH_2CH=CH_2$) was also employed for synthesis of polysiloxanes with 3-aminopropyl pendant moieties. This two-step process involves hydrosilylation in the presence of Speier's catalyst and subsequent acid hydrolysis of the formed siloxane with ketenimine moieties [37].

Finally, several aminosiloxane fluids containing aminoalkyl side groups were made *via* a ring opening copolymerization of cyclic siloxanes carrying aminoalkyl substituents and permethylated cyclic monomers such as octamethylcyclotetrasiloxane (D_4) (Scheme H) [38, 39] or copolymerization of D_4 with aminoalkyl(dimethoxy)methylsilane in the presence of strong bases such as NaOH and KOH (Scheme I) [40].



R_1 to R_3 are alkyl groups with 1-6 carbon atoms;
a and b have a value 1-10 and R_4 ia an aminoalkyl
group such as: $-(CH_2)_3NH_2$, $-(CH_2)_3NH(CH_2)_2NH_2$,
$-CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2$

Scheme H



Scheme I

APPLICATION OF AMINOSILICONES

Aminosilicones are widely used as softeners, especially for white fabrics [41]. They give excellent limp and surface smoothness to all types of fabrics. The strong adsorption silicone softeners on the surface of fabrics and their amphiphilic character largely increases durability of silicone softeners in washing processes. Molecular modelling have shown that aminoalkylsiloxanes are most efficient in the partially ionized states [8]. In acid conditions the amino group acquires cationic character ($\sim NH_3^+$) that leads to even stronger bonding to the fabrics [42—46].

Another important field of application is cosmetic industry. Aminosilicones were found to be very effective components of micro-emulsions used as hair conditioners and in a variety of personal care products [23, 46—48]. Polysiloxanes impart a smooth silky feel, easy combing characteristics, high gloss and antistatic properties to hair [49]. Among all the functionalized siloxane polymers, the amino-containing silicones were found to be the most effectively adsorbed on the hair's surface due to a strong polar interaction of the hair proteins with amino group. On a molecular level the softening properties of siloxanes are believed to come from flexibility of the siloxane backbone, and low surface free energy of the dimethylsiloxane segments [8].

Incorporation of aminoalkyl co-condensate siloxanes in emulsions used for water-repellent treatment of building materials improves wetting characteristic and durability of hydrophobizing products. They are especially effective as components of substantially non-silicatic materials comprising alkali metals or alkaline earth metals, preferably for mass hydrofobization of gypsum or gypsum plaster boards [21, 36]. A treatment of wood with siloxanes containing amino-functional groups increased water repellency [50] and showed also protective effectiveness against brown rot fungi [51].

Well defined aminoalkylsiloxanes — *e.g.* bis(aminopropyl)tetramethyldisiloxane found use as modifiers for polyimide semiconductor insulating films and as modifiers for polyamide, polyurethane and epoxy resins [18, 22, 24, 52]. Recently, aminoalkyl silicones were used as precursors for a preparation of new materials such as modified xerogel surfaces [53], large-pore ordered mesoporous silicas [28] and magnetic nanocomposites [54]. Reversible crosslinking of terminal aminopropyl siloxanes by simple triatomic molecules — CO_2 or CS_2 [7] opens up new areas of potential applications of these siloxanes *e.g.* as CO_2 capture media [55], cleaning agents in art conservation, where rheoreversibility and swelling by organic liquids are desirable attributes [56], packing polysiloxane materials for chromatography [57] and aligning media for NMR measurements [58].

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