Breathable Rubbery Skin Protectors: Design, Synthesis, Characterization, and Properties of Cyanoacrylated Silicone Rubber Networks

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Abstract

We extended our investigations of rubbery wound closure adhesives and created novel flexible networks by crosslinking cyanoacrylated silicone rubbers (i.e., commercial methylhydrosiloxane-dimethylsiloxane copolymers, PMHS-*co*-PDMS) with N,N-dimethyl-*p*-toluidine in tetrahydrofuran and hexamethyldisiloxane solvents at room temperature. Cyanoacrylation was achieved by hydrosilating (anthracene-protected) allyl cyanoacrylate with PMHS-*co*-PDMS. Steric hindrance and the molecular weight of the copolymer strongly affect the extent of hydrosilation. The rate of crosslinking is proportional with the number of cyanoacrylate groups in the copolymer and networks form in seconds with appropriate amounts of initiator. Networks on porcine skin yield well-adhering flexible optically-transparent colorless conformal coatings of good "feel" appropriate for clinically useful non-occlusive "breathable" skin or wound protectors.

Keywords: adhesives, rubber, silicones, wound protector

INTRODUCTION

The first phase of our investigations concerned clinically potentially useful rubbery wound closure adhesives and focused on the synthesis, characterization and testing of homo- and conetworks obtained by the polymerization of three-arm star cyanoacrylate-telechelic polyisobutylene [Ø(PIB-CA)$_3$], and the copolymerization of Ø(PIB-CA)$_3$ plus 2-octyl cyanoacrylate (Oc-CA), respectively.[1,2] As the continuous phase in these homo- and conetworks

is PIB, a barrier to gases and moisture, these products deemed appropriate for occlusive wound closures.

In the course of this research we theorized that similar non-occlusive (i.e., "breathable", gas and water vapor transparent) skin and wound protectors could be obtained with silicone rubbers fitted with CA groups. Silicone rubber, more precisely the polydimethylsiloxane (PDMS) moiety, is well-known to be transparent to gases (specifically to O_2, N_2, CO_2, and H_2O) but not to liquid moisture, and allows the exchange of these gases into and out of closures.[2-4] Indeed, silicone rubbers, sold under various names (e.g., Allevyn®, Tegaderm®, Mepilex®), are successful commercially available components of non-occlusive wound closures.[5,6] Silicone rubbers are biocompatible, have mechanical properties appropriate for protectors, and a good "feel' on the skin.[7]

Thus, our challenge was the synthesis of silicon rubbers fitted with CA groups (SiR-CA) and their rapid crosslinking, and to demonstrate easy deposition of such networks onto skin.

Astonishingly, our intensive and extensive search of both the scientific and patent literature (with the help of a professional librarian) remained fruitless as we could not find even a single reference disclosing silicon rubbers fitted with the CA function.

This paper concerns one of the methods we developed to attach CA groups to silicone rubbers (our patent application discloses other possibilities[8]), the crosslinking of such SiR-CAs to networks, and the structural characterization of the networks. We also describe the formation of blends obtained by the polymerization of SiR-CA in the presence of Oc-CA. We conclude with thoughts on network morphology, and demonstrate the suitability of SiR-CA networks as potential non-occlusive "breathable" skin or wound protectors.

EXPERIMENTAL

Materials

Allyl cyanoacrylate (Allyl-CA, Permabond® 919), anthracene (Aldrich), Karstedt's catalyst (platinum-divinyltetramethyldisiloxane complex, Gelest SIP6831.2), 4-dimethyl-*p*-toluidine (DMT, Aldrich), phosphorus pentoxide (EMD), hydroquinone (Aldrich), maleic anhydride (Aldrich) methanol (Aldrich), and hexamethyldisiloxane (Gelest SIH6115) were used as received. Tetrahydrofuran (THF, Fisher), benzene (Aldrich), and xylene (Alfa Aesar) were distilled over Na/benzophenone prior to use and hexane (Aldrich) over CaH_2.

Trimethylsilyloxy-terminated methylhydrosiloxane-dimethylsiloxane copolymers (PMHS-*co*-PDMS, Gelest HMS-301, HMS-053, and HMS-064) were used as received. According to Gelest's catalogue, PMHS-*co*-PDMS is prepared by the copolymerization of D_3H and D_4, so the likely structure of this copolymer is:
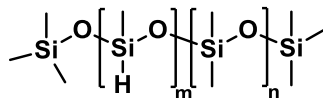
where m and n are

	M_n (g/mol)	m	n
HMS-301	1,900-2,000	8	17
HMS-053	20,000-25,000	14-17	257-322
HMS-064	50,000-60,000	40-48	640-768

Fresh porcine ventral skin was obtained from a local butcher. The skin was cut into ~3x10 cm strips and stored in a refrigerator until use. Specimens were wiped with 70v/v% aqueous isopropanol before use.

Instrumentation and Techniques

Proton (^{1}H) NMR spectra were obtained with Varian Gemini 300 MHz and 500 MHz spectrometers, using deuterated chloroform as a solvent.

Thermal characterization of polymer films was carried out by a TA Instruments Model Q2000 DSC with 6-10 mg samples and 10 °Cmin^{-1} heating runs.

Stress-strain properties were determined with a Texture Analyzer TA.XT plus tester with a 5 kilo load cell and a 5 mm/min crosshead speed. Microdumbell shaped 0.22-0.27 mm thick samples were punched from solution cast films. Exponent software was used for data analysis.

Sol fractions of polymer films were determined at room temperature using THF solvent. A well-dried film (~1 g) was extracted with THF (~18 mL) for 6 days changing the solvent every second day. After 6 days the THF was evaporated and the film dried in a vacuum oven at 35 °C till weight constancy. The sol fraction was calculated by $sol(\%) = \left(1 - \dfrac{w_a}{w_b}\right) \cdot 100$ where w_a and w_b are weight of the film after and before extraction, respectively.

Swelling behavior of polymer blends was studied at room temperature using first acetone and then hexane solvents. A well dried film (1.14 g) was swollen in acetone until equilibrium. The swelling ratio was calculated by $sr(\%) = \left(\dfrac{w_{sw} - w_{dry}}{w_{dry}} \right) \cdot 100$ where w_{sw} and w_{dry} are weight of the swollen and the dry film, respectively. The film was dried and swollen in hexane until equilibrium. Acetone and hexane soluble contents were determined by ^{1}H NMR spectroscopy.

Syntheses and Crosslinking

   a) *Synthesis of Anthracene-Protected Allyl Cyanoacrylate (allyl-11-cyano-9,10-dihydro-9,10-endoethanoanthracene-11-carboxylate, A/Allyl-CA)*

A 500 mL three neck round bottom flask equipped with a magnetic stirrer and a reflux condenser, was charged with anthracene (37.36 g, 0.21 mole), dry SO$_2$-inhibited benzene (210 mL, SO$_2$ was bubbled through benzene for 40 min), and allyl-cyanoacrylate (25.00 g, 0.18 mole). The solution was refluxed overnight, then the solvent was distilled off, and the white solid residue was recrystallized from abs ethanol. Yield: 43.04 g (75%) of A/Allyl-CA adduct. Figure 1 shows the ^{1}H NMR spectrum of the product, together with assignments. The small resonances at 1.3 and 1.5 ppm are due to traces of ethanol (<1%) used for crystallization and traces of water from chloroform, respectively. According to this evidence, the purity of A/Allyl-CA was >99%.
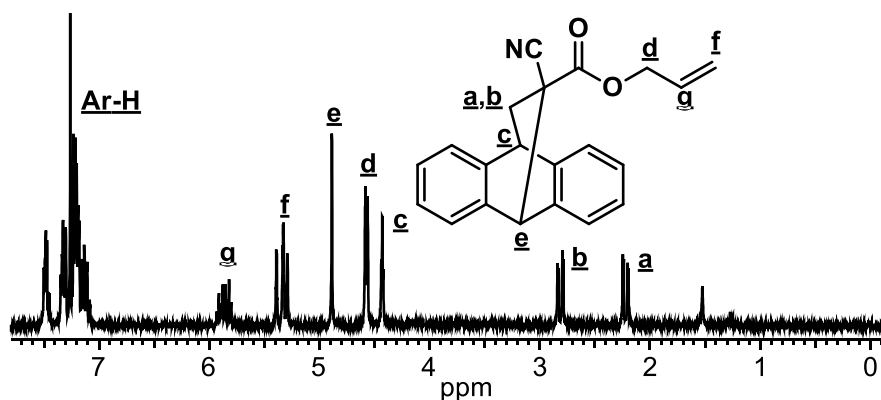

Figure 1. ^{1}H NMR Spectrum of Anthracene-protected Allyl-cyanoacrylate (A/Allyl-CA).

b) Hydrosilation of A/Allyl-CA with PMHS-co-PDMS

Hydrosilation of A/Allyl-CA with PMHS-*co*-PDMS (HMS-301) was carried out with Karstedt's catalyst in THF under a blanket of nitrogen. Thus, a 50 mL round bottom flask equipped with a magnetic stirrer was charged with PMHS-*co*-PDMS (5.00 g, 20.41 mmole SiH groups; i.e., 8 SiH groups per copolymer), A/Allyl-CA (7.08 g, 22.45 mmole) dissolved in THF (20 mL), and Karstedt catalyst (200 μL), and the solution was stirred for 5 hours at room temperature. Then the charge was precipitated into a cold methanol/water (250/50 mL) mixture, the liquid phase was decanted, and the product, a viscous (honey-like) yellow liquid, was dried by rotary evaporation. Yield: 5.677 g (50%).

Figure 2 shows the ^{1}H NMR spectrum of PMHS-*co*-PDMS carrying A/Allyl-CA groups, together with assignments. Hydrosilation produces two isomers distinguishable by NMR spectroscopy. Calculated from the intensity of the resonances associated with A/Allyl-CA (f, g, i, j) and that of Si-CH$_3$ (a), the substitution of SiH to A/CA groups was 27.5%; according to this result, the copolymer contained 2.2 A/Allyl-CA groups per molecule. This low degree of substitution is likely due to steric hindrance. In this relatively low molecular weight copolymer in which the PMHS units are close to each other after the entry of the first A/Allyl-CA the large anthracene group may hinder further hydrosilation.

The resonance at 3.49 ppm, associated with Si-O-CH$_3$ groups, indicates reaction with methanol during precipitation. The two unmarked resonances at 1.85 and 3.75 ppm are due to traces of THF.
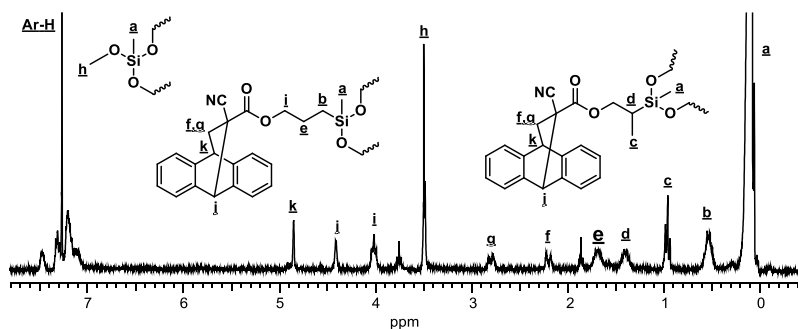

Figure 2. ^{1}H NMR Spectrum of PMHS-*co*-PDMS Carrying Anthracene-protected CA Groups (PM(A/Allyl-CA)S-*co*-PDMS).

The 20,000-25,000 g/mol PMHS-*co*-PDMS (HMS-053) contains 270-340 monomer units, i.e., 14-17 SiH groups. In this molecule the SiH groups are sterically less encumbered than in the shorter one (see above) so that substitution by A/Allyl-CA groups increased to 58%, i.e., to 8-10 A/Allyl-CA adduct per copolymer.

Substitution of SiH groups by A/Allyl-CA adducts was even higher using 50,000-60,000 g/mol PMHS-*co*-PDMS (HMS-064), which contains 680-820 monomer units, i.e., 40-48 SiH groups. This system gave 83% conversion, i.e., 33-40 A/Allyl-CA per copolymer.

c) Deprotection of PM(A/Allyl-CA)S-*co*-PDMS

The final step in the synthesis of cyanoacrylated silicone rubbers (PM(Allyl-CA)S-*co*-PDMS) was deprotection (i.e., the removal of the anthracene group) of A/Allyl-CA adducts attached to PMHS-*co*-PDMS. Deprotection was carried out by the use of 100% excess maleic anhydride.[3] Thus, a 100 mL three neck round bottom flask equipped with a magnetic stirrer and reflux condenser was charged with PM(A/Allyl-CA)S-*co*-PDMS (5.677 g, 4.64 mmole A/Allyl-CA adducts, M_n=1,900-2,00 g/mole) dissolved in xylene (20 mL), and dry SO_2 was bubbled through the solution for 20 min. Maleic anhydride (909 mg, 9.27 mmole), phosphorus pentoxide (46 mg), and hydroquinone (~10 mg) were added, and the charge was refluxed for 8 hours. The xylene was removed by vacuum distillation and the polymer dissolved in hexane (20 mL). The solution was suction filtered and the hexane removed by vacuum distillation.
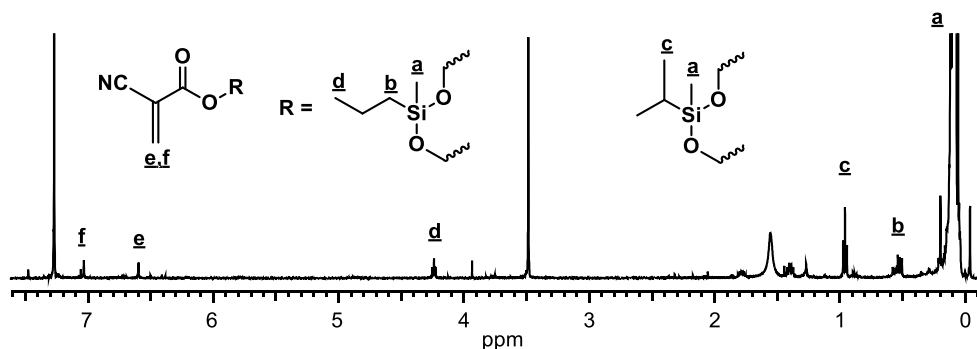

Figure 3. ^{1}H NMR Spectrum of PM(Allyl-CA)S-*co*-PDMS (M_n=1,900-2,000 g/mole)

Figure 3 shows the [1]NMR spectrum of the deprotected product, PM(Allyl-CA)S-*co*-PDMS. Integration of the resonances associated with double bond protons (e) at 6.60 and 7.03 ppm

relative to those of methyl protons at 0.08 ppm indicates an average of 2, 7-9, and 30-37 CA groups per PM(Allyl-CA)S-*co*-PDMS for the 1,900-2,000, 20,000-25,000, and 50,000-60,000 g/mole molecular weight backbones, respectively. Deprotection was close to quantitative (~92% of theory) in every case.

d) Network Synthesis: Crosslinking of PM(Allyl-CA)S-co-PDMSs with DMT

Networks were prepared by crosslinking the CA groups of PM(Allyl-CA)S-*co*-PDMS by DMT. Thus, to a charge of PM(Allyl-CA)S-*co*-PDMS (1.5 g, M_n=1,900-2,000 g/mole) dissolved in THF (4 mL) in a 15 mL test tube was added DMT (12 µL) at room temperature. The solution was briefly shaken and rapidly poured in a 7.5 X 7.5 cm Teflon mold. Subsequently, the solvent was evaporated in a hood at 43 °C for 3 days and the light yellow optically clear film was further vacuum dried at 35 °C until weight constancy. Films prepared from 20,000-25,000 and 50,000-60,000 g/mole PM(Allyl-CA)S-*co*-PDMS were colorless.

e) Blend Synthesis: Crosslinking of Oc-CA + PM(Allyl-CA)S-co-PDMSs Mixtures with DMT

Blends were made similarly to networks, except by the use of Oc-CA. The synthesis of a representative blend was as follows: To a charge of PM(Allyl-CA)S-*co*-PDMS (0.6495 g, M_n=20,000-25,000 g/mole) dissolved in THF (5 mL) in a 15 mL test tube was added 2-octyl cyanoacrylate (0.8655 g) and DMT (12 µL) at room temperature. The solution was briefly shaken and rapidly poured in a 7.5 X 7.5 cm Teflon mold. Subsequently, the solvent was evaporated in a hood at 43 °C for 3 days and the light yellow optically clear film was further vacuum dried at 35 °C until weight constancy.

f) Crosslinking PM(Allyl-CA)S-co-PDMS on Porcine Skin

Cyanoacrylated silicon rubber (0.18 g, M_n=20,000-25,000 g/mol) carrying ~9 CA groups was dissolved in hexamethyldisiloxane (100 µL) and the viscous solution was poured on a strip of porcine skin. After ~10 min an essentially tack free optically-clear transparent conformal coat formed. Stretching and twisting the skin did not dislodge the hermetically-adhering coat, and attempts to remove it from the skin surface by a tweezer failed. Experiments carried out under

the same conditions but adding 1 drop DMT to the cyanoacrylated silicon rubber solution gave tack-free coats in ~4 min.

RESULTS AND DISCUSSION

Synthesis of Silicone Rubbers Carrying CA Groups and Their Crosslinking to Networks

Figure 4 outlines a method we developed for the introduction of CA groups in silicone rubbers containing SiH functions.
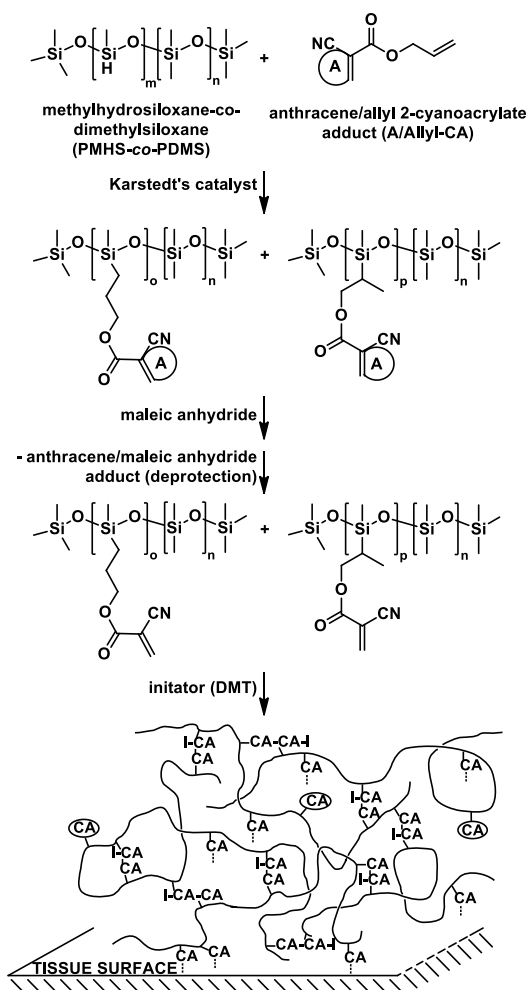

Figure 4. Synthesis Scheme of Cyanoacrylated Silicone Rubber (SiR-CA) Followed by Crosslinking, and the Idealized Microstructure of the Network (wiggly lines = silicone rubber, I = initiator (DMT) residue, CA = cyanoacrylate groups, CA--- = cyanoacrylate groups covalently attached to skin, CA in circles = unreacted buried "useless" CA groups).

All materials needed for the synthesis were commercially available (see Experimental). For silicone rubber we chose a silicone copolymer of methylhydrosiloxane-dimethylsiloxane (PMHS-*co*-PDMS), i.e., a molecule containing PDMS sequences and SiH groups for hydrosilation of A/Allyl-CA.

We found that steric hindrance (i.e., the distance between SiH groups in the silicone copolymer) strongly affects hydrosilation efficiency (the extent of A/Allyl-CA attachment to the copolymer). As the lowest molecular weight silicone we employed (M_n=1900-2000 g/mol) is made by ring opening polymerization of pentamethylcyclotrisiloxane (D_3H), the polymer consists of $Si(CH_3)_2$-O-$Si(CH_3)_2$-O-$Si(CH_3)H$-O repeats (i.e., two dimethylsiloxane groups between two methylhydrosiloxane groups). During hydrosilation the SiH bond interacts with A/Allyl-CA, carrying the bulky anthracene protecting group. Consequently, after a successful hydrosilation event neighboring SiHs become sterically encumbered by large A/Allyl-CA groups (i.e., bulky anthracene adducts retard the docking of further A/Allyl-CAs). This explains the low 27.5% hydrosilation efficiency of A/Allyl-CA by the low molecular weight silicone, equivalent to only 2.2 A/Allyl-CA per silicone molecule.

Sterically hindered SiHs that did not react by hydrosilation reacted with methanol during precipitation and yielded Si-O-CH_3 groups (identified by ^{1}H NMR spectra).

As the higher molecular weight siloxanes (M_n=20,000-25,000 and 50,000-60,000 g/mol) are made by ring opening copolymerization of D_3H plus octamethylcyclotetrasiloxane (($Si(CH_3)_2$-O-)$_4$, D_4), the distance between neighboring SiH groups is longer due to the larger number of dimethylsiloxane units between them (longer spacers). Thus, in the silicone with M_n=20,000-25,000 g/mol the average number of dimethylsiloxane units between two methylhydrosilaxane units is ~19, and in the silicone with M_n= 50,000-60,000 g/mol two SiH groups are separated by ~16 dimethylsiloxane units. Thus, due to the larger number of dimethylsiloxane units (longer spacers), the hydrosilation efficiency in the higher molecular weight silicones increased to 58 and 83%, respectively, which is equivalent to 8-10 and 33-40 A/Allyl-CA per silicone molecule. We can safely conclude that longer spacers (16 and 19 -$Si(CH_3)_2$-O- units, respectively) reduce steric congestion and thus increase hydrosilation efficiency. In other words, with SiH groups farther apart in the silicone steric hindrance is reduced (more space is available) for hydrosilation of A/Allyl-CA.

Both, protection of Allyl-CA with anthracene and deprotection (removal of the anthracene group), was effected by well-established procedures.[9,10] The length of the silicone copolymer did not affect deprotection efficiency, and deprotection was ~92% in all systems.

The products of hydrosilation of A/Allyl-CA, PM(A/Allyl-CA)S-*co*-PDMSs, are multi-(anthracene-protected)-cyanoacrylates (with 2-40 A/Allyl-CA per molecule depending on the MW of the silicone copolymer), and as such, after deprotection, can form networks upon reaction with nucleophiles. Thus, experiments were carried out to crosslink SiR-CAs by the use of DMT. After dedicated orienting experimentation a procedure was developed for the preparation of thin networks appropriate for skin protection. We found that ~0.25 mm thick homogeneous optically-clear tack-free crosslinked films can be obtained by the following procedure: In a 15 mL vial 1.5 g PM(Allyl-CA)S-*co*-PDMS (M_n=1,900-2,000 g/mol) was dissolved in 4 mL THF at room temperature, 25 μL DMT was injected, the solution was strongly shaken for a second and quickly poured in a 7x7 cm Teflon mold. The solvent was evaporated in a hood at 43 °C for 3 days.

The appropriate DMT concentration has to be carefully defined: If it is too low set time increases, if it is too high crosslinking is too fast and the system cannot be poured.

Network Characterization and Properties

Films obtained with SiR-CA of M_n=1,900-2,000 and 20,000-25,000 g/mol were very weak and could not be removed from the mold without tearing them. The products swelled but did not dissolve in THF even after 6 days at room temperature, indicating network formation. Networks prepared with SiR-CA M_n=1,900-2,000 and 20,000-25,000 g/mol, respectively, showed 94.2% and 70% gel. In contrast, films obtained with SiR-CA M_n=50,000-60,000 g/mol were sufficiently strong to be lifted from the mold without damaging them. Samples (microdumbells) punched from this film exhibited 194% elongation and 0.14 MPa tensile strength, i.e., properties that are sufficient for satisfactory skin and wound protection (elongation of human skin is ~100% and its tensile strength is 1-20 MPa).[11] All networks had a good "feel" on the skin.

Efforts were made to reinforce mechanical properties of films prepared with SiR-CA of M_n=20,000-25,000 g/mol by reaction with Oct-CA. This copolymerization strategy was successfully used earlier reinforcing three-arm star polyisobutylenes carrying CA termini (Ø(PIB-CA)$_3$) with Oct-CA.[12] Mixtures of SiR-CA and Oct-CA formed homogeneous solutions

in THF, however, the addition of DMT caused macrophase separation suggesting that SiR-CA and Oct-CA did not copolymerize but formed a blend of two polymers. Swelling studies substantiated this assumption. Thus, treating the film with acetone swelled it (swelling ratio 131%) and extracted pure poly(Oct-CA), and, similarly, treating it with hexane (swelling ratio 547%) also produced poly(Oct-CA) extract.

The fact that Ø(PIB-CA)$_3$ + Oct-CA mixtures readily copolymerize but SiR-CA + Oct-CA does not is likely due to steric encumbrance.[12] The terminal CA groups at the tips of PIB chains in Ø(PIB-CA)$_3$ are easily accessible and copolymerize with Oct-CA; in contrast, the few CA groups in SiR-CA are randomly attached to the silicone backbone and hence are sterically encumbered. Thus, the addition of DMT to SiR-CA + Oct-CA mixtures rapidly polymerizes the small Oct-CA molecules and the poly(Oct-CA) phase-separates from the SiR-CA.

Experiments were carried out to demonstrate the formation of SiR-CA coatings on skin and their covalent attachment to the skin. Thus, viscous solutions of SiR-CA (0.18 g, M_n=20,000 g/mol carrying ~9 CA groups, dissolved in 100 μL hexamethyldisiloxane) were poured onto strips of pig skin and film formation was followed visually. Transparent tack-free conformal coating strongly adhering to the surface formed after ~10 min on the skin. The same experiment carried out by adding 1 drop DMT to the SiR-CA solution, produced coats in ~4 mins. We wish to stress that the SiR-CA coats could not be removed by a tweezer from the skin without damaging the film, which suggests covalent attachment. SiR is a liquid which does not covalently attach to the skin, does not produce coatings, and it can be washed off easily with water.

Microstructure of Networks

Figure 4 helps to visualize the idealized microstructure of a network obtained by crosslinking silicone rubbers fitted with CA groups (SiR-CA) on the surface of skin. Crosslinking is initiated by the attack of nucleophilic groups (-OH, -NH-, etc.) on the skin or by purposely added initiator (e.g., DMT) on dangling CA groups, and proceeds by the addition ("polymerization") of further CA groups. Most crosslinking sites are expected to comprise two covalently linked CA groups (polymerization of three or more CA groups is possible but much less likely). The CAs in circles in the figure indicate unreacted CA groups, buried due to the high

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viscosity of the system. In view of this crosslinking mechanism, a significant number of rings, entanglements, and catenates may form that increase the load bearing capacity of the coating.

CONCLUSIONS

A simple method was developed for the synthesis of silicone rubbers carrying CA groups (SiR-CA). Thus, anthracene-protected allyl-CA was hydrosilated with silicone rubbers containing SiH groups, followed by deprotection. Hydrosilation is strongly affected by steric hindrance exerted by the bulky anthracene protecting group. SiR-CAs of various molecular weights were characterized by a variety of techniques. Crosslinking SiR-CAs with DMT produces optically-clear flexible conformal skin coatings within minutes. Films prepared with 50,000-60,000 g/mol SiR-CA exhibited mechanical properties appropriate for skin and wound protection.

ACKNOWLEDGEMENTS

REFERENCES

1. R. Gasser, J. S. Tan, J. Kennedy, G. Erdodi, WO2012109179, February 7, 2012.

2. T. C. Merkel, V. I. Bondar, K. Nagai, B. D. Freeman, I. Pinnau, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 415-434.

3. J.C. McDonald, G. M. Whitesides, *Accounts of Chemical Research* **2002**, *35*, 491-499.

4. I. Van Reeth, A. Wilson, *Cosmetics & Toiletries Magazine* **1994**

5. C. T. Hess, *Clinical Guide to Skin and Wound Care*, 7th edition, Wolters Kluwer Pub, 2013

6. C. Sussman, B. Bates-Jensen, *Wound Care*, 4th edition, Wolters Kluwer Pub, 2012

7. M-C. Belanger, Y. Marois, *J. Biomed. Mat. Res.* **2001**, *58*, 467-477.

8. J. P. Kennedy, I. Szanka, A. Szanka, WO2015054357 April 16, 2015.

9. C. J. Buck, *J Polym Sci: Polym Chem.* **1978**, *16*, 2475-2507.

10. M. Tahtouh, J. R. Kalman, B. J. Reedy, *J Polym Sci, Part A: Polym. Chem.* **2011**, *49*, 257-277.

11. G. A. Holzapfel, "Biomechanics of Soft Tissue" in Handbook of Material Behaviour Nonlinear Models and Properties, Eds. Jean Lemaitre, LMT-Cachan, France, Academic Press, 2000

12. I. Szanka, A. Szanka, S. Sen, N. Nugay, J. P. Kennedy, *J Polym Sci, Part A: Polym. Chem.* **2015**, *53*, 1640-1651.

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**Figure 2.** ^{1}H NMR Spectrum of PMHS-*co*-PDMS Carrying Anthracene-protected CA Groups (PM(A/Allyl-CA)S-*co*-PDMS).

Figure 3. ^{1}H NMR Spectrum of PM(Allyl-CA)S-*co*-PDMS (M_n=1,900-2,000 g/mole)

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Graphical table of contents

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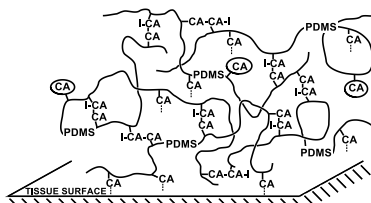
A method was developed to synthesize cyanoacrylated polydimethylsiloxane (PDMS-CA) from various molecular weight PDMS having SiH functionalities. Homonetworks and blends with 2-octyl cyanoacrylate were prepared by polymerizing the cyanoacrylate groups. The chemical attachment between PDMS-CA and skin was tested. A dry coating was formed on porcine skin which could not be removed without damaging the tissue surface.