Reversibly Cross-Linking Amino-Polysiloxanes by Simple Triatomic Molecules. Facile Methods for Tuning Thermal, Rheological, and Adhesive Properties[†]

Tao Yu,[‡] Koji Wakuda,[‡,§] Daniel L. Blair,[⊥] and Richard G. Weiss[‡,*]

Departments of Chemistry and Department of Physics, Georgetown University, Washington, D.C. 20057-1227

Received: January 6, 2009; Revised Manuscript Received: February 20, 2009

The physical properties of five siloxane polymers with different types and frequencies of amino functional groups along the polymer side chains have been manipulated from flowing liquids to gels and to rubber-like materials by the simple addition or subtraction of a neutral triatomic molecule, CO_2 or CS_2, at room temperature. The chemical changes, formation of ammonium carbamates and ammonium dithiocarbamates, create materials whose properties are totally different from those of the parent polymers as a result of the introduction of ionic cross-links. These materials can be returned to their original forms by heating (in the case of the CO_2 adducts) or to their protonated original forms by treatment with an acid (in the case of the CO_2 and CS_2 adducts). Heating the ammonium dithiocarbamates leads to loss of H_2S and permanent (covalent) thiourea cross-links between the polymer chains. The new materials adhere strongly to other surfaces and can be swelled to several times their original volumes by different liquids. The rheological, swelling, and physical properties of the new materials have been correlated with the structures of the original polymers to provide a comprehensive picture of how changes at the nanometric length scale are translated to macroscopic changes. At least for the polysiloxanes examined here, the properties of the adducts do not correlate with the molecular weights of the original polymers, but do with the frequency of amino groups. The results demonstrate a simple, new method to cross-link polysiloxanes (and, in principle, a wide range of other polymers), transforming them into materials with totally different and potentially commercially useful properties.

Introduction

Polysiloxanes are among the most studied and commercially important partially inorganic polymers in use today.[1] Their backbones are very flexible, allowing easy interconversion of conformers. They also have interesting gas permeability and unusual surface properties.[2] As a result, they are used in a myriad of applications, such as drug-delivery systems,[3] high-performance elastomers,[4] membranes,[5] adhesives,[6] coatings,[7] soft lithography stamps,[8] and self-healing materials.[9] The low energy of interaction among polysiloxane chains is responsible for two of their interesting attributes, high malleability and relatively low viscosity. These can also be disadvantageous because polysiloxanes cannot be made into fibers and immobilized films without significant structural modifications (N.B., cross-links between chains). It would be advantageous to be able to interconvert polysiloxanes between low and high interaction energy states so that they can be processed for different purposes without expending a large effort or expense.

Many modifications of the parent polysiloxane structure are known. Usually, a fraction of the methyl groups of the most common polysiloxane, poly(dimethylsiloxane) (PDMS), are substituted by a group containing a different length or functionality (i.e., a one-dimensional structural change).[10] Ladder polysiloxanes possess two-dimensional structural features,[11] while cross-linked polysiloxanes,[12] including tubular and pseudosieve plate polysiloxanes, are three-dimensional structures.[13] The nature and extent of the chain cross-links can be varied and each change leads to materials with different chemical and physical properties. The cross-links can be covalent or noncovalent (e.g., hydrogen bonding,[14] metal coordination,[15] etc.). Although the cross-linking can be reversed in some cases, it does not yield the original materials without performing significant physical or chemical manipulations. Clearly, a *reversible* cross-linking strategy that requires benign changes to the material mild conditions, and allows the noncross-linked and cross-linked forms to be recovered intact without significant effort would be desirable. We describe such strategies here and explore how the properties of the noncross-linked and cross-linked states differ.

The basis for our approaches is grounded in simple organic chemical transformations that have led to the development of reversible organogels,[16] ionic liquids,[17] and reversible solvents,[18] CO_2 fixation-release systems,[19] and supermolecular polymers.[20] It is known that simple, neutral X=Y=X triatomic molecules, in which the X atoms are much more electronegative than the Y atom (e.g., CO_2 and CS_2), can become "bridge-linkers" for amino groups.[21,22] We reasoned that it should be possible to exploit the general chemistry shown in eqs 1 and 2 to transform *weakly* interacting chains of uncharged polysiloxanes with substituent amino groups into *strongly* interacting chains via attractive electrostatic attractions between positive and negative charged centers that lead to cross-links. In a medium of low polarity, such electrostatic forces can be very strong because they vary with the inverse of dielectric constant,[23] and the dielectric constant of silicone polymer is only 3.0−3.5.[24]

Reversal of the CO_2-generated ammonium carbamate cross-links can be effected by warming the material under air or, more

---

[†] Part of the "Hiroshi Masuhara Festschrift".

[*] To whom correspondence should be addressed. E-mail: weissr@georgetown.edu.

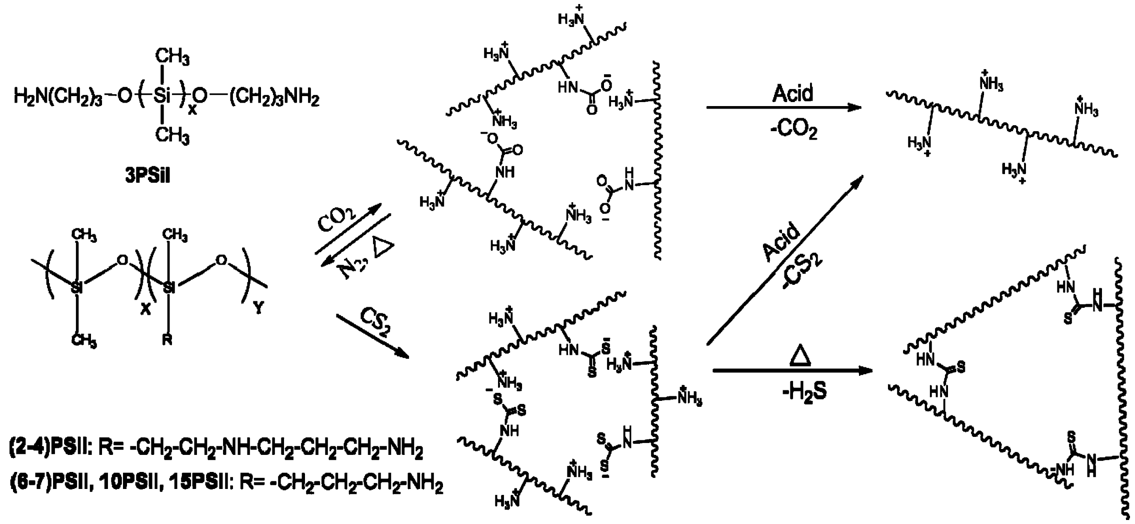
[‡] Department of Chemistry.

[§] Current address: Chemistry Department, Engineering Science School, Osaka University, Machikaneyamamachi, Toyonaka, Osaka 560-8531, Japan.

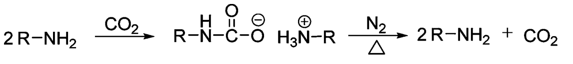
[⊥] Department of Physics.

10.1021/jp900115g CCC: $40.75

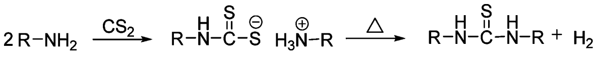
SCHEME 1: Structures of Polysiloxane Samples and a General Scheme for Their Reactions with CO_2 and CS_2



rapidly, by bubbling an inert (displacing) gas, such as molecular nitrogen, through the sample (eq 1). Our experience is that the analogous ionic cross-links achieved with CS_2, ammonium dithiocarbamates, are not amenable to reversal, [22] but heating produces (permanent) covalent thiourea cross-links instead (eq 2).[25] Clearly, the degree of cross-linking can be controlled by the amount of amine functionality of polysiloxanes (as well as by the amount of the triatomic molecule added to the polymer; vide infra). In this way, the thermal and rheological properties of the polysiloxanes can be tuned easily. Compared with conventional cross-linking methods, this strategy has the advantages of being rapid, isothermal, inexpensive, and (with CO_2) reversible.



$$2\,R{-}NH_2 \xrightarrow{CO_2} R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{O}\ \ H_3\overset{\oplus}{N}{-}R \xrightarrow[\Delta]{N_2} 2\,R{-}NH_2 + CO_2 \qquad (1)$$



$$2\,R{-}NH_2 \xrightarrow{CS_2} R{-}\overset{H}{N}{-}\overset{S}{\overset{\|}{C}}{-}\overset{\ominus}{S}\ \ H_3\overset{\oplus}{N}{-}R \xrightarrow{\Delta} R{-}\overset{H}{N}{-}\overset{S}{\overset{\|}{C}}{-}\overset{H}{N}{-}R + H_2S \qquad (2)$$

Here, we describe how these simple cross-linking methods change the thermal, rheological, and adhesive properties of polysiloxanes with up to 15% (by monomer content) of amino-functional groups (PSil). The resulting polymers after addition of a triatomic, PSil-CO_2 or PSil-CS_2, possess viscosities and adhesiveness that are several orders of magnitude higher than those of the PSil. As expected, the PSil-CO_2 can be reconverted to their PSil forms by warming and bubbling N_2 through them (Scheme 1); this cycle has been repeated without detectable degradation. Also, as expected, warming the PSil-CS_2 results in permanent thiourea cross-links and loss of H_2S.[25] However, the triatomic adduct can be removed from both the PSil-CS_2 and the PSil-CO_2 by treatment with an acid such as acetic acid or trifluoroacetic acid, to produce protonated PSil that are flowing liquids. The results demonstrate that the simple chemical changes effected by addition or removal of a triatomic molecule to one of the PSil as a bulk polymer can change its properties in extraordinary fashions of both fundamental an applied interest. Furthermore, the magnitude of those changes can be tuned by the amount of amino functionalities in the PSil.

Experimental Section

Instrumentation. IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer interfaced to a PC, using an attenuated total reflection accessory or NaCl plates. Thermal gravimetric analysis (TGA) measurements were conducted under a dynamic nitrogen atmosphere (60 cm^3/min unless stated otherwise) at a 5 deg/min heating rate on a TGA Q50 thermo gravimetric analyzer (TA Instruments, New Castle, DE) interfaced to a computer. Differential scanning calorimetry (DSC) measurements were recorded on a DSC Q200 calorimeter (TA Instruments, New Castle, DE) interfaced to a TA Thermal Analyst 3100 controller, and equipped with a refrigerated cooling system (RCS90) to control the cooling rates. Samples were sealed in aluminum cells and heated at 10 deg/min under a N_2 atmosphere. Rheological experiments were performed on an Anton Paar Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria), using a parallel plate (radius 25 mm, gap 0.5 mm) or cone-and-plate (radius 25 mm, gap 0.5 mm, cone angle 1 , truncation 49 μm) geometry. Samples were equilibrated at 25 C for about 5 min before starting measurements (at 25 C) in order to eliminate any mechanical hysteresis. Dynamic frequency-sweep spectra were conducted in the linear viscoelastic regime of each sample as determined by dynamic stress-sweep tests. All measurements were carried out within one week of sample preparation. The percentage of CO_2 uptake (percent CO_2, based upon the stoichiometric amount calculated from the amino content of a PSil) was measured with a mercury buret apparatus that is based on a design described in ref 26.

Materials. 3-[(2-Aminoethyl)amino]propylmethoxysiloxane−dimethylsiloxane copolymer with 2−4% amino content ((2−4)PSil), 3-aminopropylmethylsiloxane−dimethylsiloxane copolymer with 6−7% amino content ((6−7)PSil), and 3-aminopropyl-terminated polydimethylsiloxane with (3.2−3.8)% amino content (3PSil) were from Gelest, Inc. which supplied the characterization data also. For (2−4)PSil: bp >205 C, mp <−60 C, and dynamic viscosity = 200−300 mPa·s;M_w not reported. For (6−7)PSil): bp >205 C, mp <−60 C, weight-average molecular weight $M_w \approx 4000-5000$, and dynamic viscosity = 80−120 mPa·s. For 3PSil: $M_w \approx 850-900$ and viscosity = 10−15 mPa·s. 3-Aminopropylmethylsiloxane−dimethylsiloxane copolymers with 10% and 15% amino groups (10PSil and 15PSil, respectively) were gifts from Dr. Dmitri Katsulis and Mr. Kenneth E. Zimmerman of Dow-Corning Corp., who also supplied their characterization data. For 10PSil: $M_w \approx 9950$, polydispersity (PD) = 1.71, and dynamic viscosity = 100 mPa·s. For 15PSil: $M_w \approx 9650$, PD = 1.71, and dynamic viscosity = 100 mPa·s. All reagents were used as received unless stated otherwise. Organic solvents for the swelling of gels were reagent grade or better (Aldrich). Carbon disulfide (anhydrous, 99.9%) was purchased from Aldrich. Carbon dioxide gas was generated by warming dry ice and was dried by passing it through a tube filled with Drierite ($CaSO_4$).

Sample Preparations. ***Synthesis of Ammonium Carbamate Polysiloxanes (PSil-CO_2).*** Dry CO_2 gas was bubbled gently through a stirred polysiloxane sample in a glass vial for 1 h. The vial was placed in a water bath during the CO_2 addition to dissipate the heat from the exothermic reaction.

Synthesis of Ammonium Dithiocarbamate Polysiloxanes (PSil-CS_2). Two molar equivalents of carbon disulfide were slowly added to a PSil in a closed glass vial. (*Warning*: *Carbon disulfide is a pungent*, *poisonous*, *highly volatile liquid that should be used with appropriate precautions*.) The vial was sonicated in an ultrasonic cleaner for 1 h and allowed to stand for 2 days, then the contents were placed under a house vacuum for 24 h to remove excess CS_2.

Synthesis of Thiourea Cross-Linked Polysiloxanes (PSil-CS_2-H). The procedure above was followed but the sample was heated to 120 °C for 1 h and cooled to room temperature 3 times instead of being placed under a house vacuum. The resulting material was kept in a vacuum oven at 40 °C for 24 h to remove any dissolved H_2S and residual CS_2. The thiourea-containing samples are slightly yellow. (*Warning*: *H_2S is a very toxic gas that should be handled with appropriate precautions.*)

Acidification Experiments. Either acetic acid or trifluoroacetic acid (1 mL) was added to 1 g of PSil-CO_2 or PSil-CS_2 in a closed glass vial and the mixture was stirred for 1 h.

Procedure for Swelling. A weighed aliquot (ca. 50 mg) of polymer and 3 mL of a liquid were placed in a closed screw-cap glass vial for 24 h. The polymer was removed, its surface was dried quickly on a piece of filter paper, and it was reweighed. The swelling ratio (S%) was calculated by eq 3, where W_g and W_p are the weights of swelled and dry polymer, respectively.

$$S\%(w/w) = [(W_g - W_p)/W_p] \times 100\% \tag{3}$$

The temporal uptake of liquid was determined by removing the polymer at different times from the liquid, weighing it, and placing it anew into the liquid until no weight increase could be detected.

Adhesion Test Procedures. An aliquot of polymer was placed on the steel base plate of the rheometer, and the upper parallel steel plate was moved into contact with the upper surface of the polymer. The initial gap was set at 0.15 mm. The system was left undisturbed for 10 min to form an equilibrated interfacial contact. Then, the top plate was lifted vertically to a plate gap of 0.50 mm. The normal force response in this process was recorded by the rheometer. All measurements were performed at 25 °C. No data were collected with PSil-CS_2 because the force required exceeded the capabilities of the rheometer.

Results and Discussion

Characterization of Polysiloxanes. Bubbling CO_2 through the stirred polysiloxanes for a few minutes resulted in a noticeable and significant increase in viscosity (Figure 1). In a separate experiment reported in Figure S4 of the Supporting Information, a flowing 15PSil sample like that at the left was regenerated by bubbling N_2 gas through its nonflowing 15PSil-CO_2 analogue at 80 °C (to increase the rate of displacement of CO_2). The cross-linking from formation of ionic pairs, as ammonium and carbamate centers are created (Scheme 1), can be monitored conveniently by FT-IR spectroscopy (Figure S1 of the Supporting Information with (6−7)PSil as an example). After CO_2 bubbling, a C═O stretching band at 1640 cm^{-1}, typical of a carbamate,[27] was observed as a shoulder. In addition, a medium strong band, centered at 1586 cm^{-1}, can be assigned to the N−H bending;[28] the corresponding peak was located at 1598 cm^{-1} in (6−7)PSil before CO_2 bubbling and after passing N_2 through (6−7)PSil-CO_2. Also, a band ascribed to the asymmetric vibration of C−Si−C shifted to 1472 cm^{-1} upon bubbling CO_2 through the (6−7)PSil. The change in the IR frequency demonstrates that a chemical change occurred, and it is reasonable to ascribe it to the uptake of CO_2.

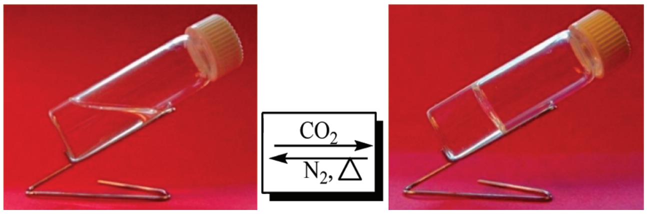


Figure 1. Before (left) and after (right) bubbling CO_2 through neat (6−7)PSil at 25 °C.

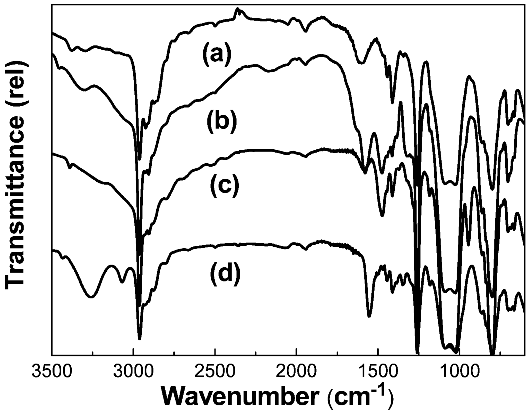


Figure 2. Vertically offset IR spectra of 3PSil (a), 3PSil-CO_2 (b), 3PSil-CS_2 (c), and 3PSil-CS_2-H (d).

Similarly, exposure of the amino-terminated polysiloxane 3PSil to CO_2 led to a rapid increase in its viscosity. The infrared spectrum in Figure 2 for the product of the reaction is consistent with the 3PSil-CO_2 structure; its new absorption bands are almost the same as those found in the spectrum of 15PSil-CO_2. The formation of ammonium dithiocarbamates in polysiloxanes upon addition of CS_2 is also indicated by FT-IR spectra. An N−H bending band was found at 1552 cm^{-1}, and the bands at 1370 and 945 cm^{-1} can be assigned to C═S and C−S stretchings, respectively.[29] Upon heating a 3PSil-CS_2 sample to 120 °C (to form 3PSil-CS_2-H), the N−H stretching band shifts from 3190 cm^{-1} to 3068 cm^{-1} as a result of H-bonding interactions. The C−S stretching band at 945 cm^{-1} is no longer present and the C═S stretching band shifts to 1348 cm^{-1}.[30] The IR frequencies for the thiourea groups in 3PSil-CS_2-H are very similar to those found in the spectrum of *N*,*N′*-dialkylthioureas obtained by heating alkylammonium alkyldithiocarbamates.[31]

Weight Percent CO_2 Uptake. The temporal course of uptake of (1 atm) CO_2 by the polysiloxanes has been followed. Because the uptake rate is dependent on the surface area of the polysiloxanes exposed to the CO_2 gas and the rate of stirring, neither of which can be reproduced exactly, no attempt has been made to compare quantitatively rates of uptake by the different PSil polymers. However, the surface area and stirring rate in each run were nearly the same, so that the order of rates among

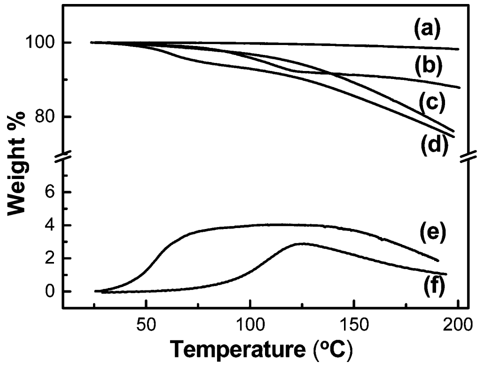


Figure 3. TGA curves of 3PSil-CS$_2$-H (a) heated from room temperature, neat 3PSil (b), 3PSil-CO$_2$ (c), and 3PSil-CS$_2$ (d). Difference curves between 3PSil and 3PSil-CO$_2$ curves (e) and between 3PSil and 3PSil-CS$_2$ curves (f) are shown as well.

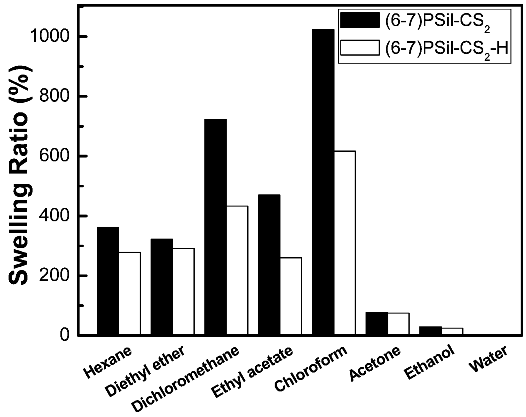


Figure 4. Swelling ratios of (6−7)PSil-CS$_2$ (■) and (6−7)PSil-CS$_2$−H (□) in various liquids at 25 C.

the PSil is known qualitatively. The plateau (saturation) values for uptake are independent of both variables and, therefore, are reproducible quantitatively.

A typical plot for (6−7)PSil is shown in Figure S5 of the Supporting Information. The other polysiloxanes behaved in an analogous fashion. The uptake was rapid during the first 5 min and reached its maximum, ∼130% of the expected amount for complete reaction, after ca. 60 min. The 30% excess is ascribed to physically adsorbed CO$_2$.[32]

Thermally Induced Changes and Stabilities. Examples of the weight losses from heating 3PSil, 3PSil-CO$_2$, 3PSil-CS$_2$, and 3PSil-CS$_2$-H by TGA are collected in Figure 3. The difference curve between 3PSil-CO$_2$ and 3PSil shows a 4.0% higher loss at 80 C from 3PSil-CO$_2$ than from 3PSil; the calculated weight of CO$_2$ in 3PSil-CO$_2$, assuming complete conversion, is ca. 4.0%. We assume that the excess (i.e., physically adsorbed) CO$_2$ is lost over time as the 3PSil-CO$_2$ samples equilibrate with air.

Similarly, heating 3PSil-CS$_2$ results in a 2.8% weight loss at 120 C. This value is close to the 3.1% loss predicted if each of the ammonium dithiocarbamate ion pairs loses one molecule of H$_2$S.[25] As expected, the thiourea-containing polysiloxane, 3PSil-CS$_2$-H, is more stable thermally than its ionically cross-linked analogue, 3PSil-CS$_2$.

Representative DSC thermograms of polysiloxanes are collected in Figures S6 and S7 of the Supporting Information. The first-heating thermogram of 15PSil-CO$_2$ includes a broad endotherm that extends from 60 to 120 C that is attributed to loss of CO$_2$. The first-heating thermogram of 15PSil-CS$_2$ has a broad endotherm from 75 to 150 C that is in good agreement with the expectation from the TGA results that H$_2$S is being lost. No subsequent exotherms or endotherms were detected during the first cooling or second heating of the sample; conversion of ammonium dithiocarbamate to thiourea is complete after the initial heating.

The isothermal stability of DPAS-15-CO$_2$ was monitored by TGA. The reversion of the ionic to uncharged forms of the polysiloxanes is very slow at 25 C in the presence of a dry nitrogen gas flow of 60 cm^3/min (0.70% weight, corresponding to ∼0.16 equiv of CO$_2$, was lost during 60 min) and is even slower in the absence of a wind (0.08% or $\sim 2 \times 10^{-2}$ equiv of CO$_2$ was lost during 60 min) (Figure S8b of the Supporting Information). At 75 or 100 C, 96% of the weight loss calculated for total removal of the CO$_2$ is achieved after less than 5 min with N$_2$ flow (Figure S8a of the Supporting Information).

Taken together, these results clearly demonstrate that the PSil-CO$_2$ have good thermal stability at room temperature without nitrogen flow, and good reversibility at elevated temperature with nitrogen flow.

Swelling and Kinetics of Swelling. The cross-linked PSils can be swollen into gel states by a variety of liquids. An example, the increase in size of (6−7)PSil-CS$_2$ swelled by hexane, is shown in Figure S9 of the Supporting Information and the weight increases observed after swelling with a variety of liquids are displayed in Figure 4. We attribute the greater swelling capacity of (6−7)PSil-CS$_2$ than (6−7)PSil-CS$_2$-H to the ability of the ionic cross-links of the former to “float” from one position to another in a manner that maximizes the network stability in the presence of a liquid; covalent cross-links are “fixed” and, therefore, unable to readjust to the presence of a swelling liquid. Even before swelling, (6−7)PSil-CS$_2$-H is a much stiffer material than (6−7)PSil-CS$_2$. The swelling ratios reported here are larger than those from other cross-linked poly(dimethylsiloxane) gels,[33] probably as a result of the longer side chains in the PSil and the triatomic cross-linkers which leave the 3-D networks more flexible (i.e., the cationic and anionic centers remain paired, but the specific groups constituting the pairs can change with time and degree of swelling).

As mentioned above, the degree of cross-linking can be controlled also by the amount of the triatomic molecule added to the polymer. Thus, 0.4 equiv of CS$_2$ was added to 15PSil to simulate the degree of cross-linking in fully reacted (6−7)PSil. Under these conditions, swelling ratios in hexane were 330% for 15PSil-0.4CS$_2$ and 250% for 15PSil-0.4CS$_2$-H (i.e., the sample of 15PSil-0.4CS$_2$ that was heated and then swelled). The corresponding (6−7)PSil samples have swelling ratios in hexane, 360% and 280%, that are very near these values. From this observation, we conclude that the ammonium dithiocarbamate cross-links are not affected in an important fashion by the presence of free amino groups on the polymer chains. However, when the nature of the amino groups differs, as they do between (2−4)PSil, in which each side chain contains one primary and one secondary amino group, and 15 PSil, in which each side chain contains only one primary amino group (see Scheme 1), the properties of the partially reacted 15PSil do not match those in which all of the amino groups of (2−4)PSil are thought to be reacted (vide infra).

The kinetics of swelling[34] of these two polysiloxanes by hexane has been investigated as well (Figure S10 of the Supporting Information).[35] Swelling of (6−7)PSil-CS$_2$ is rapid during the first several minutes and reaches an equilibrium after ca. 2 h; its rate and its equilibrium value are higher than those of (6−7)PSil-CS$_2$-H. The smaller spaces intrinsically available to hexane molecules between chains in the thiourea-cross-linked

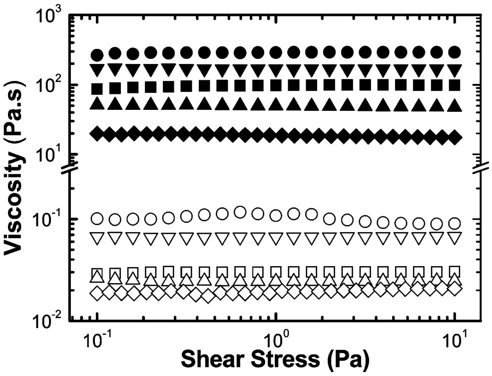


Figure 5. Viscosities (Pa·s) of samples before and after bubbling CO_2 as a function of shear stress (Pa) at 25 °C: 15PSil-CO_2 (●), 10PSil-CO_2 (▼), (6−7)PSil-CO_2 (■), (2−4)PSil-CO_2 (▲), 3PSil-CO_2 (♦), 15PSil (○), 10PSil (▽), (2−4)PSil (□), (6−7)PSil (△), and 3PSil (◇).

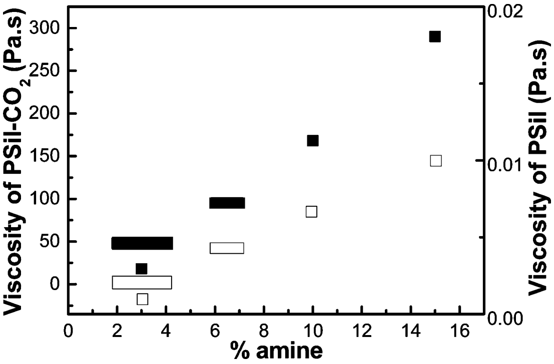


Figure 6. Viscosities of PSil (□, right Y-axis) and PSil-CO_2 (■, left Y-axis) versus % amine functionality.

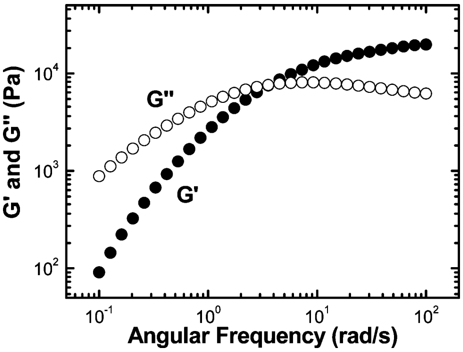


Figure 7. Storage (G', ●) and loss moduli (G'', ○) of (2−4)PSil-CS_2 at 25 °C.

polysiloxane networks (vide ante) can account for both observations.

Rheological Properties. To determine the relationships among amine content, polymer structure, and viscoelastic properties, both static and dynamic rheological studies have been conducted on the polysiloxanes before and after exposing them to one of the triatomic molecules. Figure 5 displays steady-shear rheological data for the polysiloxanes before and after cross-linking by CO_2. Viscosities (η, Pa·s) are independent of shear rate, as expected of Newtonian liquids.[36] However, η increases by ca. 3 orders of magnitude after each PSil is exposed to CO_2. The increase in viscosity is especially noticeable in the two polysiloxanes with the highest amino group contents, 10PSil-CO_2 and 15PSil-CO_2.

The viscosities of the PSil-CO_2 increase in a regular fashion with increasing amino group content (Figure 6). Although there is no apparent relationship between amino group content and the *ratio* of the PSil-CO_2 and PSil viscosities (Table S2 of the Supporting Information), the viscosities of the neat PSil polymers are known to be proportional to their molecular weights.[37] We emphasize here that cross-links within the 3PSil-CO_2 network do not result in a true 3-dimensional network—the amino end-groups can extend the lengths of the chains only and, thus, produce 1-dimensional topological networks that can appear to be pseudo-3-dimensional networks if the chains intertwine or their cation−anion pairs aggregate in pairs, providing quadrupolar interactions.

The rheological properties of two polysiloxanes containing comparable frequencies of amino groups but one, (2−4)PSil, capable of making 3-D cross-linked networks and the other, 3PSil, capable of making extended 1-D structures with increased molecular weights, have been compared. Addition of CO_2 or CS_2 increased the viscosities of both (Supporting Information, Figure S14). Also, the stronger attachment of CS_2 than CO_2 to the amine groups and the greater polarizability of the dithiocarbamate make the viscosity of 3PSil-CS_2 higher than that of 3PSil-CO_2, but both are less viscous than their (2−4)PSil analogues which can form 3-dimensional cross-linked networks in the presence of one of the triatomic molecules.

The viscosity of the (thiourea-containing) 3PSil-CS_2-H, made by heating 3PSil-CS_2 to ca. 120 °C, is ca. 20× that of its immediate precursor. The large increase can be attributed to the covalent nature of the thiourea links between 3PSil chains and the ability of the thiourea groups to establish strong H-bonding networks.[38,39] The loss modulus G'' of this material exceeds the storage modulus G' over the entire range of frequencies examined and is a strong function of frequency (Figure S15 of the Supporting Information), whereas G' is nearly independent of frequency; G' of all of the polysiloxanes with amino groups on side chains is strongly dependent on frequency (Figure S11, Supporting Information). In addition, the viscoelastic properties of 3PSil-CS_2 indicate that this material is like both a viscous liquid and a gel.[40]

However, (2−4)PSil-CS_2 exhibits a different rheological behavior from the other polysiloxane samples, whether they are treated with CO_2 or CS_2 (Figure 7). Its viscoelastic response can be divided into two regimes: at lower frequencies, G'' exceeds G' (a viscous response); at higher frequencies, above the crossing point (ω_c, where the system relaxation time, t_R, is ca. $1/\omega_c$), G'' becomes lower than G' (an elastic response of a transient entangled network[41]). Its steady-shear rheology differs from those of the other CO_2- and CS_2-treated polysiloxanes as well (Figure S12 of the Supporting Information): at low angular frequencies, viscosity increases with increasing shear stress (Pa); above the critical shear stress, the viscosity becomes independent of shear stress, as expected for a Newtonian liquid: in behavior typical of viscous liquids, both G' and G'' increase with increasing angular frequencies (Figure S11 of the Supporting Information); these are extremely viscous fluids without gel-like properties.

As mentioned above, partial reaction of 15PSil with CS_2 to effect cross-links has a different consequence than that when a polysiloxane with amino groups of a different type and in a different distribution along a chain, such as (2−4)PSil, is completely reacted with CS_2. Thus, addition of 0.2 equiv of CS_2 to 15PSil, to simulate the frequency of ammonium dithiocarbamate groups in (2−4)PSil-CS_2, led to polymers with very different rheological properties (Figure S13 in the Supporting Information). These results, in combination with those from swelling 15PSil-0.4CS_2 (to simulate (6−7)PSil-CS_2),

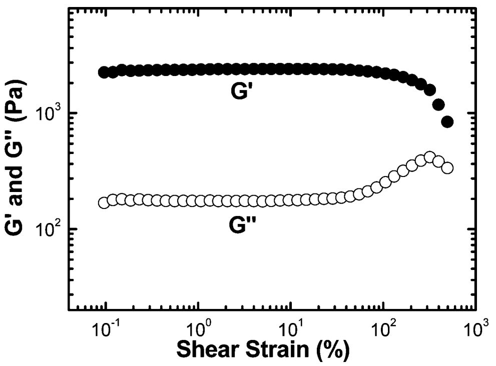


Figure 8. Storage (G', ●) and loss (G'', ○) moduli of (6−7)PSil-CS_2 at 25 C.

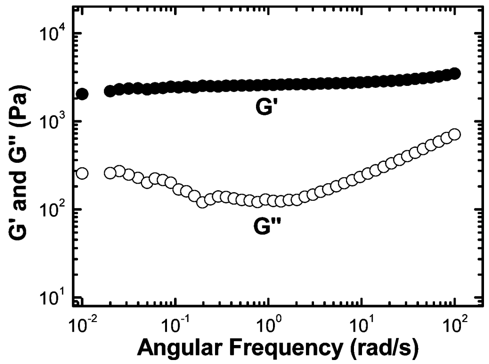


Figure 9. Storage (G', ●) and loss (G'', ○) moduli of (6−7)PSil-S_2 at 25 C

demonstrate that the structure of the amino-containing polysiloxane must be considered carefully when attempting to understand the consequences of adding an X=Y=X cross-linker.

According to the dynamic strain sweep measurements in Figure 8, (6−7)PSil-CS_2 is a soft elastic material; G' decreases as shear strain increases. However, G'' increases and then decreases in the high-strain region. This behavior, a "weak strain overshoot", arises from the strain-induced imbalance between the formation and destruction of network junctions.[42] If the polysiloxane backbones with ammonium dithiocarbamate groups (as well as those with ammonium carbamate groups) are highly extended as a result of the electrostatic repulsion from the charged centers, the resultant microstructure networks can resist deformation while a weak strain is imposed and G'' increases. However, the microstructures are destroyed by large strains, decreasing G''.

On the basis of the observations in Figure 8, the dynamic rheological data for (6−7)PSil-CS_2 in Figure 9, showing a gel-like behavior—the storage modulus G' greatly exceeds the loss modulus G'' over the entire range of frequencies and both moduli are almost independent of angular frequencies—are not surprising. The lack of frequency dependence indicates that the sample does not relax in the time frame of ≤ 100 s. The (6−7)PSil-CS_2 swollen by chloroform and ethyl acetate and PSil-CS_2-H swollen by hexane also behave rheologically like gels (Figures S16 and S17 in the Supporting Information).

Adhesion Tests. PSil-CO_2 samples adhered[43] strongly to several different surfaces. Figure S18 of the Supporting Information provides quantitative data for the adhesion to steel as a function of amino group content. Although adhesion is highest for 15PSil-CO_2, the dependence on amino group content is not linear. The ability of the PSil-CO_2 to adhere to other rigid substrates has been examined only qualitatively as a result of instrumental limitations. The results indicate that the PSil-CO_2 have strong adhesive forces to glass in the opening mode (i.e., pulling the plates apart by applying a force perpendicular to the plate surfaces); the forces are weaker for Teflon, paper, cardboard, and copper, but all are substantial. Adhesion to any of the materials tested was much stronger for the PSil-CO_2 than for the corresponding PSil. We note that adhesion of 15PSil-CO_2 even to Teflon was rather strong.

We also evaluated the qualitative adhesiveness of the PSil-CO_2 under different environmental conditions. There was no discernible difference in the adhesion of 15PSil-CO_2 to copper plates during 24 h when the sandwiched samples were left in air or submerged under tap water. In both cases, the contact surface area of the polymer to the outside environment was very small, conditions that disfavor loss of CO_2 via out-diffusion and entry of water via in-diffusion. However, the substrates could be separated much more easily when a sandwich was warmed for several minutes to 40 C (i.e., below the CO_2 loss temperature according to DSC and TGA measurements); recooling the same sandwich to room temperature increased again the adhesive strength.

Acidification Treatment. It is known that protonation of the carbamate of the dithiocarbamate groups results in a rapid loss of their triatomic moieties and formation of ammonium groups.[21c] When the ammonium carbamate being treated is part of a polymeric material, addition of acid causes a precipitous decrease in viscosity, analogous to that experienced by ammonium carbamates when they are heated to remove CO_2.[16c,44] Similarly, decarboxylations of the PSil-CO_2 were effected upon application of an acid to their surfaces; the viscosities were reduced and small bubbles (presumably CO_2) were formed in the materials when acetic acid (pK_a 4.8) was added. However, the PSil-CS_2 was converted to flowing liquids only after addition of the stronger trifluoroacetic acid (pK_a 0.5).

Summary and Conclusions

We have developed a facile method for the cross-linking of polysiloxanes with amino functionalities via addition of an uncharged triatomic molecule, CO_2 or CS_2.The cross-linking with CO_2 can be reversed easily by mild heating while that with CS_2 cannot be—warming the ammonium dithiocarbamates that are formed upon exposure of the PSil to CS_2 results in covalent thiourea cross-links and expulsion of H_2S. The changes of the thermal, rheological, and adhesive properties of the polysiloxanes before and after ionic and covalent cross-linking have been examined as a function of the degree of amino substitution on the polymer chains—several of the properties of the systems can be "tuned" by varying the amino group content along the polymer chains. A remarkable aspect of this work is the extremely large increases in the viscosity and adhesiveness that can be attained simply by bubbling CO_2 (or adding CS_2) through the polymers. Although there is a direct relationship between the absolute viscosity and the amount of amine functionality in the polymers after addition of a triatomic, no correlation was obvious before, where molecular weight of the polymer chains appears to be the most important factor. The strong adhesion of the PSil-CO_2 polymers to various substrates, combined with their reversibility to the original PSils (and loss of adhesive strength) opens prospects for creating reversible, stimuli-responsive adhesives[45] or sealants in which adhesion can be controlled by environmental conditions.[46]

The PSil-CS_2 and the PSil-CS_2-H materials that they yield upon heat treatments are also polymer gels, and their gel-like properties are apparent from their ability to be swelled to several-fold their original volumes by some organic solvents. Again, this ability to be swelled and deswelled may lead to interesting new applications for polysiloxanes. Although heating the PSil-CS_2 cannot reconvert them to their PSil forms, as can the PSil-CO_2, exposing them to a strong acid produces ammonium groups along the chains (i.e., protonated PSil) that flow again like liquids, have lost their gel-like properties, and are no longer strong adhesives.

In summary, we have demonstrated that simple organic chemistry can be applied to a set of complex polymers to change enormously their macroscopic properties.The nature of those changes have been documented step-by-step through a combination of spectroscopic and rheological measurements.This facile strategy provides not only an effective alternate to the more classical method to cross-link polymers, but also an easily accessed route to two classes of novel materials with interesting physical and chemical properties.

Potential new applications include the use of polysiloxanes as cleaning agents in art conservation, where rheoreversibility and swelling by organic liquids are highly desirable attributes.[47] In addition, our swollen polysiloxanes may be useful packing materials for chromatography[48] and as aligning media for NMR measurements.[49] This approach may also be useful in the synthesis of new polymers from monomers pretreated with CO_2 or CS_2.[50] Experiments to exploit some of these uses and to expand the range of polymers that are cross-linked by these methods are underway.

Acknowledgment. We thank the U.S. National Science Foundation for its support of this research. We also gratefully acknowledge Dr. Dimitri Katsoulis and Mr. Kenneth E. Zimmerman of Dow-Corning Corporation for synthesizing and providing the 10PSil and 15PSil polymers.

Supporting Information Available: IR spectra, figures of percent CO_2 uptake as a function of time, isothermal TGA weight loss curves, DSC thermograms, photographs of polysiloxane gels before and after swelling, swelling kinetic curves, steady-shear and dynamic rheology, and a table of viscosity values before and after bubbling CO_2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) *Silicon-Based Polymer Science: A comprehensive resource*; Advances in Chemistry Series 224; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990. (b) Clarson, S. J.; Smith, S. D.; Owen, M. J. *Silicones and Silicone-Modified Materials*; American Chemical Society: Washington, DC, 2000. (c) Manners, I. *Angew. Chem., Int. Ed.* **1996**, *35*, 1602–1621. (d) Mark, J. E. *Acc. Chem. Res.* **2004**, *37*, 946–953.

(2) *Physical Properties of Polymers Handbook*, 2nd ed.; Mark, J. E., Ed.; Springer: Berlin, Germany, 2007. (b) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*, 2nd ed.; Oxford University Press: New York, 2005; pp 154−199. (c) Erman, B.; Mark, J. E. *Structures and Properties of Rubberlike Networks*; Oxford University Press: New York, 1997.

(3) Gao, Z.; Nahrup, J. S.; Mark, J. E.; Sakr, A. *J. Appl. Polym. Sci.* **2003**, *90*, 658–666.

(4) Batra, A.; Cohen, C.; Archer, L. A. *Macromolecules* **2005**, *38*, 7174–7180.

(5) (a) Kato, D.; Masaike, M.; Majima, T.; Hirata, Y.; Mizutani, F.; Sakata, M.; Hirayama, C.; Kunitake, M. *Chem. Commum.* **2002**, *2616*, 2617. (b) Park, H. B.; Kim, J. K.; Nam, S. Y.; Lee, Y. M. *J. Membr. Sci.* **2003**, *220*, 59–73. (c) Miller, A. L., II; Bowden, N. B. *Chem. Commum.* **2007**, *20*, 2051–2053.

(6) Verma, M. K. S.; Majumder, A.; Ghatak, A. *Langmuir* **2006**, *22*, 10291–10295.

(7) Oomen, A. G.; Mayer, P.; Tolls, J. *Anal. Chem.* **2000**, *72*, 2802–2808.

(8) (a) Paul, K. E.; Prentiss, M.; Whitesides, G. M. *Adv. Funct. Mater.* **2003**, *13*, 259–263. (b) Mcdonald, J. C.; Whitesides, G. M. *Acc. Chem. Res.* **2002**, *35*, 491–499.

(9) (a) Cho, S. H.; Andersson, H. M.; White, S. R.; Sottos, N. R.; Braun, P. V. *Adv. Mater.* **2006**, *18*, 997–1000. (b) Wu, D. Y.; Meure, S.; Solomon, D. *Prog. Polym. Sci.* **2008**, *33*, 479–522.

(10) (a) Abe, Y.; Gunji, T. *Prog. Polym. Sci.* **2004**, *29*, 149–182. (b) Abbasi, F.; Mirzadeh, H.; Katbab, A. A. *Polym. Int.* **2001**, *50*, 1279–1287.

(11) (a) Zhang, X.; Xie, P.; Shen, Z.; Jiang, J.; Zhu, C.; Li, H.; Zhang, T.; Han, C. C.; Wan, L.; Yan, S.; Zhang, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3112–3116. (b) Zhou, Q. L.; Yan, S. K.; Han, C. C.; Xie, P.; Zhang, R. B. *Adv. Mater.* **2008**, *20*, 2970–2976.

(12) (a) Zhang, Z. C.; Sherlock, D.; West, R.; West, R.; Amine, K.; Lyons, L. J. *Macromolecules* **2003**, *36*, 9176–9180. (b) Ngoumeni-Yappi, R.; Fasel, C.; Riedel, R.; Ischenko, V.; Pippel, E.; Woltersdorf, J.; Clade, J. *Chem. Mater.* **2008**, *20*, 3601–3608.

(13) Zhang, Y.; Cao, M.; Guo, G. Q.; Sun, J.; Li, Z.; Xie, P.; Zhang, R. B.; Fu, P. F. *J. Mater. Chem.* **2002**, *12*, 2325–2330.

(14) Nair, K. P.; Breedveld, V.; Weck, M. *Macromolecules* **2008**, *41*, 3429–3438.

(15) Serpe, M. J.; Craig, S. L. *Langmuir* **2007**, *23*, 1626–1634.

(16) (a) George, M.; Weiss, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 10393–10394. (b) George, M.; Weiss, R. G *Langmuir* **2002**, *18*, 7124–7135. (c) Carretti, E.; Dei, L.; Baglioni, P.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 5121–5129.

(17) (a) Yamada, T.; Lukac, P. J.; George, M.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 967–969. (b) Yamada, T.; Lukac, P. J.; Yu, T.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 4761–4768. (c) Yu, T.; Yamada, T.; Gaviola, C. G.; Weiss, R. G. *Chem. Mater.* **2008**, *20*, 5337–5344.

(18) (a) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. *Nature (London)* **2005**, *436*, 1102. (e) Phan, L.; Andreatta, J. R.; Horvey, L. K.; Edie, C. F.; Luco, A.-L.; Mirchandani, A.; Darensbourg, D. J.; Jessop, P. G. *J. Org. Chem.* **2008**, *73*, 127–132.

(19) (a) Endo, T.; Nagai, D.; Monma, T.; Yamaguchi, H.; Ochiai, B. *Macromolecules* **2004**, *37*, 2007–2009. (b) Ochiai, B.; Yokota, K.; Fujii, A.; Nagai, D.; Endo, T. *Macromolecules* **2008**, *41*, 1229–1236.

(20) (a) Xu, H.; Hampe, E. M.; Rudkevich, D. M. *Chem. Commum.* **2003**, 2828–2829. (b) Xu, H.; Rudkevich, D. M. *Chem.—Eur. J.* **2004**, *10*, 5432–5442. (c) Rudkevich, D. M.; Xu, H. *Chem. Commum.* **2005**, 2651–2659.

(21) (a) Hori, Y.; Nagano, Y.; Nakao, J.; Taniguchi, H. *Chem. Express* **1986**, *1*, 173–176. (b) Hori, Y.; Nagano, Y.; Nakao, J.; Fukuhara, T.; Taniguchi, T. *Chem. Express.* **1986**, *1*, 224–227. (c) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857–3897.

(22) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 1017–1025.

(23) Laidler, K. J.; Meiser, J. H. *Physical Chemistry*, 3rd ed.; Houghton Mufflin: Boston, MA, 1999; p 267

(24) DeLassus, P. T.; Whiteman, N. F. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999; p V/168.

(25) Schroeder, D. C. *Chem. Rev.* **1955**, *55*, 181–228.

(26) House, H. O. *Modern Synthetic Reaction*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 2.

(27) Corset, C.; Froment, F. *J. Phys. Chem.* **1990**, *94*, 6908–6911.

(28) Lobo, H.; Bonilla, J. V. *Handbook of Plastics Analysis*; Marcel Dekker: New York, 2003..

(29) (a) Nakamoto, K.; Fujita, J.; Condrate, R. A.; Morimoto, Y. *J. Chem. Phys.* **1963**, *39*, 423–427. (b) Gosavi, R. K.; Agarwala, U.; Rao, C. N. R. *J. Am. Chem. Soc.* **1967**, *89*, 235–239.

(30) Boas, U.; Karlsson, A. J.; de Waal, B. F. M.; Meijer, E. W. *J. Org. Chem.* **2001**, *66*, 2136–2145.

(31) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 1017–1025.

(32) Guadagno, T.; Kazarian, S. G. *J. Phys. Chem. B* **2004**, *108*, 13995–13999.

(33) (a) Brennan, D. P.; Dobley, A.; Sideris, P. J.; Oliver, S. R. *Langmuir* **2005**, *21*, 11994–11998. (b) Favre, E. *Eur. Polym. J.* **1996**, *32*, 1183–1188.

(34) (a) Sonmez, H. M.; Wudl, F. *Macromolecules* **2005**, *38*, 1623–1626. (b) Wang, C.; Li, Y.; Hu, Z. *Macromolecules* **1997**, *30*, 4727–4732.

(35) We have not treated these data according to Fick's[35a,b] second law because the samples employed do not have constant thicknesses. (a) Comyn, J. *Polymer permeability*; Elsevier: London, U.K., 1985. (b) Crank, J. *The Mathematics of Diffusion*; Oxford University Press: Oxford, U.K., 1975.

(36) Khan, S. A.; Royer, J. R.; Raghavan, S. R. *Aviation Fuels with Improved Fire Safety: A Proceeding*; National Academy Press: Washington, DC, 1997; pp 3146.

(37) Carraher, C. E. *Seymour/Carraher's polymer chemistry*, 7th ed.; CRC Press: Boca Raton, FL, 2008; pp 4982.

(38) Custelcean, R. *Chem. Commum.* **2008**, *295*, 307.

(39) (a) Menger, F. M.; Caran, K. L. *J. Am. Chem. Soc.* **2000**, *122*, 11679–11691. (b) Yabuuchi, K.; Marfo-Owusu, E.; Kato, T. *Org. Biomol. Chem.* **2003**, *1*, 3464–3469. (c) Pèrez-Folch, J.; Subirana, J. A.; Aymami, J. *J. Chem. Crystallogr.* **1997**, *27*, 367–369. (d) Ramanathan, A.; Siakumar, K.; Subramanian, K.; Janarthanan, N.; Ramadas, K.; Fun, H.-K. *Acta Cryatallogr. Sect. C* **1995**, *51*, 2446–2450.

(40) (a) Ketner, A. M.; Kumar, R.; Davies, T. S.; Elder, P. W.; Raghavan, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 1553–1559. (b) Tung, S. H.; Huang,

Y. E.; Raghavan, S. R. *Langmuir* **2007**, *23*, 372–376. (c) Tung, S. H.; Huang, Y. E.; Raghavan, S. R. *Soft Matter* **2008**, *4*, 1086–1093.

(41) (a) Macosko, C. W. *Rheology: Principles, Measurements and Applications*; VCH Publishers: New York, 1994. (b) Winter, H. H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367–382.

(42) (a) Hyun, K.; Kim, S. H.; Ahn, K. H.; Lee, S. J. *J. Non-Newtonian Fluid Mech.* **2002**, *107*, 51–65. (b) Sim, H. G.; Ahn, K. H.; Lee, S. J. *J. Non-Newtonian Fluid Mech.* **2003**, *112*, 237–250.

(43) Veselovskii, R. A. *Adhesion of polymers*; McGraw-Hill: New York, 2002.

(44) Carretti, E; Dei, L; Macherelli, A.; Weiss, R. G. *Langmuir* **2004**, *20*, 8414–8418.

(45) Khongtong, S.; Ferguson, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 7254–7255.

(46) We envision that these polysiloxanes can be employed as reversible, temperature-dependant adhesives. Specifically, substrates strongly adhere at room temperature to the polysiloxanes exposed to CO_2, and their adhesive strength can be tuned by changing the temperature.

(47) (a) Carretti, E.; Dei, L.; Weiss, R. G. *Soft Matter* **2005**, *1*, 17–22. (b) Carretti, E.; Dei, L.; Weiss, R. G.; Baglioni, P. *J. Cult. Heritage* **2008**, *9*, 386–393.

(48) Chang-Chien, G. P.; Lee, W. S.; Tsai, J. L.; Jeng, S. H. *J. Chromatogr. A* **2001**, *932*, 97–105.

(49) Freudenberger, J. V.; Spiteller, P.; Bauer, R.; Kessler, H.; Luy, B. *J. Am. Chem. Soc.* **2004**, *126*, 14690–14691.

(50) (a) Alauzun, J.; Besson, E.; Mehdi, A.; Reyè, C.; Corriu, R. J. P. *Chem. Mater.* **2008**, *20*, 503–513. (b) Soutullo, M. D.; Odom, C. I.; Wicker, B. F.; Henderson, C. N.; Stenson, A. C.; Davis, J. H. *Chem. Mater.* **2007**, *19*, 3581–3583.

JP900115G