

Telechelic Siloxanes with Hydrogen-Bonded Polymerizable End Groups. I. Liquid Rubbers and Elastomers

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ABSTRACT: Functional siloxanes are widely used in the synthesis of model networks used in rubber elasticity studies, and various functional siloxanes are also used in the synthesis of silicone rubbers. We present here the results of studies of two classes of telechelic, free-radically polymerizable siloxanes carrying either amide or urea groups attached at both ends of siloxane chain. The presence of polar, hydrogen-bonding end-groups favors the formation of aggregates which is reflected in the drastically increased viscosity of the resulting "liquid rubbers." In addition, such aggregation accounts for high local concentrations of reactive groups thus making it possible to have high molecular weight precursors undergo facile room temperature polymerization. In this article, we study the effect of the nature of these functional groups on the viscosity of polymerizable "liquid rubbers," finding that the different endgroups lead

to dramatically different viscosities. We also study the silicone rubber films obtained by a UV-initiated free-radical polymerization of the liquid rubbers, using dynamic mechanical analysis and large-strain uniaxial deformation. We find here that important properties such as plateau modulus and Young's modulus are highly dependent on both endgroup type and precursor molecular weight. The crosslinking of telechelic siloxanes in dilution was also studied to further explore the effect of crosslink density of the mechanical properties of the model networks. Finally, we evaluated the role of dangling ends within the networks through the incorporation of monofunctional macromers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 756–766, 2010

Key words: elastomers; functionalization of polymers; networks; polysiloxanes; viscosity

INTRODUCTION

Although "the area of rubber-like elasticity has had one of the longest and most distinguished histories in all of polymer science,"¹ only in the recent decades has considerable progress been made in an attempt to elucidate molecular aspects of the correlation between elastic behavior and the structure of polymer networks.² These efforts justified much interest in the synthesis and characterization of various "model" elastomeric networks, that is, networks whose structures are controlled through specific synthetic procedures involving selective crosslinking reactions. A group of polymers that attract special attention in the studies of model networks are silicones because a broad spectrum of well-characterized functional silicone polymers is potentially readily available and many curing chemistries can be applied to form "model" networks. Knowledge of imperfections in the network structure is essential if the absolute values of moduli are to be interpreted meaningfully in studies of model networks. By using siloxane systems, it has been shown that side reac-

tions (incomplete reactions) give inelastic free chain ends (dangling ends) and reduce the modulus while entanglements cause the modulus to increase, with the result that an apparently perfect, affine behavior can be observed.^{3,4} Another type of imperfection that occurs naturally in end-linking polymerization is the formation of inelastic loops, a result of intramolecular reaction.² The effect of both entanglements and dangling ends and of inelastic loop formation on polymeric networks deserves much more attention. One of the possible means of varying the amounts of such structures is by the formation of "model" networks in dilution,^{5–7} but such a procedure can introduce still more artifacts, for example, by affecting the completeness of cure. Recent such work on model silicone networks has been described in a number of articles and summarized in numerous textbooks and reviews.^{8–12}

Telechelic siloxanes based on high purity silicone diamines have been extensively studied in this laboratory as new methods of synthesis of silicone precursors were developed.¹³ Some very early results of studies of free-radically polymerizable telechelic siloxanes have been presented.¹⁴ These initial results revealed the applicability of those materials in the study of fundamental issues of network theory and rubber elasticity, and selected materials from this group have been used in model studies elsewhere.¹⁵

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It is the aim of this article to present the results of studies of silicone networks formed by free-radical polymerization of terminally functional polydimethylsiloxanes with a wide range of molecular weights (5,000 (5k)–50,000 (50k) g/mole), having different free-radically polymerizable functional end-groups: methacrylate, (meth)acrylamide, α -methylstyryl. These end-groups are connected to the siloxane backbone via short, strongly polar, hydrogen-bonding spacers (urea, or amide linkages). The combination of a nonpolar polysiloxane backbone with polar end-groups promotes phase separation of the end-groups and their aggregation, enhanced by the hydrogen bonding of the urea or amide groups. This provides a system with unique polymerizability features, including a high degree of conversion at high dilution. Also, dangling ends can be deliberately and quantitatively introduced into such systems by the use of monofunctional siloxane macromers (macromonomers). Hydrogen-bonding interactions in the uncured “transient networks” and in the elastomers obtained upon cure are reported in a subsequent article.

The contribution of both very short and long polymer chains to the ultimate mechanical characteristics of resulting bimodal¹⁶ and trimodal¹⁷ networks has been extensively studied by Mark and co-workers with the use of difunctional silicones as models. The reinforcing affect has been attributed to the limited chain-extensibility of the very short silicone chains. Our results demonstrate that bimodality plays an important role in affecting the mechanical properties of silicone elastomers even at a relatively high molecular weight (5,000 g/mole) of the short chain components.

Free-radically polymerizable telechelic siloxanes may prove their practical importance as room temperature polymerizable liquid silicone rubbers with controlled mechanical properties. In many instances, silicone rubbers with properties comparable to heat-curable silicone elastomers were obtained.

The use of telechelic free-radically polymerizable silicones in the formation of silicone–acrylate copolymer networks has been recently reported.¹⁸

MATERIALS AND METHODS

All monomers, initiators, and capping agents, as well as photoinitiators and solvents were purchased from commercial vendors and used as supplied unless indicated otherwise.

IEM - 2-(Methacryloyloxy)ethyl isocyanate—Aldrich
VDM, vinyl dimethyl azlactone: 2-ethenyl-4,4-dimethyl-1,3-oxazolin-5-one,

and IDM, isopropenyldimethyl azlactone: 2-isopropenyl-4,4-dimethyl-1,3-oxazolin-5-one were made according to the method described by Rasmussen et al.¹⁹

m-TMITM, *m*-isopropenyl- α,α -dimethyl benzyl isocyanate—Cyanamide

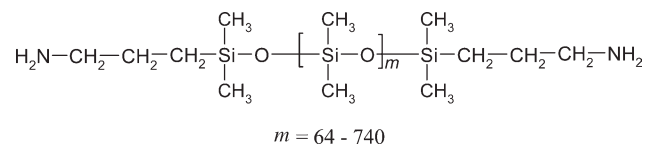
Acryloyl ethyl carbonic anhydride—made according to the method of Hatada and Kondo.²⁰

DarocurTM 1173, 2-hydroxy-2-methyl-1-phenylpropane-1-one—EM Industries.

Siloxane precursors

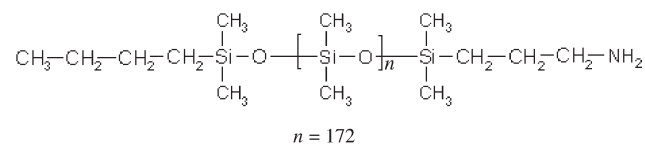
Difunctional siloxanes

Reactive free-radically curable polysiloxanes used in this study were synthesized using telechelic primary amine terminated polydimethylsiloxanes as starting materials. These polymeric precursors with molecular weights in the range 5,000–55,000 g/mole, having good functionality (high degree of end-labeling), were prepared by the modified method of the base-catalyzed equilibration of D₄ with 3,3'-bis-aminopropyl tetramethyldisiloxane, as described by Hoffman and Leir.¹³ The number average molecular weights of polymers having normal distribution were determined by an acid titration of the amine end groups. In some experiments, different lots of materials with somewhat different molecular weights were used. In this article, references will be given to the abbreviated, approximated molecular weights, e.g. 5k will refer to the liquid rubbers with a number average molecular weight 5,000 g/mole ($\pm 10\%$).



Siloxane macromer

Monofunctional siloxanes with narrow molecular weight distribution were synthesized by the standard method of siloxane macromer synthesis,^{21,22} by using D₃ as a monomer and the lithium butyldimethylsilanolate as an initiator. The propagation reaction was carried out in tetrahydrofuran at room temperature and capping was achieved with aminopropyldimethyl fluorosilane, a capping agent, the synthesis of which was described elsewhere.²³ 3-Aminopropyl-functional siloxane macromer, molecular weight 13,000 g/mole, was obtained with narrow molecular weight distribution ($M_w/M_n < 1.2$)



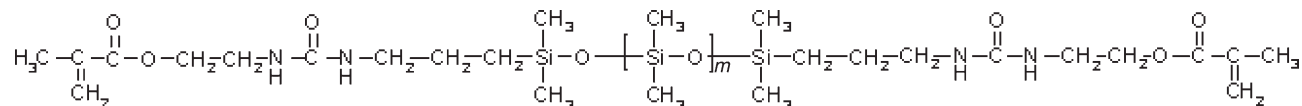
Free-radically polymerizable polysiloxanes

Both difunctional and monofunctional primary amine terminated siloxanes were further functionalized by reacting them at room temperature (the

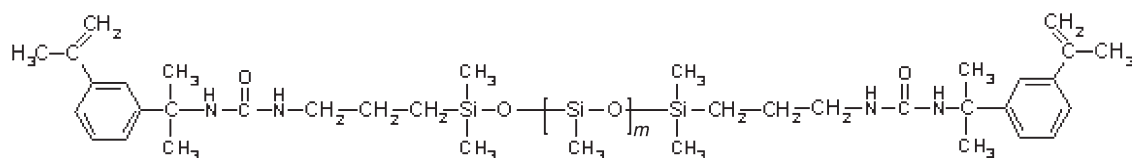
exotherm observed in the reaction of lower molecular weight siloxanes needed control) with vinyl functional isocyanates or azlactones. The scheme below shows the methods of preparation of the five groups of reactive difunctional siloxanes. Analogously, the reaction of semitelechelic aminofunctional polysiloxane with vinylazlactone led to the formation of acrylamidoamido-functional macromer.

The functionalization reactions were performed in bulk by mixing stoichiometric amounts of the appropriate capping agent (IEM, TMI, VDM, or IDM) with the corresponding amine-terminated polysiloxane for several hours at room temperature.

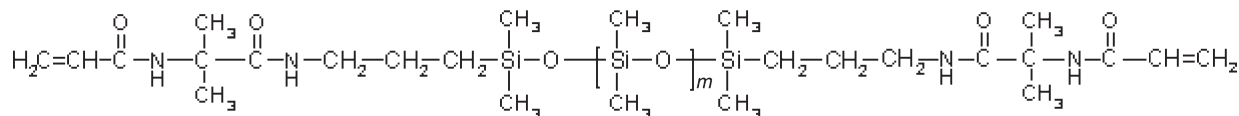
The reaction of amine-terminated polysiloxanes (PDMS diamine) with IEM leads to the formation of MethAcryloxyUrea Siloxane (MAUS) derivatives:



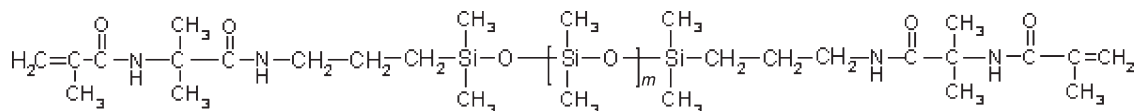
Correspondingly, the reaction of PDMS diamine with m-TMI leads to the formation of α -MethylStyrylUrea Siloxane (MeStUS) derivatives:



The reaction of PDMS diamine with VDM leads to the formation of Acrylamidoamido Siloxane (ACMAS) derivatives:

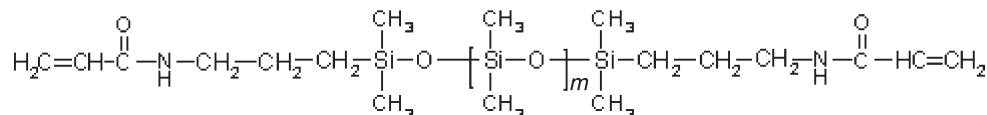


Correspondingly, PDMS diamine forms MethacrylamidoAmido Siloxanes (MACMAS), when reacted with IDM:

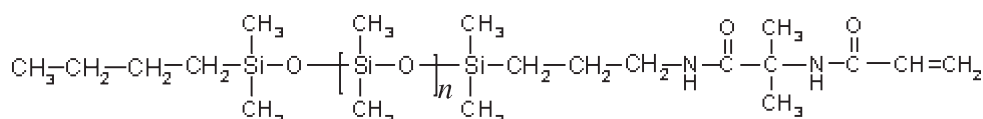


Acrylamido-functional polysiloxanes (ACMS series) having a free-radically polymerizable acrylamide group directly linked to PDMS (no polar spacer group) were obtained in the reaction of amine-terminated polysiloxanes with acryloyl ethyl carbonic anhydride, prepared by the method described by Hatada and Kondo²⁰ and were used in some comparative experiments.

Monofunctional siloxane—ACMAS macromer—was synthesized by reacting 3-aminopropyl-functional siloxane macromer with VDM:



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The completeness of the capping reactions was monitored by infrared (IR) spectrometry.

Curing procedures

DarocurTM1173 photoinitiator was added (0.2 wt %) to the telechelic siloxane, and the solution was well mixed and degassed. For lower viscosity samples, the liquid was poured into the center of a clamped laminate structure consisting of two sheets of plate glass sandwiching two sheets of polyester which in turn sandwiched a 1-mm-thick spacer. Higher viscosity samples were pressed into the space created between two polyester films separated by a 1-mm-thick spacer. The samples were exposed to low intensity ultraviolet (UV) lights (Sylvania Blacklight, 2.6 mW/cm²) for 5 min on each side.

Test methods

Viscosity

The bulk viscosity of functional polysiloxanes was determined using a Model RVTDV-II BrookfieldTM Viscometer with a programmable temperature controller. Liquid polymer of 15 g was poured into the chamber and placed in the thermostat. The measurement was taken after thermal equilibrium was reached. Spindles #21 or #27 were used depending on the viscosity of the sample.

DMTA

Dynamic-mechanical properties of a few select samples were characterized in shear mode using a RheometricsTM RDA II rheometer in the temperature sweep mode (5°C/min) at frequencies of 0.3, 3.0, or 30 Hz.

Mechanical properties

Mechanical testing was performed on an InstronTM Model 4501 tensile tester. Testing was performed according to a modification of ASTM D412-83. The samples were prepared according to Method B (cut ring specimens). Type 1 rings (5.1 cm circumference) were produced with a specially-designed precision ring cutter. Modifications to the ASTM were as follows:

1. Crosshead speed was 12.7 cm/min rather than 50.8 cm/min
2. The test fixture shafts (0.48-cm diameter for both upper and lower jaw) rotated at 30 rpm in the same direction to maintain uniform strain throughout the entire ring
3. The thickness of the rings was 0.5 mm

RESULTS AND DISCUSSION

Liquid silicone rubbers

The term “liquid rubber” is often applied in the literature to describe functional polymers having rela-

tively low viscosities used as precursors of silicone elastomers, usually in respect to systems curable by hydrosilation, and most often used in injection molding. However, it also adequately describes the system of free-radically polymerizable siloxane polymers. In the systems described in this article, nonpolar siloxane chains are terminated with strongly polar end groups able to form hydrogen bonds. This leads to aggregation of the end-groups as reflected in the strong increase in viscosity upon functionalization of the aminopropyl-terminated polysiloxanes with isocyanate or azlactone capping agents.

Urea groups are known to form bifurcated hydrogen-bonded structures²⁴ and are capable of formation of “2D networks” in polyureas and polyureaurethanes²⁵ and also in bridged silsesquioxanes having urea linking groups.²⁶ Such “ordered” hydrogen bonded structures display characteristic IR spectral shifts of the affected groups. The IR variable temperature spectra of the telechelic siloxanes terminated with the urea groups (MAUS and MeStUS) and amide groups (e.g. ACMAS, MACMAS, ACMS), and of the corresponding networks formed by their polymerization, reported separately,²⁷ confirm the formation of strongly hydrogen-bonded assemblies of end-groups at room temperature.

In our study of the effect of temperature on the viscosities of uncured liquid silicone rubbers, it was expected that hydrogen-bonding interactions between end-groups should weaken at elevated temperatures and thus lead to a strong viscosity decrease. The data presented in Table I show that the viscosity of all functional siloxanes studied asymptotically approaches the level characteristic of the corresponding amino-functional polysiloxanes, although even as the temperature reaches 110°C the viscosities of most of the liquid rubbers were still somewhat higher than the viscosity of silicone diamines.

It should be noted that some of the studied functional polysiloxanes of relatively large differences in molecular weights (each having a normal distribution of molecular weights) are immiscible, and this behavior can be considered as an additional measure of the strength and the specificity of interactions between the end-groups. For example, at a 50/50 weight to weight (w/w) ratio, 5k ACMAS is immiscible with 35k ACMAS—while sheared the blend appears to be transparent, but it quickly becomes hazy upon standing. However, 5k ACMAS is miscible (that is, it forms a clear mixture) with 20k ACMAS. It was further found out that 35k ACMAS can be blended at any ratio with 10k ACMAS if clarity of the mixture is considered a measure of homogeneity of the system. (This miscibility would most likely be affected by the molecular weight distribution, which was not studied). Similarly, 5k

TABLE I
Viscosity of Telechelic Polysiloxanes (in cPS) at Various Temperatures

Siloxane	M_w	Temperature					
		25°C	35°C	50°C	70°C	90°C	110°C
Diamine	5k	131	104	80	59	47	35
	10k	358	292	219	159	116	91
	20k	1640	1430	1080	776	582	441
	35k	7060	5220	4050	2960	2230	1700
MAUS	5k	4920	2720	1450	637	310	165
	10k	6500	4060	2190	1040	445	245
	20k	21600	13000	6350	2900	1420	830
	35k	51600	31800	16800	8150	4320	2860
MeStUS	5k	59200	28800	10300	2780	1020	330
	10k	29400	20200	8500	2920	1090	417
	20k	81600		17700	6400	2600	1160
	35k	137000	71200	31600	11800	4840	2780
ACMAS	5k	49200	33200	16700	7300	245	102
	10k	52400	17700	5400	1270	348	217
	20k	83600	39600	13700	2540	1090	668
	35k	84000	56000	17500	6950	3840	2780
MACMAS	5k	3270	1160	462	180	97	57
	10k	2530	1210	582	294	174	120
	20k	6080	2940	1840	1100	721	494
	35k	11300	7440	5220	3300	2300	1770
ACMS	5k	486	324	194	112	71	46
	10k	774	568	363	221	147	101
	20k	2750	1990	1370	910	636	474
	35k	8160	6460	4560	3100	2270	1700

MAUS is immiscible with 35k MAUS, but 10k MAUS is miscible. Similar behavior was observed in the MeStUS series. The immiscibility of 35k ACMAS and 5k ACMAS was studied in some detail. Up to about 25 wt % of 5k ACMAS could be added to 35k ACMAS to form apparently homogeneous mixtures, but even a small amount (< 1%) of 35k ACMAS added to 5k ACMAS caused hazing of the blend. However speculative it might be, it is not unlikely that in a highly ordered pseudo- (transient-) network formed by the higher molecular weight liquid rubber, at lower concentrations the low molecular weight component can be “packed-in” between the closed-packed spheres of the statistical coils of the higher molecular weight chains to form its own domains without disrupting the continuity of the pseudo-network formed by the high molecular weight component. However, as the concentration of the low molecular weight component increases, it causes the higher molecular weight coils to contract, as in the presence of a poor solvent. The opposite—low concentration of high molecular weight component behavior—cannot be true: however, there is no space for an incompatible, high molecular weight component to form its own domains without disrupting the continuity of a pseudo-network formed by the low molecular weight liquid rubber.

The strong interactions of end-groups in the liquid rubbers described in this article lead to a high localized concentration of polymerizable end-groups,

which, in turn, accounts for the facile polymerizability of the systems even at a very low molar concentration of functional groups (e.g. at molecular weights as high as 50k), or even at high dilution (see the next sections). On the other hand, the highly ordered structures, such as postulated for the urea linkages, might affect the polymerizability of the vinyl groups by limiting their mobility. In this article, only UV-initiated free-radical polymerization of telechelic siloxanes is described, but the telechelic siloxanes described here might be reacted by means of other radical polymerization methods.

Silicone elastomers

As explained earlier, liquid silicone rubbers available in a broad range of molecular weights and with different functional groups were used to prepare silicone elastomers by the simple method of free-radical polymerization initiated by photoinitiators. In the following sections, data will be presented regarding the mechanical and dynamic-mechanical properties of our silicone elastomers:

- made of liquid rubbers with different end-group chemical structures
- made of liquid silicone rubbers of different molecular weights, including blends of high and low molecular weight materials

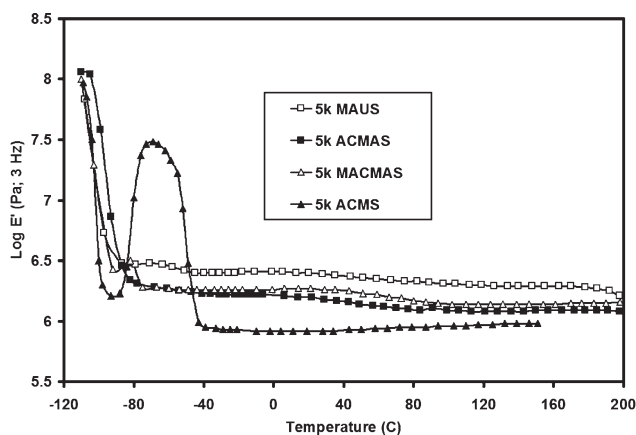


Figure 1 Storage Modulus measured at 3 Hz as a function of temperature for four different endgroup types, all at 5k molecular weight.

- cured in the swollen state
- coreacted with monofunctional siloxanes to introduce dangling ends

Network structure

The studied liquid silicone rubbers, having strongly polar, hydrogen bonding end-groups, polymerize easily to form elastomers with good mechanical properties. The only exception in this family is MeStUS, which is incapable of homopolymerization, but which easily copolymerizes with other vinyl-functional siloxanes. The method of synthesis of silicone elastomers described in this article is straightforward and versatile. The polymerization reaction is carried out at room temperature in the presence of photoinitiator (or at elevated temperatures, if a thermal free-radical initiator is used, as has been demonstrated in these studies²⁸) and results in elastomers with precisely controlled properties. However, as is the case with any free-radically polymerizable systems, the systems discussed here are sensitive to oxygen inhibition, which must be excluded either by surface cover or by nitrogen inerting. The fact that the polymerization reaction requires a few minutes exposure to low-intensity UV lights for completion might be related to the fact that diffused oxygen present in the system might need to be consumed first to overcome its inhibiting effect. Indeed, systems purged with nitrogen before curing polymerize more readily.

An important task was to determine the extent to which the aggregation phenomena of end groups influenced the completeness of the curing reactions. The literature is full of conflicting data regarding the effect of curing conditions on the degree of conversion of reactions leading to network formation. It is well known that after a system reaches the gel point,

the chain mobility dramatically decreases and the intermolecular reactions slow down correspondingly. This behavior leads to the formation of dangling ends, inelastic loops, and—in extreme cases—to residual nonincorporated macromolecules.

It seems reasonable to expect preorganized (transient) networks of the systems studied to cure more effectively, as the curing reaction should primarily proceed within the domains formed by the end-groups. As the curing reactions proceed via a free-radical polymerization of vinyl groups, one has to assume the existence of crosslinking sites composed of oligomeric acrylates or acrylamides, with siloxane chains extending from those sites to form star-like structures.

Small strain experiments (DMTA)

The effect of end groups of precursors

The rheological behavior of various types of cross-linked networks studied depends primarily on the nature of the end-group involved in the crosslinking, as well as on the molecular weight of telechelic prepolymer. Obviously, the relative importance of each of these two factors depends on the relative concentration of the end-groups in the mixture. This can be illustrated by Figures 1 and 2.

Figure 1 shows the temperature dependence of the storage modulus for networks made by the polymerization/crosslinking of 5k molecular weight telechelic siloxanes having four different end-groups. Not shown in these plots are the glassy plateaus, which occur at temperatures below about -120°C . The dramatic decrease in storage modulus at the glass transition can be seen for all four end groups, but in the case of ACMS end-groups, the end of the transition is marked by an increase in modulus due to cold crystallization between roughly -90°C to

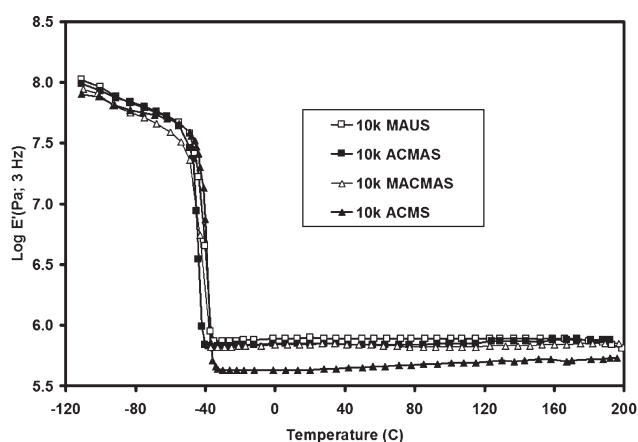


Figure 2 Storage Modulus measured at 3 Hz as a function of temperature for four different endgroup types, all at 10k molecular weight.

-70°C. This increase is then followed by a decrease in modulus as the crystalline regions begin to melt, until they are entirely molten at -40°C.

A close examination of the curves from -40°C to ~80°C reveals an augmentation of the storage modulus for all the curves except ACMS. We believe that this augmentation is due to the hydrogen-bonding nature of the end-groups. The results of the supporting IR temperature studies are reported in a subsequent article.²⁷

Above ~80°C, the hydrogen bonding is overwhelmed by thermal energy, and the remaining storage modulus behavior is dictated by the distribution of functionalities of the end-group loci. By "distribution of functionality" we mean the relative number of chain ends that are either

1. dangling ends
2. simply chain-extended to another chain
3. tied to two other chains
4. tied to three other chains etc.

Note that more complex arrangements could occur. For instance, a chain may have its two ends crosslinked (connected) together. In this case, the molecular loop may also be permanently entangled with other chains or not. One could also envision two chains parallel-linked with end-groups crosslinked to each other at both ends of both chains (ladder structure). More complex arrangements can occur with increased functionalities.

Silicone polymers typically exhibit excellent high temperature behavior, and the elastomers studied are no exception. The thermal stability of silicone elastomers is considered as one of their most attractive features in comparison with common organic polymers. Having inferior properties at ambient temperatures, silicone elastomers outperform most of their organic counterparts at both low temperatures and at high temperature applications. The rubber plateau modulus, except as hypothesized above with respect to hydrogen bonding, is very flat up to 200°C.

Figure 2 demonstrates how doubling the average molecular weight between end-groups (from 5,000 to 10,000 g/mole)—and thereby decreasing the average density of end-groups—causes a convergence of the measured rheological behavior of the networks made of various liquid rubbers. There is virtually no difference in the temperature dependence of the networks derived from MAUS, ACMS, and MACMAS. ACMS differs somewhat in that its rubber plateau modulus is slightly lower than those of the networks made of telechelic siloxanes with three other end-groups.

We hypothesize that the ACMS endgroup is unique among the endgroup types because it is much less prone to hydrogen bonding and most likely oligomerizes to form dimers. That is, we believe that the distribution of end-group topology within the ACMS-ter-

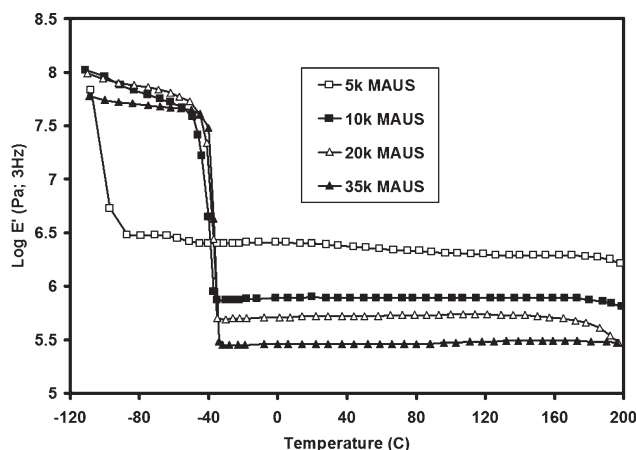


Figure 3 Storage Modulus measured at 3 Hz as a function of temperature for four different molecular weights of MAUS.

minated chains is dominated by chain extension. The resulting network would be expected to be less constrained and, therefore, freer to cold crystallize and possessing of a lower plateau modulus, consistent with the behavior shown in Figures 1 and 2.

The effect of molecular weight of siloxane precursors

As mentioned earlier, the molecular weight of liquid rubbers used in their preparation is a major factor affecting the mechanical and dynamic-mechanical properties of the resulting elastomers. In an idealized system, crosslink density and thus the modulus of the elastomer should be defined by the molecular weight of telechelic prepolymer and by the multiplicity of the crosslinking sites.

We present two figures supporting this assumption within our studied systems. Figure 3 demonstrates the temperature dependence of dynamic mechanical storage modulus (measured at 3 Hz) of MAUS for four different molecular weights of precursor liquid rubber. Figure 4 characterizes similar behavior in MACMAS, but measured at 30 Hz (all the samples were characterized at frequencies of 0.3, 3.0, and 30.0 Hz).

As demonstrated earlier in Figure 1, it can be clearly seen also in Figures 3 and 4 that the low temperature behavior of the networks made of 5k molecular weight precursor is very different from networks made of the higher molecular weight precursors. The latter show a characteristic T_g transition around -120°C accompanied by a relatively small drop in E' , as silicone elastomers remain crystalline up to the temperature of -40°C. In this temperature range, an abrupt decrease in E' is observed as melting takes place. However, no sharp melting transition in this temperature range was observed for silicone elastomers made of telechelic siloxanes with molecular weights of 5k with the exception of 5k ACMS-based

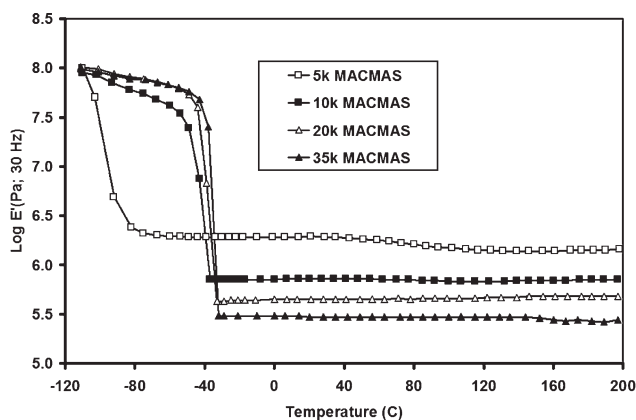


Figure 4 Storage Modulus measured at 30 Hz as a function of temperature for four different molecular weights of MACMAS.

elastomer which cold-crystallizes upon heating and then undergoes a melt transition, as discussed earlier.

Additionally, both Figures 3 and 4 show the rubbery plateau moduli decreasing with an increase of the molecular weight of siloxane precursors, as one would expect from rubber elasticity theory. With the molecular weight roughly doubling between different samples in the series, one might expect to see the log of the modulus decreasing by 0.3 between samples. While the decreases shown in Figures 3 and 4 are of the order of 0.2 to 0.4, we are unable to analyze this trend quantitatively without a more detailed understanding of the distribution of both end-group functionality and the molecular weights within each sample elastomer.

The effect of curing in the presence of diluent

To elucidate the role of the distribution of crosslinking sites in determining the dynamic-mechanical properties of siloxane networks, the formation of *in-situ* swollen siloxane networks has been studied. This approach was possible because of the tendency toward strong aggregation of the end-groups in our systems, as discussed earlier, which allows for the polymerization of telechelic siloxanes even in relatively dilute systems. A series of solutions of 35k MAUS in cyclohexane ranging from 73% down to 20 wt % siloxane was prepared and the samples were cured in the swollen state. As the chain length of siloxanes between the crosslinking sites was the same in all samples, any measured differences in mechanical properties of the cured sister samples after the solvent was dried off must therefore be due to the differences in the distribution of

- functionalities of the crosslinking sites
- number and types of chain entanglements

One might hypothesize that the average multiplicity of crosslinking sites decreases with an increase in dilution resulting in an increased concentration of

chain-extended units (dimers) and perhaps the formation of dangling ends. Both of these effects would tend to lower the rubbery plateau modulus. Figure 5 shows the dynamic mechanical data obtained for a 35k molecular weight MAUS cured undiluted compared to volume dilutions 73%, 47%, and 20% polymer with cyclohexane. Consistent with the hypothesis aforementioned, the plateau modulus does indeed decrease with increasing dilution.

Large strain experiments

All of the experiments discussed so far explored the temperature dependence of dynamic mechanical characteristics of materials under small strains deformations. In addition, we have characterized the large strain behavior of silicone elastomers using uniaxial tension. As is common for uniaxial tensile measurements, we have used a constant crosshead rate of 127 mm/min with an initial gauge length of 25 mm.

The effect of end groups of precursors

Stress-strain measurements were used in the analysis of the effect of the end-groups in a series of networks made of 5k siloxane precursors. This data are illustrated in Figure 6. We find that, in a manner consistent with the data of Figure 1, there is clear differentiation between the curves of MAUS, ACMS and the pair ACMS and MACMAS, and the tensile moduli rank similar to the dynamic storage moduli of Figure 1. We also find that the 5k siloxane precursors provide crosslinking at a level high enough to render all four samples linear-elastic.

The effect of molecular weight of siloxane precursors

Similarly, large strain experiments were conducted for series of elastomers made of different molecular

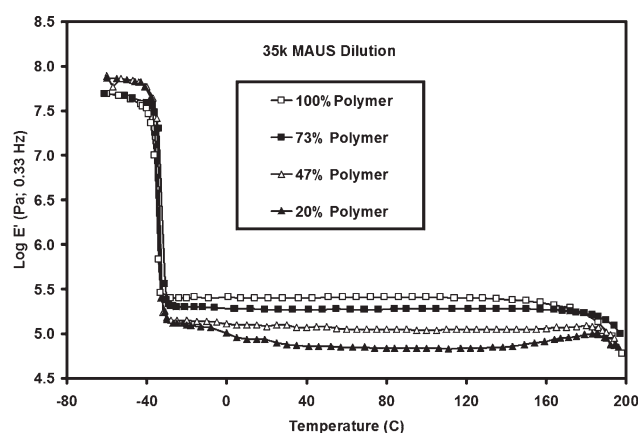


Figure 5 Storage Modulus measured at 0.33 Hz as a function of temperature for four different dilution ratios of MAUS.

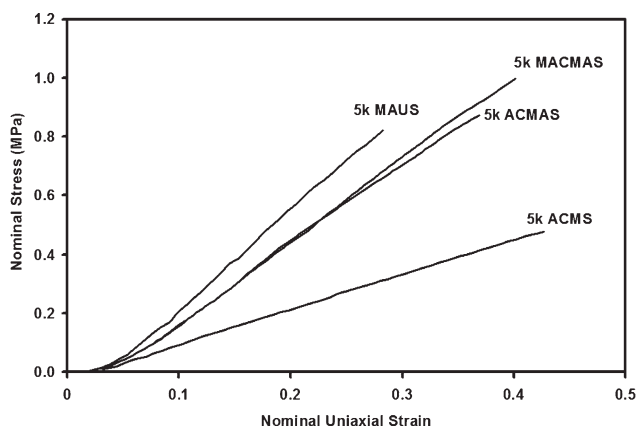


Figure 6 Nominal stress in megaPascals as a function of nominal uniaxial strain for four different endgroups at a molecular weights of 5k.

weight precursors. Figure 7 illustrates tensile behavior of elastomers made of MAUS precursors of varying molecular weights. This data may be compared with the dynamic mechanical data shown in Figure 3 and demonstrates that as the molecular weight of the telechelic prepolymer increases, the tensile modulus decreases as expected and the large strain behavior changes from linear-elastic to nonlinear-elastic.

The effect of blending of high and lower molecular weight precursors

An interesting question in the field of large-strain elasticity theory (and one with practical consequences) is the behavior of silicone networks made of telechelic siloxanes having bimodal molecular weight distributions. The mechanical response of elastomers can be controlled if silicone networks are made of blends of high molecular weight and very low molecular weight silicone components, as demonstrated earlier in the extensive studies by Mark.^{8,9} According to Mark et al., the limited chain extensibility of

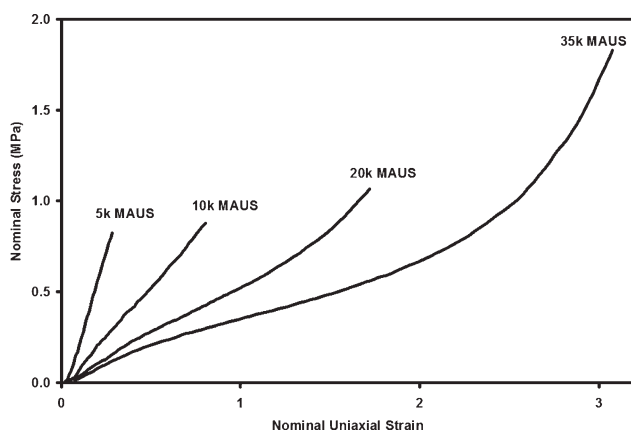


Figure 7 Nominal stress in megaPascals as a function of nominal uniaxial strain for four different molecular weights of MAUS.

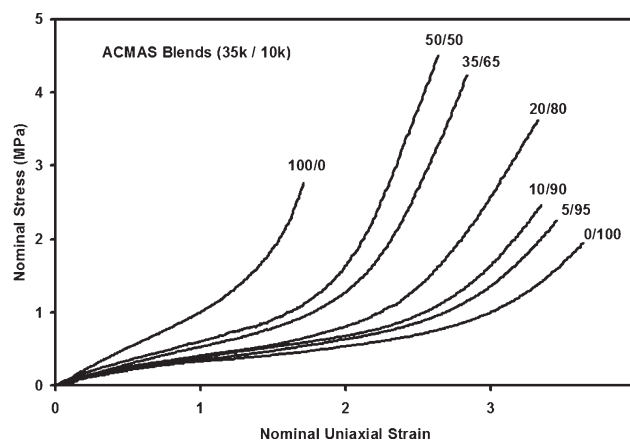


Figure 8 Nominal stress in megaPascals as a function of nominal uniaxial strain for seven different ratios of 35k ACMAS with 10k ACMAS.

short chains is responsible for an upturn in the modulus observed when oligomers with molecular weight of several hundred g/mole are used in mixtures with higher molecular weight reactive siloxanes, for example, 20k. These kinds of bimodal networks have significantly increased ultimate strength and energy at rupture when compared with unimodal reference samples. Figure 8 presents the large-strain tensile data for ACMAS blends of 35k/10k ranging from 100/0 to 0/100. While the dependence of Young's Modulus and the strain at break on composition is monotonic, the behavior of the stress at break is clearly more complex. The elastomers made of blends containing more equal weight fractions of the higher and lower molecular weight components have a stress at break much higher (>50%) than the networks made of more uneven component fractions. The data should be viewed carefully, considering that no effort was made to study the effect of the molecular weight distribution of the starting materials on the mechanical properties of the networks formed of the blends. However, the fact that such a relatively small differences in the average molecular weights of the two components (35k and 10k) cause such a significant reinforcement of the networks could suggest that the limited chain-extensibility may not be a primary factor in determining mechanical properties of the bimodal networks.

The effect of dangling ends

We also studied the effect on siloxane network characteristics of the addition of monofunctional free-radically polymerizable siloxane (siloxane macromer) to telechelic siloxane systems using high-strain test methods. Silicone macromer coreacted with difunctional siloxanes could be considered as a source of dangling ends in such formed networks. As illustrated in Figure 9, increasing the

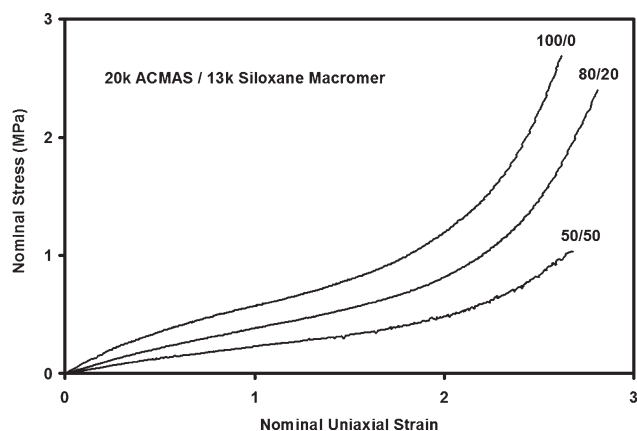


Figure 9 Nominal stress in megaPascals as a function of nominal uniaxial strain for three different ratios of 20k ACMAS mixed with 13k siloxane macromer.

concentration of siloxane macromer (13k ACMAS macromer) in networks formed of 20k ACMAS resulted in a decrease of the rubber modulus of the resulting network.

CONCLUSIONS

In this article, some of the more important rheological features of liquid silicone rubbers having polar, free-radically polymerizable end groups were discussed. The combination of low polarity siloxane chains with end groups that are able to form strong hydrogen bonds between themselves provides systems which are preorganized in transient networks. Curing these liquid rubbers by reacting the end-groups in a free-radical polymerization then creates true (permanent) networks. This preorganization of transient networks is responsible for a strongly increased viscosity of the neat liquid silicone rubbers, particularly evident in the case of acrylamido-amido (ACMAS) and urea groups. Infrared spectra (which are discussed in a subsequent article) confirm the existence of strong hydrogen-bonded groups in both urea and amide derivatives. Upon temperature increase, the hydrogen bond interactions must become weaker, which is reflected both in the decreased viscosities, and in pronounced changes in the IR spectra.²⁷

Strong interactions between the end groups provide for a high local concentration of polymerizable groups even when the overall concentration of polymerizable groups is very low, as in the case of 55k liquid rubbers. It is thus reasonable to assume that crosslinking would proceed within a domain formed by an aggregation of end-groups. In such a case, the average degree of aggregation would be a factor determining the maximum degree of oligomerization of the end-groups that would correspond to the maximum number of chain-ends attached to the

crosslinking site. However, it is possible to imagine that within a particular domain more than one kinetic chain can be initiated, as conformational restrictions of the aggregated end-groups can negatively affect their polymerizability. That would lead to the formation within the domains of more than one crosslinking- or chain-extension site, which could maintain an ability to hydrogen bond. It is believed that the liquid silicone rubbers described in this article can provide useful models in the studies of various aspects of rubber elasticity, as pointed out by the earlier work by Gent et al.¹⁵

From the same silicone diamine starting materials, telechelic siloxanes with different functional groups were derived. These liquid silicone rubbers are capable of low temperature curing via UV-initiated free-radical polymerization. The effect of the nature of the functional group and the siloxane molecular weight on the dynamic-mechanical and stress-strain characteristics of networks made of those materials was studied. Interestingly, blends of liquid rubbers with somewhat different molecular weights (e.g. 10,000 and 35,000 g/mole) showed significantly enhanced mechanical properties when compared with rubbers made of either of the pure components of the blend. This data seem to indicate that the reinforcement observed in the extensively studied bi- and multimodal networks is of more general nature and is by no means related to the limited chain extensibility of the oligomeric chains.

The hydrogen bond association of the reactive groups allows for formation of networks even when diluted in nonpolar solvents. This allows for studies of the effect of the diluting medium on some of the basic network characteristics, which might be important in the fundamental studies of model networks. The effect of dangling ends on the properties of silicone networks was also demonstrated by the deliberate incorporation of monofunctional free-radically polymerizable siloxane (siloxane macromer) into the system.

Finally, free-radically polymerizable siloxanes can be used in the preparation of copolymer networks with other vinyl monomers, as described elsewhere.¹⁸

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