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Graphical Abstract for:

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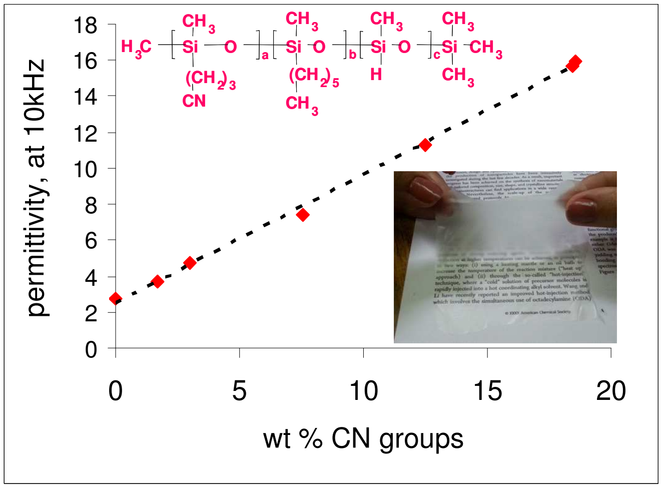

Polysiloxanes were modified by (co-)hydrosilylation with γ-cyanopropyl and hexyl groups, to finely tune their composition and properties, especially dielectric permittivity, as a way towards active component in dielectric elastomer transducers. Un-modified Si-H groups can be further used to obtain cross-linked thin films.

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ARTICLE TYPE

Chemical modification of polysiloxanes with polar pendant groups by co-hydrosilylation

Carmen Racles*[a], Mihaela Alexandru[a], Adrian Bele[a], Valentina Musteata[a], Maria Cazacu[a], and Dorina M. Opris*[b]

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New polymers with tuneable dielectric properties were prepared by modifying trimethylsilyl end-terminated poly(methylhydro)siloxane with polar γ-cyanopropyl groups. The amount of polar groups was tuned by adjusting the allyl cyanide / n-hexene ratio in poly(methylhydro)siloxane *co*-hydrosilylation. The copolymers were characterized by FTIR and NMR spectroscopy. The distribution of the polar groups along the chain was evaluated based on ^{1}H NMR spectroscopy. The influence of the amount of polar γ-cyanopropyl on the glass transition temperature (T_g) and on the dielectric properties was investigated by DSC and impedance spectrometry. All polymers showed T_gs well below room temperature. A linear increase in permittivity (ε') with increasing the amount of γ-cyanopropyl groups was observed. A maximum ε' value of 15.9 for the copolymer containing 89 mol% polar groups was achieved, which is 6-fold higher than polydimethylsiloxane. The incomplete conversion of Si-H groups observed in all hydrosilylation reactions with allyl cyanide opened up the possibility of using the prepared copolymers as cross-linkers.

Introduction

Dielectric elastomer actuators (DEA) are stretchable capacitors that respond to an electric field by changing their size and convert electrical energy directly into mechanical work.[1] Due to their large achievable strain and stress, high power density, as well as excellent electromechanical coupling at a certain electric field, large varieties of applications were proposed and explored.[1] Unfortunately despite of their considerable potential, some applications of DEA are still hindered by the large driving voltage required for actuation. Since their performance is directly influenced by the stiffness of the dielectricum (elastic moduli (Y)) and its ε', scientists try to develop new elastomers with high ε' and low Y.[2] To achieve materials with increased ε' different paths were followed which include: blending the polymeric matrix with metal oxides, ceramics,[3-7] or conductive fillers[8-10] or chemical modification.[11-15]

One class of materials of high interest for DEA applications are silicone elastomers since they have large strain at break,[16,17] are resistant to oxygen, water and sunlight,[18] and are biocompatible.[19,20] But probably the most attractive properties of silicones for DEA are their good elastic properties over a wide range of temperatures and frequencies.[21] Additionally, silicones have very high dielectric strength of more than 80 V/μm[22, 23] and high energy density.[24] However, the use of silicones in some DEA products is limited by the high driving voltage necessary for actuation mainly due to their ε' which is lower than 3. Therefore, much research is presently being devoted to increase their ε' while maintaining the electrical conductivity and the Y at low values. Modification of silicones with functional side groups is one approach that was recently explored.[13,14,25] Although countless side-chain modified polysiloxanes are reported, only a few were especially designed for actuator applications.[13,25]

Hydrosilylation is a powerful tool for the modification of siloxane compounds.[26,27] However, its application can be sometimes problematic due to catalyst's sensitivity. For example, we recently used allyl cyanide for hydrosilylation of hydroxyl end-functionalised poly(dimethyl-*co*-methyhydro)siloxanes and found that the conversion of the hydrosilyl (Si-H) groups to cyanopropyl was incomplete even when a large excess of allyl cyanide was used.[14] Additionally, a spontaneous self-cross-linking of the starting materials as well as of the functionalised product was observed when stored in a non-protected atmosphere for a long time.

Therefore, the first goal of this work was to clarify some aspects of (*co*-)hydrosilylation reaction with allyl cyanide and platinum divinyltetramethyldisiloxane complex (Pt(dvs)) catalyst and to verify whether the hydroxyl end-groups are responsible for the spontaneous cross-linking reactions mentioned above. The second goal was to find out how the ε' is influenced by the amount of cyanopropyl groups and which is the maximum value of the ε' which can be reached with this system. To achieve such goals, a trimethylsilyl end-terminated poly(methylhydro)siloxane, which by structure carries a Si-H group on every repeat unit, was used in hydrosilylation reactions. To obtain polymers with different content of polar cyanopropyl groups, a mixture of allyl cyanide and n-hexene was used, whereby their proportion was varied. To find out how the cyanopropyl groups are distributed on the polymer chain, the ^{1}H NMR spectra of the resulting copolymers were carefully analysed.

Experimental

Materials and Methods

The following reagents were used as received: trimethylsilyl-terminated poly(methylhydro)siloxane (ca. 1900 g/mol) from Alfa Aesar, allyl cyanide, n-hexene, and Pt(dvs) solution in xylene (Karstedt catalyst) from Sigma-Aldrich. Toluene was stored over molecular sieves and distilled from sodium wire.

The infrared spectra were recorded on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 300-4000 cm^{-1} range (resolution 2 cm^{-1}, 32 scans) at ambient temperature. ^{1}H NMR spectra were recorded on 400 MHz Bruker spectrometer in $CDCl_3$. Differential scanning calorimetry (DSC) investigations were done on a Pyris Diamond DSC (Perkin Elmer USA) instrument. The sorption capacity of water vapours was measured in dynamic regime at 25 ^{o}C (298 K) by using an IGAsorp equipment (Hiden Analytical, Warrington UK) at different relative humidity (RH). The vapour pressure was increased and decreased in 10% RH steps between 0 and 90% for sorption and reverse for desorption, each having a pre-established equilibrium time of 15 and 30 min, respectively. The complex dielectric permittivity was measured using Novocontrol Dielectric Spectrometer Concept 40 Alpha Analyzer equipped with a Quatro temperature controller. Measurements were carried out at frequencies between 1 and 10^6 Hz at room temperature. For the temperature dependence experiment, frequency scans were performed in 5 ºC steps, in temperature range from – 150 to + 60 ºC. The liquid polymers were placed between two golden plated stainless steel electrodes (diameter 20 mm) and the distance between electrodes was adjusted to 140 μm using spacers.

Hydrosilylation of poly(methylhydro)siloxane

The hydrosilylation reactions were carried out in a multireactor, in order to maintain the same reaction conditions for 6 experiments, i.e. 70 ^{o}C, 90 rpm, 6 h. Prior to the synthesis, all the glass pieces were carefully dried in an oven at 120 ^{o}C. For feed ratios, final compositions and molecular weights please see Table 1.

As an example, the procedure for copolymer B3 is described. Poly(methylhydro)siloxane (5 g), allyl cyanide (4.24 g, 5.05 mL, 63.3 mmol) and n-hexene (1.78 g, 2.6 mL, 21 mmol), i.e. a total of 1.1 mol un-saturated reagents per mol of Si-H, were dissolved in dry toluene (10 mL). To the resulting solution, Karstedt's catalyst (0.4 mL, i.e. 5.2 μL per mmol of Si-H) was added and the reaction mixture was stirred at 70 °C for 6 h. Then the solvent and un-reacted reagents were removed by rotary evaporation.

^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 0.17(Si-CH_3, 116 H); 0.57(CH_3-$(CH_2)_4$-$C\underline{H}_2$-Si, 17H); 0.76 (NC-CH_2-CH_2-$C\underline{H}_2$-Si, 38 H); 0.93($C\underline{H}_3$-$(CH_2)_4$-CH_2-Si, 26 H); 1.35 CH_3-$(C\underline{H}_2)_4$-CH_2-Si, 68 H); 1.75 (NC-CH_2-$C\underline{H}_2$-CH_2, 41 H); 2.43 (NC-$C\underline{H}_2$-CH_2-CH_2, 42 H); 4.75 (un-reacted Si-H, 3.5H).

^{13}C NMR (400MHz, $CDCl_3$) δ, ppm: -0.63 ($\underline{C}H_3$)-Si; -0.35 $\underline{C}H_3$-Si(CH_2-CH_2-CH_2-CN); 1.89($\underline{C}H_3$-Si$(CH_2)_5$-CH_3); 14.14 Si-$(CH_2)_5$-$\underline{C}H_3$; 16.84 Si-$\underline{C}H_2$-CH_2-CH_2-CN; 17.55 Si-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2-CH_3; 19.70 Si-CH_2-$\underline{C}H_2$-CH_2-CN; 20.41 Si-CH_2-CH_2-$\underline{C}H_2$-CN; 22.62 Si-CH_2-CH_2-CH_2-CH_2-$\underline{C}H_2$-CH_3; 22.98 Si-CH_2-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_3; 31.61 Si-CH_2-CH_2-$\underline{C}H_2$-CH_2-CH_2-CH_3; 33.00 Si-CH_2-CH_2-CH_2-$\underline{C}H_2$-CH_2-CH_3; 119.55 Si-CH_2- CH_2- CH_2-$\underline{C}$N.

The ^{1}H NMR and ^{13}C NMR spectra are presented in Figures 1S and 2S (Supporting Information).

In the case of copolymers B4-B6 an exothermic reaction was observed when the catalyst was introduced and therefore the reaction vessel was cooled in an iced bath within the first few minutes then mounted in the multireactor.

For copolymer B7, only n-hexene was used and therefore the procedure was slightly modified. The reaction was done in a two-neck vessel, equipped with condenser and magnetic stirring. After slow addition of the catalyst, the reaction mixture was kept at room temperature until no exothermic effect was observed. The reaction was continued for 6 h at 70 °C. The solvent and the un-reacted n-hexene were removed by rotary evaporation.

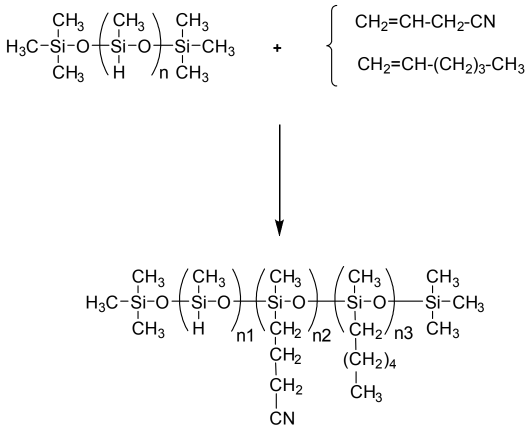
^{1}H NMR (400MHz, $CDCl_3$) δ, ppm: 0.02-0.09 (Si-CH_3, 116 H); 0.50 (CH_3-$(CH_2)_4$-$C\underline{H}_2$-Si, 65H); 0.93 ($C\underline{H}_3$-$(CH_2)_4$-CH_2-Si, 98 H); 1.3 CH_3-$(C\underline{H}_2)_4$-CH_2-Si, 260 H); 4.70 (un-reacted Si-H, 0.14H).

Results and Discussion

Trimethylsilyl end-terminated siloxane copolymers containing different amounts of polar cyanopropyl pendant groups were prepared by *co*-hydrosilylation reactions of a commercial trimethylsilyl-terminated poly(methylhydro)siloxane with allyl cyanide and n-hexene (Scheme 1). The molecular weight of the starting polymer M_n = 2122 g/mol was calculated from ^{1}H NMR spectrum (Figure 1S) and found to be slightly higher than indicated by the producer (M_n ca. 1900 g/mol). While allyl cyanide allowed us introducing polar side groups to the silicone chain, n-hexene was used to ensure the same overall conversion of the Si-H groups. For most of the reactions, the alkene/Si-H stoichiometry was maintained 1.1, except for polymer B1 where the proportion of allyl cyanide to Si-H was increased to 2, to force the reaction towards 100% conversion. Additionally, a model homopolymer containing only hexyl groups (B7) was also synthesized.

In FT-IR spectra (Figure 3S) the main absorption bands were assigned to: siloxane bonds at 1022-1093 cm^{-1} (Si-O-Si asymmetric stretch, typical pattern for polymers), γ Si-CH_3 at

743 and 801 cm^{-1}, δ Si-CH$_3$ at 1261 cm^{-1}, un-reacted Si-H bonds at 2157 cm^{-1}, and CN groups at 2247 cm^{-1}.



[B1-B7]

Scheme 1. Synthesis of copolymers B1-B7 by hydrosilylation with allyl cyanide/n-hexene.

^{1}H NMR spectrum of copolymer B3 is given in Figure 1 and the calculation of the composition is given in Figure 1S. Table 1 summarizes the composition of all copolymers. Although an excess of allyl cyanide was used, the conversion of Si-H groups was in all cases around 90%.

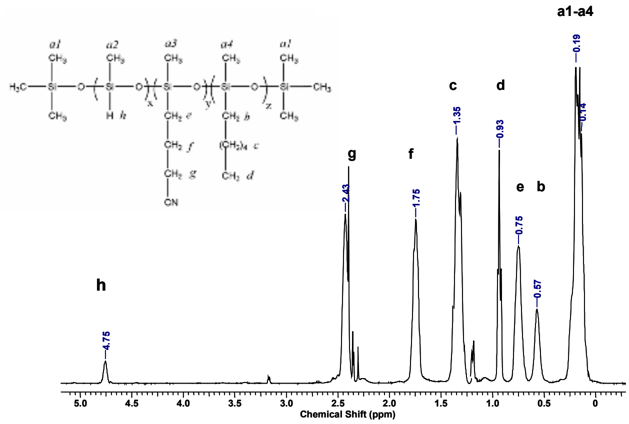


Figure 1. ^{1}H NMR spectrum of copolymer B3.

Due to the electron withdrawing cyano group, allyl cyanide is less reactive then n-hexene in hydrosilylation. An exothermic reaction was observed when the proportion between n-hexene and allyl cyanide was increased, i.e. in reactions B4-B7. Therefore, the hexyl group content found by ^{1}H NMR was very close to the prescribed one or even higher in B3 and B4 (Table 1). Only in B6, the hexyl content was lower than prescribed (82.9% instead of 87.5%). This might be due to evaporation of n-hexene due to the above mentioned exothermic reaction, despite the precautions taken as to cool the reaction mixture in an iced bath. For copolymer B7 the conversion was 99.6% and the ^{1}H NMR and FT-IR spectra showed little residual Si-H groups.

The polar group content was in all cases lower than expected (Table 1). Since the amount of hexyl groups is close to that prescribed, the incomplete overall conversion for the hydrosilylation is due to lower reactivity of allyl cyanide.

Table 1. Composition of copolymers in B series, calculated by ^{1}H NMR

Entry	C_4H_5N [% mol] (feed)[a]	C_6H_{12} [% mol] (feed)	Conversion [%][b]	M_n calculated [g/mol]
B1	87.8 (200)	-	87.8	4050
B2	89 (110)	.	89	4070
B3	62.1 (82.5)	26.9 (27.5)	89	4220
B4	38.8 (55)	51.1 (55)	89.9	4380
B5	16 (27.5)	74 (82.5)	90	4505
B6	9.2 (13.2)	82.9 (96.8)	92.1	4620
B7	-	99.6 (110)	99.6	4860

[a] The feed amounts were calculated as 10% (mol) excess reported to prescribed composition, except for polymer B1 (see text)

[b] Total conversion for hydrosilylation

A precise assignment of the 0-0.4 ppm region of the ^{1}H NMR spectra is challenging (Figure 2). Four types of methylsilyl protons are present in this region: the $(CH_3)_3Si$ chain ends (E), the Si(hexyl)C$\underline{H_3}$ non-polar groups (D^N), the Si(cyanopropyl)C$\underline{H_3}$ polar groups (D^P) and the un-reacted methylhydrosiloxane units (D^H). The assignments of triad sequences in series B as well as of the starting homo-polymer are given in Table 2. A straightforward assignment can be done only in the case of B7, where practically all Si-H groups were replaced by non-polar hexyl groups, which determined important modifications in the chemical shifts as compared to the starting homopolymer, i.e. 0.13 $(CH_3)_3Si$ chain ends (E), 0.08 Si(hexyl)C$\underline{H_3}$ (D^N) groups and 0.06 D^N in the middle of the chain.

In the other spectra of copolymers the Si(cyanopropyl)C$\underline{H_3}$ polar groups (D^P) are located between 0.16 and 0.25 ppm, with a maximum at 0.19 ppm in B1 polymer (for which full functionalisation with allyl cyanide was intended). In the low field region, the methyl protons of the un-reacted methylhydrosiloxane units (around 10%) are also present, but a precise assignment of the signals is rather difficult. In copolymers B3-B6, in addition to methyl groups from D^H units, new signals due to the D^P and D^N are present which makes the interpretation even more challenging. It is reasonable to assume that the methyl groups in polar units would be located at lower field, while those in nonpolar units at higher field. This trend is clearly observed in Figure 2.

Table 2. ^{1}H NMR chemical shifts and assignments

Polymer	Peaks (δ, ppm) and sequences						
Homopolymer	0.25 $D^HD^HD^H$	0.20 D^HD^HE	0.17 E				
B1	0.25 $D^PD^HD^P$	0.23 $D^HD^PD^P$	0.19 $D^PD^PD^P$	0.16 D^PD^PE	0.15 E		
B3	0.25 -0.23 (sh) $D^PD^HD^P$, $D^PD^HD^N$, $D^ND^PD^H$		0.19 $D^PD^PD^P$	0.17 $D^PD^PD^N$,$D^ND^PD^N$	0.15 $D^PD^ND^P$, $D^PD^ND^N$	0.14 D^ND^ND, E	
B4		~0.23- 0.18 $D^PD^HD^P$, $D^PD^HD^N$, $D^ND^PD^H$		0.16 $D^PD^PD^P$	0.15-0.14 $D^PD^ND^P$, $D^PD^ND^N$, $D^PD^PD^N$, $D^ND^PD^N$	0.11; 0.07 $D^ND^ND^N$	0.09 E
B5		0.21 $D^PD^HD^P$	0.19 $D^PD^HD^N$, $D^ND^PD^H$	0.17 $D^PD^PD^P$	0.14 $D^PD^ND^P$ $D^PD^PD^N$, $D^ND^PD^N$	0.12-0.11 $D^PD^ND^N$, E	0.09; 0.07 $D^ND^ND^N$
B6		0.21 $D^PD^HD^P$	0.18 $D^PD^HD^N$, $D^ND^PD^H$	0.16 $D^PD^PD^P$	0.13 $D^PD^ND^P$ $D^PD^PD^N$, $D^ND^PD^N$	0.12-0.11 $D^PD^ND^N$, E	0.09; 0.07 $D^ND^ND^N$
B7						0.09 E	0.04; 0.02 $D^ND^ND^N$

The proportion of protons of the methyl groups from most polar triads $D^PD^PD^P$ (located at 0.19 ppm in B3 and at 0.16 ppm in the other samples) to that of the total number of CH_3 protons in the polar units was around 60% in all copolymers. On the other hand, the proportion of the methyl groups in nonpolar triads $D^ND^ND^N$ (generaly at 0.11 ppm and at 0.09 ppm in B3) to the total number of CH_3 protons gave variable results. The nonpolar groups in nonpolar triads were around 35% for B3 and B4, and about 65% for B5 and B6 copolymers

To explain this trend, a model hydrosilylation reaction of a poly(dimethyl-*co*-methylhydro)siloxane was done according to Racles et al.[14] Figure 4S shows the ^{1}H NMR spectra of a poly(dimethyl-*co*-methylcyanopropyl)siloxane and the corresponding starting poly(dimethyl-*co*-methylhydro)siloxane. The assignments of chemical shifts for methylsiloxy groups in the initial copolymer (calibrated at 7.30 ppm for $CHCl_3$) were as follows (ppm) (Figure 4Sa and 4Sd top): 0.09 $(CH_3)_3Si$; 0.12 $(CH_3)_2Si$ in $D\underline{D}D$, 0.14 $D\underline{D}D^H$ and $D^H\underline{D}D^H$; 0.16 $(CH_3)SiH$ in $D\underline{D^H}D$; 0.19 $D\underline{D^H}D^H$; 0.21 $D^H\underline{D^H}D^H$. In the spectrum of the cyanopropyl modified copolymer (Figure 4Sb and 4Sd bottom), all the protons in D^H centered triads disappeared and a new peak appeared at 0.135 ppm due to addition of allyl cyanide. The less reactive D centered triads remained. The same trend can be observed in the region of the Si-H protons (Figure 4S-c). The most polar protons (at 4.74 ppm) disappeared, while the Si-H protons in the vicinity of D units were un-reacted (less polar, at 4.73 and 4.70 ppm). Thus, it can be concluded that the most polar Si-H groups are consumed in the hydrosilylation reaction while the less reactive Si-H groups which are isolated between two dimethylsiloxy units (DD^HD) remained unmodified. This is in agreement with previous studies which show that neighbor Si-H groups are more reactive.[27]

Coming back to the series B copolymers, we concluded that, due to the higher reactivity of n-hexene as compared to allyl cyanide, n-hexene is less selective than allyl cyanide and therefore occupies random positions on the polysiloxane chain. Allyl cyanide prefers the more reactive Si-H neighbour positions, increasing the tendency to form short polar segments. Therefore, the proportion of nonpolar short segments is reduced in copolymers containing more cyano groups.

Additional experiments were carried out, where the alkene reagents were added stepwise. Partial hydrosilylation of poly(methylhydro)siloxane with allyl cyanide or n-hexene (0.55 mol alkene to 1 mol Si-H) allowed formation of B8a and B9a, respectively. These copolymers were subsequently reacted with the complementary alkene co-reagent to afford copolymers B8 and B9. The ^{1}H NMR spectra of the partially hydrosilylated copolymers B8a and B9a are shown in Figure 3. When allyl cyanide was used first (B8a) most of the methyl protons from D^P units were in polar triades $D^PD^PD^P$, while when n-hexene was used first (B9a), only half of the methyl protons in D^N units were in nonpolar triades $D^ND^ND^N$. This shows the tendency of allyl cyanide to occupy vicinal positions and the more random addition of the more reactive n-hexene. It should be also mentioned here that the second hydrosilylation step done to obtain B8 was slow, e.g. 5 h after the n-hexene was added only around 10% was consumed. When additional catalyst was added, total conversion of Si-H groups was achieved. The low conversion of the n-hexene in the second step might be due to the catalyst poisoning by allyl cyanide. For the synthesis of B9 the addition of allyl cyanide in the second step afforded about 87% overall conversion of Si-H groups after 5 h.

Thus, the NMR data point towards a tendency of allyl cyanide to form short polar blocks, which is favoured by the presence of Si-H vicinal groups. However, the high reactivity and low selectivity of the n-hexene "limits" the length of the polar blocks where a mixture of alkene is used (B3-B6).

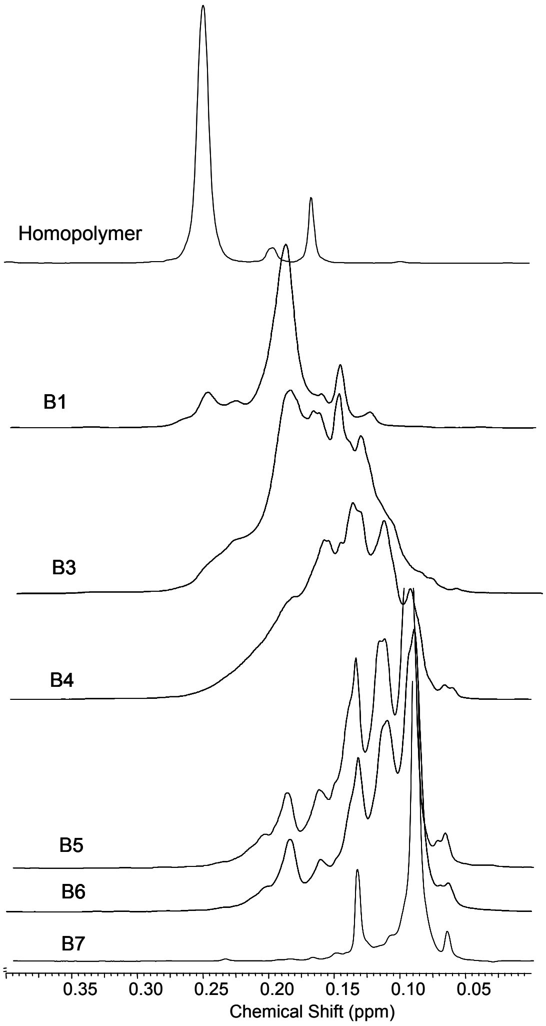


Figure 2. ^{1}H NMR spectra (0-0.4 ppm region) of the copolymers

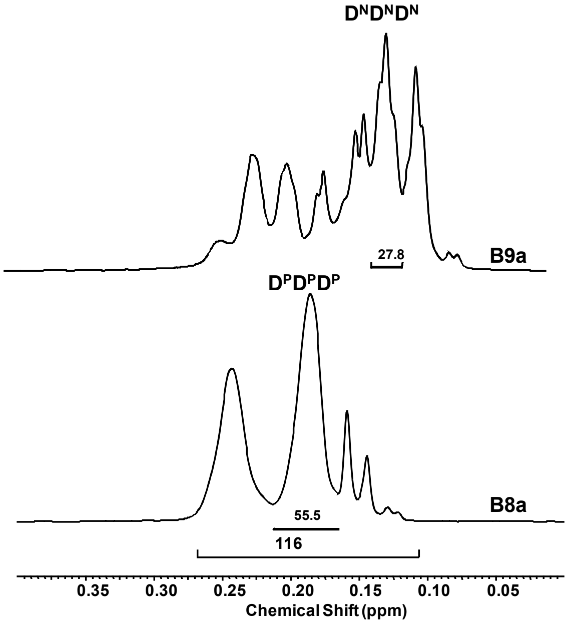


Figure 3. ^{1}H NMR of intermediary copolymers obtained by reacting 55% of Si-H groups in poly(methylhydrosiloxane) with either allyl cyanide (B8a) or n-hexene (B9a).

For the hydrosilylation several factors proved to have an influence on the kinetics and on the final composition of the copolymers. For example, when allyl cyanide was used either alone or in combination with n-hexene, incomplete hydrosilylation was observed. The incomplete conversion in hydrosilylation was reported before[28] and discussed in relation with different reactivity of vicinal and isolated Si-H groups. In our case, attempts to increase the conversion by using excess of allyl cyanide (50%) or more catalyst (25 μL per mmol Si-H) and longer reaction time (24 h) were not successful, the ^{1}H NMR spectrum still showed about 2.3% un-reacted Si-H groups.

General characterization of the copolymers

Due to the polarity of cyanopropyl groups, water absorption might be favoured for these polymers. To verify this, dynamic water vapour sorption (DVS) analysis was conducted. An increase in water vapour sorption capacity with increasing the polar group content was observed (Figure 4). However, the maximum sorption capacity was around 1 %, for a polymer with 87 mol% polar groups, which is rather low. It should be mentioned that this value was obtained after keeping the sample at relative humidity of over 80%.

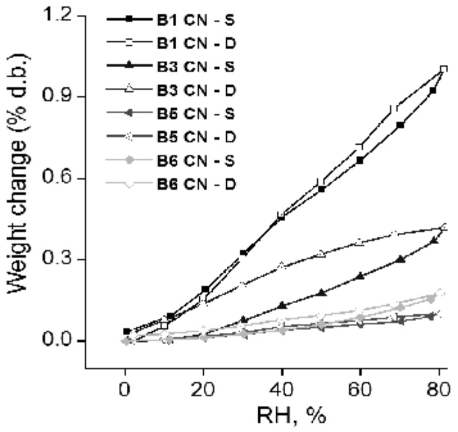


Figure 4. DVS data (S-sorption; D-desorption) for cyanopropyl-modified silicones.

The glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) in the second heating curves. Single T_g values were obtained and no other transition was observed during DSC scans. A linear increase in T_g with increasing the cyanopropyl content was observed from -111 °C for B7 to -62 °C for B1 (Figure 5 and Figure 5S). The non-polar hexyl groups act as softener for the copolymers, while the polar groups tend to increase the T_g. Compared to the starting poly(methylhydro)siloxane (T_g = -139.7 °C), all copolymers exhibited higher T_g values. The presence of a single T_g for all copolymers is an indication that no phase separation occurs. Similar results were reported for poly(dimethyl-*co*-methylcyanopropyl)siloxanes with polar groups content from 8.5 to 100% synthesized by ring opening polymerization of dimethyl and cyanopropyl containing monomers.[29]

Gordon-Taylor equation (1) was used to calculate the glass transition temperatures for copolymers and blends. In our system with three types of structural units, it can be written as follows:

$$1/T_g = w_A/T_g^A + w_B/T_g^B + w_C/T_g^C \qquad (1)$$

where w_X represents the weight fraction and T_g^X the glass transition of each homopolymer, i.e. methylhydro-, methylhexyl and methylcyanopropyl- polysiloxane.

The T_g value of poly(methylcyanopropyl)siloxane (100% modification degree) was taken from the literature (T_g = -64.5 °C).[29] Although this value is lower than that obtained by us for the copolymer with 89% modification degree, a good correlation between the calculated and experimental data was obtained (Figure 5).

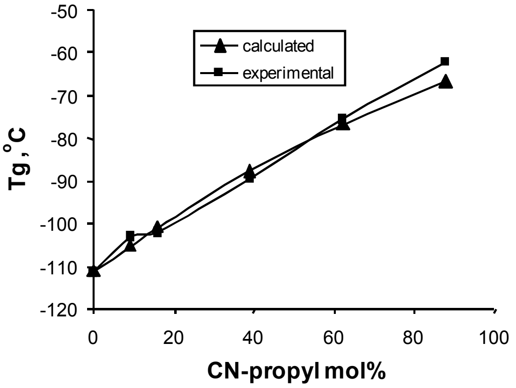


Figure 5. Variation of glass transition temperature in B series of copolymers as function of polar cyanopropyl groups: experimental (■) and predicted according to Gordon-Taylor equation (▲).

Dielectric properties

The dielectric properties of the prepared copolymers were measured as liquids. Table 3 summarizes the dielectric permittivity (*ε'*), dielectric loss (*ε''*) and conductivity (σ) at 10 kHz for all copolymers. The values for the *ε'* varied from 3.7 to 15.9 at the same frequency, for polar group content roughly between 9.2 and 89 mol % (i.e. 1.7 - 18.6 cyano group wt%) (Table 3, Figure 6). The *ε'* was plotted versus cyano groups wt% (Figure 7). A linear increase in the *ε'* with increasing the amount of cyano groups is observed.

Table 3. Dielectric properties of the cyanopropyl –containing copolymers, measured in liquid state

Entry	mol % CN-modified siloxane units	wt % CN groups	*ε'* at 1 Hz	*ε'* at 10 kHz	*ε''* at 10 kHz	σ (S cm^{-1}) at 10 kHz
B7	0	0	3.15	2.74	5×10^{-3}	2.8×10^{-11}
B6	9.2	1.7	3.8	3.7	1.9×10^{-2}	1.1×10^{-11}
B5	16	3.0	5.1	4.7	2×10^{-2}	1.1×10^{-10}
B4	38.8	7.5	13.7	7.4	1.4×10^{-1}	8×10^{-10}
B3	62.1	12.5	26.2	11.3	6.2×10^{-1}	3.5×10^{-9}
B1	87.8	18.5	261.6	15.7	3.5	1.9×10^{-8}
B2	89	18.6	174.9	15.9	2.5	1.4×10^{-8}

The ability of a material to be polarized in an electric field increases with the polar group content. Thus, the increase in *ε'* with increasing the polar cyano group content is not surprising. However, it is important to note that the maximum value for the *ε'* that can be achieved with cyano polar groups is ca. 16, which means an increase by a factor of 6 compared to polydimethylsiloxane.

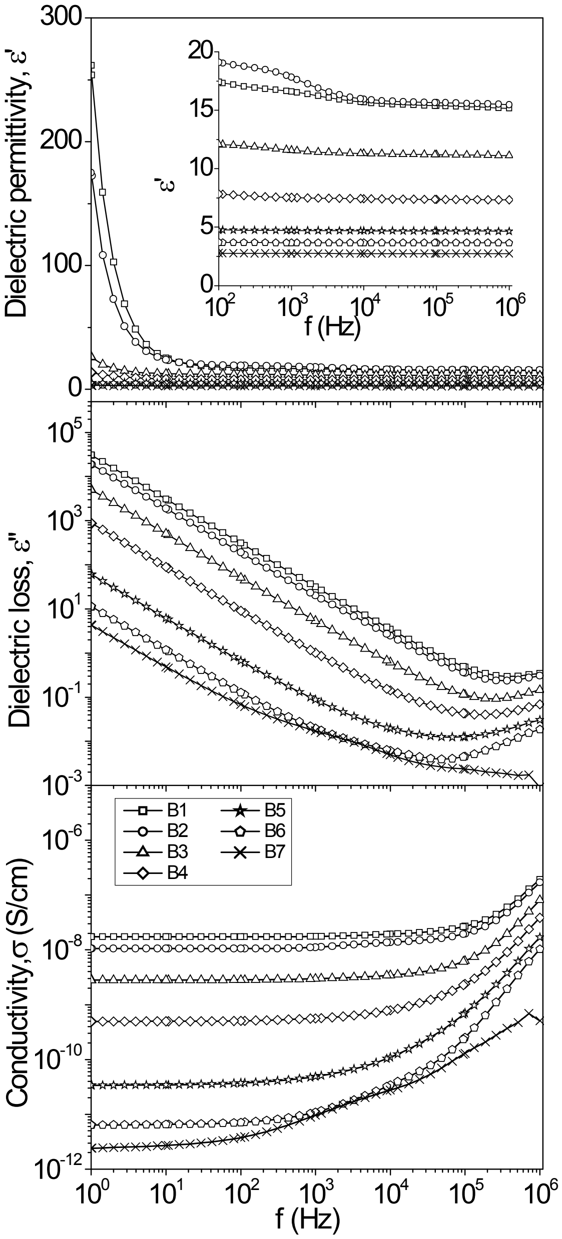


Figure 6. Dielectric properties of the copolymers: dielectric permittivity (top), dielectric loss (middle), and conductivity (bottom).

The *ε'* increases very much at low frequencies, which is a universal phenomenon known as the low frequency dispersion.[30] A strong increase in the dielectric loss for the polymers with high content of polar groups was also observed, as well as an increase in conductivity with increasing the content of cyanopropyl groups. However, in all cases, the conductivity values remained in the limits of the dielectric materials (Table 3).

The high *ε''* at low frequency, with values as high as 10^5, correlated with the frequency dependence – linear at low frequencies in a double logarithmic scale, with the slope of log ε''(f) close to -1 – indicate that the nature of dielectric loss is mainly conductive.

The increase in *ε'* at lower frequencies was reported before, for example, in silicone films blended with cyanopropyl-modified polysiloxanes[31] and was assigned to adsorbed water. Indeed, by increasing the polarity of a polymer, the amount of absorbed water from atmosphere should increase. DVS data show that the vapour sorption capacity of our copolymers is low and slightly increases with the polar groups even when exposed to high humidity. Another explanation for the dielectric relaxation in this case may be the ion conductivity. It is known that ppm concentrations of ion impurities are enough to significantly increase the ionic conductivity especially for low viscosity materials.[30] The Pt catalyst was not removed from the final copolymers. Since the amount of Pt catalyst used was the same in all the reactions, the strong increase in the dielectric loss for the polymers with high content of polar groups might be due to Pt ions, formed by complexation involving CN groups, instead of Pt(0), as in the case of n-hexene addition. Thus the amount of Pt ions would increase with the number of CN groups. This is suported by the observed "poisoning" effect of allyl cyanide on Pt(dvs) catalyst. Further investigations are required to clarify this hypothesis.

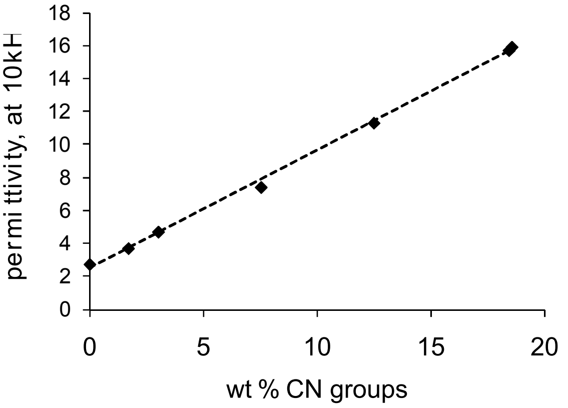


Figure 7. Dielectric permittivity at 10 kHz of copolymers as function of polar cyano group mass content.

The temperature dependency of dielectric properties was also investigated, within -150 to +60°C temperature range. In Figure 8 the *ε'* and *ε''* of copolymer B3 at variable frequencies are plotted versus temperature.

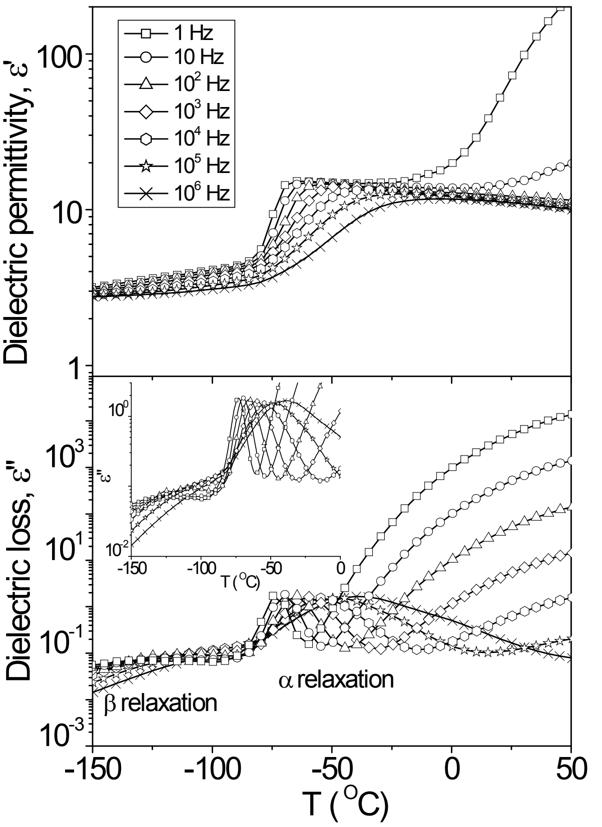


Figure 8. Temperature dependence of ε' and ε'' in 1 to 10^6 Hz frequency range

The variation of both dielectric permittivity and loss suggest structural relaxation processes. In the dielectric loss curve, a low amplitude peak with maximum at about -130°C at 1 Hz was assigned to the secondary β relaxation process due to localized motions of side groups. This peak is shifted towards higher temperature as the frequency increases, till approximately -100 °C at 10^6 Hz, as is characteristic for dielectric relaxation processes.

An α relaxation process associated with the glass transition was observed at -75 °C at 1 Hz, which is very close to the T_g value registered by DSC (-75.6 °C). As expected, this peak shifted to higher temperature with increasing frequency, till -40 °C at 10^6 Hz. The α relaxation process is also clearly visible as a stepwise increase in the dielectric permittivity (ε') curve, which is also shifted towards higher temperatures with frequency increase.

At high temperatures and low frequencies, an abrupt increase of ε' and ε'' was observed, as a result of enhanced mobility of charge carriers.

Cross-linking via un-modified Si-H groups

As mentioned in the Introduction, when hydroxyl end-functionalised polysiloxanes containing Si-H groups were used as precursors in the hydrosilylation with allyl cyanide, an uncontrolled cross-linking occured.[14] A similar process was observed for copolymers B: when stored in open vessels for few days, insoluble materials formed. We supposed that the cross-linking occurred due to the presence of atmospheric humidity. Since copolymers B are trimethylsilyl- terminated, we can exclude the possibility of cross-linking via chain ends. The first step toward cross-linking is the hydrolysis of the unmodified Si-H groups, followed by dehydrocoupling between the formed Si-OH and Si-H groups in the presence of Pt catalyst or by an inter-molecular dehydration between two Si-OH groups. Figure 9 compares the FT-IR spectra of copolymer B2 taken after reaction (1) and after storage in normal atmosphere for 6 months as concentrated toluene solution (2) and pure (3). An absorption band at around 3400 cm^{-1} characteristic for H-bonded OH groups and a decrease of Si-H absorption band was observed for both stored samples. Calculation of the ratio between Si-H absorbance and CN absorbance (A_{2156}/A_{2245}) gave the following results: (1) 0.788; (2) 0.377; (3) 0.062 which clearly indicate that Si-H groups are hydrolysed in atmosphere humidity and participate farther in a condensation reaction.

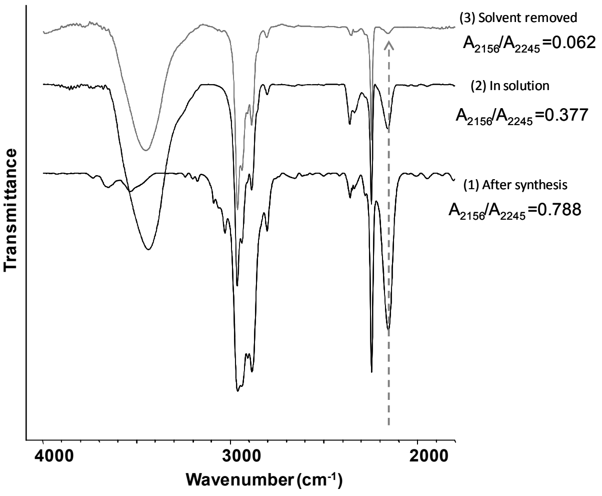


Figure 9. Modification of the IR spectrum (1800-4000 cm^{-1} region) of B2 stored in different conditions for 6 months

This process is accelerated when a solution of DBTDL catalyst in methanol is used, where after 1 h the Si-H absorption band decreased to half as compared to Si-CH$_3$ band. Therefore, the incomplete conversion of the Si-H groups opens up the possibility of using the prepared copolymers as cross-linkers. First experiments show that homogenous thin elastomeric films with increased permittivity and good elastic properties formed (Figure 6S). Work regarding the preparation and full characterization of such materials will be discussed in a forthcoming publication.

Conclusions

A series of cyanopropyl-modified polysiloxanes containing trimethylsilyl end groups was synthesized by hydrosilylation of poly(methylhydro)siloxane with a mixture of allyl cyanide / n-hexene, whereby their proportion was tuned. Irrespective of the amount of allyl cyanide used, incomplete hydrosilylation was observed (about 11% un-reacted Si-H groups). The ^{1}H NMR spectra indicated the formation of short polar segments. A linear increase of glass transition temperature with the polar group content was observed. Low water sorption capacity (below 1%) at over 80% humidity was measured by DVS, even for highly polar silicones. A linear increase of ε' with increasing the amount of cyanopropyl group content was observed. A maximum ε' value of 15.9 (@ 10 kHz) was measured for copolymer B2 with 89% cyanopropyl groups. The residual Si-H groups in copolymers can be used further as cross-linking points in a condensation reaction with hydroxyl end-functionalised polysiloxane and opens the access to a new class of dielectric elastomers to be used for actuation.

Dedication

This paper is dedicated to the 65th anniversary of "Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania.

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Notes and references

[a] *Petru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, Iasi, 700487, Romania. Fax: +40232211299; Tel:+40232217454; E-mail: raclesc@icmpp.ro*

[b] *Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Functional Polymers, Ueberlandstr. 129, CH-8600, Dübendorf, Switzerland.E-mail: dorina.opris@empa.ch*

† Electronic Supplementary Information (ESI) available: [^{1}H and ^{13}C NMR spectra, FTIR spectra, DSC curves and photos of cross-linked films]. See DOI: 10.1039/b000000x/

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