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Amphiphilic sorbents based on polysiloxanes crosslinked by an *N*,*N*′-heterocycle

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New amphiphilic sorbents have been synthesized by crosslinking of the chloromethyl side-functionalized polysiloxanes with piperazine. Three structures, differing by the crosslinking degree, have been synthesized as potential sensitive materials for humidity sensors able to work at high humidity or as metal sorbents. Correlations between structure and morphology of the polymeric matrix, as well as their swelling capacity in solvents with different polarities, are discussed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: polysiloxanes; crosslinking; amphiphiles; swelling; piperazine

INTRODUCTION

The measurement and control of humidity are important in many areas, including industry (paper, food, electronic), domestic environments (air conditioning) and medicine (respiratory equipment).[1] Polymers,[2–4] polymer composites[5–7] and modified polymers[8] with hydrophilic properties have been used in humidity sensor devices. Polymer electrolytes containing hydrophilic groups such as —COOH, SO_3H or $-N^+R_3Cl$ are excellent materials for sensing low humidity but cannot operate at high humidity because of their solubility in water.[1] Such problems have been overcome by blending with a hydrophobic polymer, or by chemical modification of the hydrophobic polymers to generate ionic groups, resulting in materials sensitive to humidity. Crosslinkable polymers are also used to generate ionic sites, in the crosslinked state, for sensing humidity.[1]

The hydrophobic character of polysiloxanes is well known and commonly used in water repellency.[9] An approach to promoting water sorption into silicone rubber is mixing with hydrophilic compounds such as ethylene glycol, glycerin, polyethylene glycols and lactose.[10] Polysiloxanes may be also modified by the introduction of various hydrophilic functions to the attached organic radicals, which considerably affects their properties. The great flexibility of polysiloxane chains makes these functions easy accessible. Thus, quaternary ammonium salt (QAS) and hydroxyalkyl groups have been introduced in polysiloxanes of various topologies to confer hydrophilic properties.[9] Polysiloxanes containing a low proportion of highly hydrophilic groups have been proved to be very hygroscopic and strongly swell in water.[9] Crosslinked organopolysiloxane with hydrophilic groups such as NH_2, $N^+(CH_3)_3Cl$, SO_3H, OH have been grafted onto a pressed silica gel or a sintered alumina plate to make humidity sensors.[1]

In this paper, we report the acquisition of crosslinked structures by the reaction between polysiloxanes containing chloromethyl side groups and piperazine when the simultaneous formation of hydrophilic groups (ammonium salt) and crosslinking occurred.[2,9] The presence of the hydrophilic functions, the ionic ammonium salt and ionizable tertiary amine should lead to particularly strong water affinity due to the electrostatic and hydrogen bond forces.[9] Thus, it is expected that a completely water-insoluble polymer (polysiloxane) would be converted into a permanent, three-dimensional network capable of absorbing high proportions of water without passing into solution. Non-polar solvents also can be absorbed due to the hydrophobic siloxane matrix. It is also known that piperazine can form complexes with metal ions, and the development of a piperazine-based hydrogel with metal chelating properties has already been described.[11] Such polymeric material can be used to remove metal ions from polluted surface waters through complexation and ion-exchange mechanisms.[12,13]

EXPERIMENTAL

Materials

Chloromethylmethyldichlorosilane (b.p. = 121.5–122 °C, $d_4^{20} = 1.2858$), CMCl, supplied by ABCR GmbH & Co

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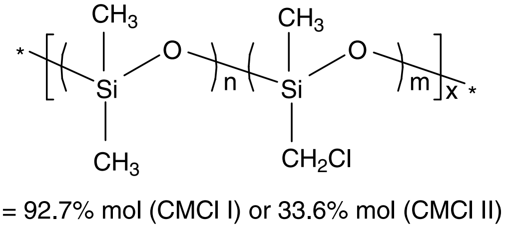
(Germany) was used as received. This is susceptible to hydrolysis in the presence of environmental humidity, releasing gaseous HCl.

Octamethylcyclotetrasiloxane (D_4) (purum, >98%; m.p. = 16–19 °C, b.p. = 175 °C/760 mmHg; $n_D^{20} = 1.3960$, $d_4^{20} = 0.955$) supplied by Fluka AG (Switzerland) was used as received. Piperazine anhydrous (1,4-diethylenediamine), PPA, was supplied by Fluka AG (Switzerland), m.p. = 106 °C. This is corrosive and causes burns.

α,ω-Trimethylsiloxy polymethylchloromethylsiloxane, MCl, was synthesized according to a modified procedure as described in Sauvet *et al.*[14] A 3.6 ml (0.2 mol) aliquot of water was slowly added to a stirred solution containing 16.35 g (0.1 mol) methylmethylchloromethyldichlorosilane and 0.2606 g (0.0024 mol) trimethylchlorosilane as endblocker in 40 ml diethylether. The reaction mixture was stirred for 4 h at room temperature, after which time the mixture was neutralized by repeated washing, first with a 5% $NaCO_3$ solution and then with water. The etheric solution was dried over $CaCl_2$. After filtration the solvent was removed. The yield was 70% (7.60g) polymer having an average number molecular mass, M_n (determined by GPC) of about 4000.

α,ω-Trimethylsiloxy-polydimethylmethylchloromethylsiloxane, CMCl (Scheme 1), with an average methylchloromethylsiloxane units content of 56% on the chain (determined by ^1H NMR spectrometry) and an M_n of about 30 000, was obtained by acid equilibration of MCl with octamethylcyclotetrasiloxane.[15] A cation-exchanger, Purolite CT-175 was used as a catalyst (2.5 wt% reported for the reaction mixture). The equilibration was performed at 90 °C for 10 h, after which time the catalyst was removed by filtration. The reaction mixture was devolatilized by heating at 150 °C/5 mmHg. A viscous, slow, opaque oil was obtained. Two fractions were extracted from the above copolymer by precipitation with methanol from toluene solution: fractions I and II with 92.7% mol (CMCl I) and 33.6% mol (CMCl II) methyl(chloromethyl)siloxane units, respectively. The copolymer fraction compositions were estimated by ^1H NMR spectra based on the ratio between the signals assigned to protons from dimethyl (0.1 ppm) and chloromethylsiloxane (2.7 ppm) units, respectively.

A sample of crosslinked polydimethylsiloxane (c-PDMS) was prepared using a polydimethylsiloxane α,ω-diol with molar mass of about 70 000 and methyl-triacetoxysilane as a crosslinker. The crosslinking occurred[16] at room temperature under the influence of environmental humidity.



m = 92.7% mol (CMCl I) or 33.6% mol (CMCl II)

Scheme 1.

Techniques

^1H NMR spectra were recorded on a JEOL C-60 HL spectrometer using $CDC1_3$ as a solvent, and chemical shifts were obtained relative to signal assigned for residual $CHC1_3$. IR spectra were run on a Specord M80 Carl Zeiss Jena Spectrometer using the KBr pellet technique. Gel permeation chromatographic analysis (GPC) was carried out on a PL-EMD 950 Evaporative Mass Detector instrument using $CHCl_3$ as eluant after calibration with standard polystyrene samples.

Scanning electron microscopy, SEM, images on films (with thickness <100 nm, estimated by SEM in film fracture) deposited on Al supports and coated with Au were recorded with a Tesla BS 301 SEM at 25 kV and a magnification of 2300–2600.

Contact angle measurement

Static water-drop contact angles were measured using the tangent method on a home-made goniometer. The equipment consists of a horizontal stage for the sample, a source of illumination, and a telescope equipped with a goniometer eyepiece. The multiplication power of the assembly is in the range 50–100×. Measurements were performed at room temperature using the water sessile drops on the surfaces cast from reaction mixture solutions by solvent evaporation, followed by extraction with water and chloroform and draying in a vacuum. Double-distilled water was used as liquid for measurement. The water drops were produced with a Hamilton syringe of 1 μL. The measurements were repeated at least four times on different parts of the film sample.

Procedure

Crosslinking

The chloromethyl side-functionalized polysiloxane, CMCl, and piperazine, PPA, in a pre-established molar ratio (related to the functional groups) according to Table 1, were together dissolved in a $DMF/CHCl_3$ 1 : 1 mixture for a solution of about 5 wt% vol. The reaction mixture was stirred in a nitrogen atmosphere for about 20 h at 70 °C. Then the solvents were removed by vacuum in a rotavapor. The remaining solid material was extracted, first with water and then with chloroform by immersion for 24 h, each time followed by drying in vacuum at 50 °C and maintaining on P_2O_5, and weighed in order to determine the soluble fraction content. The insoluble fractions were analyzed by IR, SEM and contact angle measurements. All crosslinked products were light, brittle, white-opaque foils.

Swelling experiments

Crosslinked samples previously dried in vacuum at 50 °C and maintained on P_2O_5 for one week were used in order to determine, by gravimetry, the swelling capacity in two solvents: water and chloroform. For this, each sample was soaked for 24 h in solvent, then taken out, tapped with filter

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Table 1. Some synthesis and analytical data of the synthesized networks

Sample	Siloxane reactant	Feed ratio of the functional groups (−Cl : NH−)	Main parameters[a] of the crosslinked structures (%)[b] h	k	l	n	Soluble fraction[c] (wt%)
PPAS1	CMCl II	0.5 : 1	8.6	18.9	0	72.5	69.3
PPAS2	CMCl II	1 : 1	24.7	0	2.0	73.3	53.4
PPAS3	CMCl I	1 : 1	76.8	0	5.4	17.8	46.1

[a] According to Scheme 2.

[b] Estimated on the basis of the found chloro and nitrogen contents in the extracted network.

[c] Soluble fraction that is lost during purification process by extraction in water and chloroform. This fraction contains unreacted piperazine and uncrosslinked polysiloxanes (original or partially modified polysiloxanes).

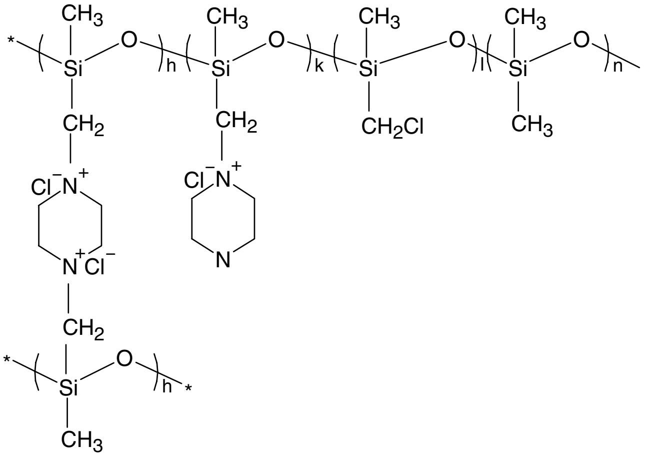
paper to remove the excess surface solvent, and weighed. The gels were dried to a constant weight as above was described. The dry weight values were used to determine the weight-swelling ratio (W) defined as: $W =$ (wet weight − dry weight)/dry weight.[11] All experiments were carried out with three samples and average values were considered.

RESULTS AND DISCUSSIONS

Synthesis

Side-chloromethyl functionalized polysiloxanes were reacted with piperazine, resulting in ionic crosslinked structures of the type presented in Scheme 2. To our knowledge, no similar structures with piperazine have been reported until now. The same types of oligo[dimethyl(chloromethyl)siloxane]s were reacted with 4,4′-bipyridyl leading to water-soluble or crosslinked polymers (depending on the ratio between the two reactants) able to interact with divalent metal chlorides.[17] The reaction of the halo-alkyl groups with amine had already been used in the surface modification of the silica gel.[18]

Two polysiloxanes differing in the chloromethyl groups content and two ratios between functional (chloro and amine) groups were used in this work (Table 1). Reactions occurred in solution using a DMF–$CHCl_3$ solvent mixture in 1 : 1 volume ratio. Piperazine acts as a nucleophile forming ammonium salt with chloromethyl groups side-attached to polysiloxane chains.



Scheme 2. The synthesized crosslinked structures.

A modification of the IR spectra, as compared with that of the starting linear chloromethyl-functionalized polysiloxane, can be observed as a result of the reaction (Fig. 1). Thus, in the IR spectra of PPAS2 the band at 1180 cm^{-1} from chloro-alkyl functionalized polysiloxane, as well as the bands at

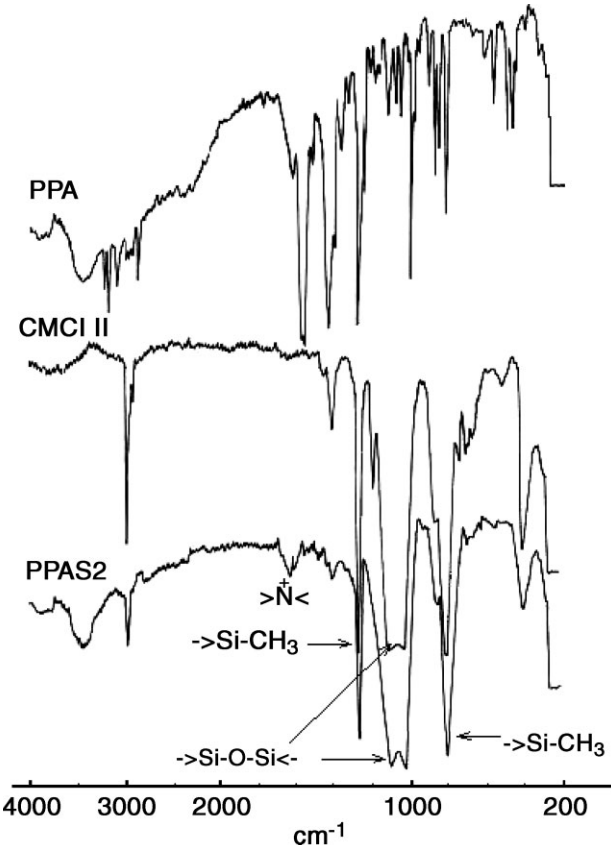


Figure 1. IR spectrum of a crosslinked structure (PPAS2) in comparison with those of the starting reactants.

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1560 and 1430 cm^{-1} from piperazine disappeared and a new band appears in the product at 1650 cm^{-1} as a result of the ammonium salt formation.

Because the piperazine is bifunctional, crosslinked structures having estimated crosslinking degrees of 24.7 for PPAS2 and 76.8 for PPAS3 (Table 1) are formed when the stoichiometric ratio of reacting groups is used. By using an excess of amine groups, a soluble product is expected to result. However, in the case of PPAS1, a network with a crosslinking degree of about 8.6 was also formed, although in low yield (34.8%). The crosslinking degrees are expressed as molar percentages of groups in which the piperazine links two chains by chloro methyl groups (h in Scheme 2) were calculated on the basis of elemental anlaysis (chloro and nitrogen).

Swelling experiments

Since the proposed crosslinked systems have been developed for use for humidity sensors or to remove toxic metal ions from aqueous solutions, their swelling behaviors in distilled water were investigated. For comparison, the uptake ability of a nonpolar solvent such as chloroform was also determined. The swelling behavior of the hybrid networks was established by measuring the increase in mass due to solvent uptake, relative to the mass of the dry extracted network (Table 2).

The swelling behavior of a polymer network depends on a number of factors, like hydrophilic/hydrophobic balance in the network, the presence of ionic or ionizable groups in the polymeric segments and the crosslinking extent of the network.[12,19] A polymer capable of absorbing high proportions of water without passing into solution is considered as a hydrogel. This implies that the polymers used in these materials must have hydrophilic character. Generally, it is commonly to use synthetic polymers that are water-soluble when they are in non-crosslinked form. A completely water-insoluble polymer, namely polysiloxane, is converted into a gel, this time by crosslinking with water-soluble piperazine. Therefore, differently from the classical gels where the amount of water absorbed decreases as crosslinking degree increasing, an inverse dependence is visible in this case. Thus, it can be observed that a highly crosslinked sample, (Table 1, PPAS3 based on a high functionalized polysiloxane precursor, CMCl I), has a higher uptake ability, both in polar and nonpolar solvents. This is different from the crosslinked pure PDMS, which has a negligible water sorption capacity but absorbs chloroform in high amounts. Such behavior is due to the fact that the crosslinker is a hydrophilic that favors the water sorption. In addition, the presence of highly flexible siloxane between crosslinking points permits mobility or relaxation of macromolecular chains in the matrix, providing enough space for accommodation of water molecules in the network.[12] Therefore, the synthesized networks have high weight-swelling ratios both in polar (water) and in nonpolar (chloroform) solvents: 2.38–8.14 and 6.64–9.81, respectively. For comparison, networks based on the polybutadiene–polydiethylsiloxane copolymers crosslinked by siloxane bonds have swelling capacities in toluene in the range 3.1–13.00, depending on the copolymer composition.[20]

Table 2. Equilibrium swelling of crosslinked structures in different solvents

	W (weight-swelling ratio)[a]		
Sample	Water	Chloroform	Contact angle
PPAS1	2.38	6.64	103
PPAS2	5.94	8.40	93
PPAS3	8.14	9.81	96.4
c-PDMS	0.015	11.56	109

[a] After 1 day immersion in a solvent at room temperature, calculated with relationship: $W = (\text{wet weight} - \text{dry weight})/\text{dry weight}$.[11]

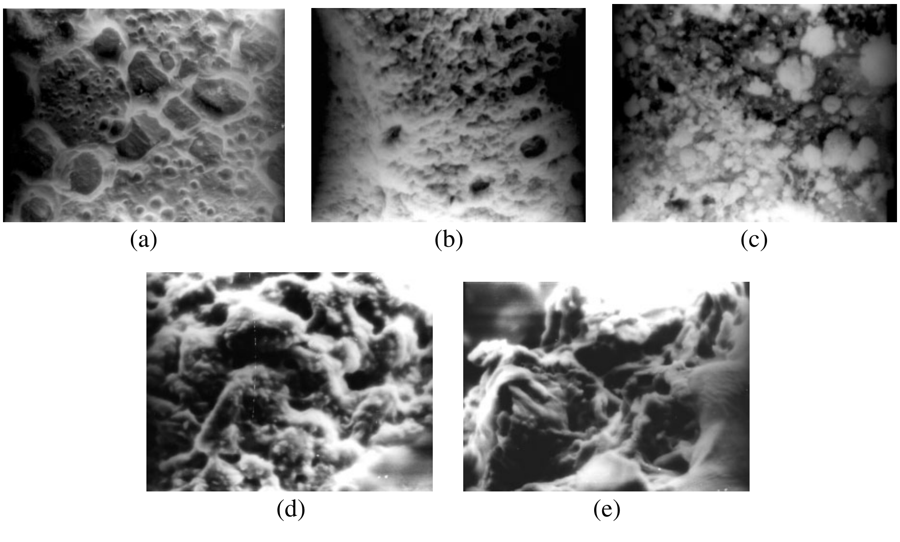
(a) (b) (c)
(d) (e)

Figure 2. Scanning electron micrographs of the thin films deposed on Al supports and coated with Au: (a) extracted PPAS1 (×2600); (b) extracted PPAS2 (×2500); (c) extracted PPAS3 (×2600); (d) unextracted PPAS1 (×2300); (e) unextracted PPAS2 (×2300).

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Scanning electron microscopy was used to analyze the supramolecular aggregation of the compounds. In Fig. 2 are shown the electron micrographs obtained by investigation with secondary electrons of the film topography for all crosslinked polysiloxane types. Globular microdomains with diameters in the hundreds of nanometers range, disposed into intergranular matrices, are visible on the film surfaces in all cases, differing by packing densities (in dependence on the crosslinking degree). The images are clearer in the samples extracted in water and chloroform [Fig. 2(a–c)] compared with those unextracted [Fig. 2(d,e)]. Thus, in the case of extracted PPAS1 having a reduced crosslinked degree (8.6%), zones with cavities are visible on the surface, limited by unstructured material [Fig. 2(a)]. The globular aggregates can be distinguished in the cavities. The extracted PPAS2 presents compact zones having superficial pores, beside the corpuscular formation [Fig. 2(b)]. The same topographic aspects can also be observed in the case of PPAS3 [Fig. 2(c)], but the pore densities on the surface are lower and the dispersity of the globular formation dimension is very large. These microscopic observations can be explained by segregation of the piperazine moieties into polar microdomains. The hydrophobic polysiloxane matrix facilitates the phase segregation of the piperazine by secondary intermolecular interactions.[19]

The high measured values for the contact angles (Table 2) are due to the presence of siloxane on the surface. The low surface energy of the siloxanes provides a thermodynamic driving force for their migration to the polymer-air or vacuum interface.[21] However, all samples exhibited surfaces with slight lower contact angles as compared with a pure PDMS crosslinked with methyltriacetoxysilane. Further, an analysis of the contact angle values suggests that the different crosslinking degrees result in surfaces of different hydrophilicity. The increased values for the contact angle in the case of PPAS1 with high content in hydrophilic component is assigned to the low crosslinking degree, which facilitates phase segregation and confers freedom of movement for polysiloxane moieties, which will migrate to the surface.[21]

CONCLUSION

Polisiloxanes having chloroalkyl side groups were crosslinked with piperazine. As a result of the reaction, ionic groups were formed in networks that conferred the ability to behave like hydrogels, which led to uptakes of 238–814% water. It has been emphasized that, with increasing crosslinking degree, water swelling capacity increases due to the polar nature of the crosslinks. This was also correlated with the morphology of the networks and their surface hydrophilicity.

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