Preparation and Morphology of a Silicone-Acrylate Copolymer System

TODD R. WILLIAMS, *Life Sciences Research Laboratory, 3M Corporation, 3M Center, Bldg. 201-2W-17, St. Paul, Minnesota 55144*

Synopsis

This paper presents the synthesis and analysis of a new series of silicone acrylate (SiAc) copolymers. The building block oligomers are linear polydimethylsiloxanes with alkylene urethane methacrylate end groups (M_n 1000–3000). A variety of analyses were performed in order to elucidate the morphology of these copolymers. Data are presented from differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), permeability testing, small angle x-ray scattering (SAXS), and electron microscopy. These data indicate that these copolymers possess a two-phase morphology in the range of compositions studied. Conclusions are drawn about the continuity, shape, and size of the domains. Some comparisons are made between data for these "ladder" polymers and data for siloxane-containing alternating block copolymers reported in the literature.

INTRODUCTION

Copolymers of acrylic-functional polysiloxane derivatives have been known for some years[1] and are of use in such diverse applications as release coatings,[2] contact lenses,[3] electronics adhesives,[4] and etching resists.[5] These copolymers present interesting combinations of physical properties, such as low-temperature toughness, physical strength, and gaseous permeability. It has been suggested that these copolymers exist with a phase-separated morphology.[6] The degree of phase separation and the morphologies of the phases are of interest in designing new and improved polymers for a number of applications. In this paper are presented the results of a variety of analytic investigations of the morphology of one such silicone-acrylate (SiAc) system.

EXPERIMENTAL

Oligomer Synthesis

The silicone-containing oligomers used in this investigation are called silicone urethane methacrylates (SiUMA) and are synthesized by the scheme shown in Figure 1. The molecular weight is adjusted at the equilibration-polymerization step in well-established fashion.[7] Note that the product of such a reaction sequence is a strictlly linear polysiloxane with nominal acrylic functionality of two. In this paper, SiUMA-x denotes a silicone urethane methacrylate with a polysiloxane chain with a number average of x silicon atoms.
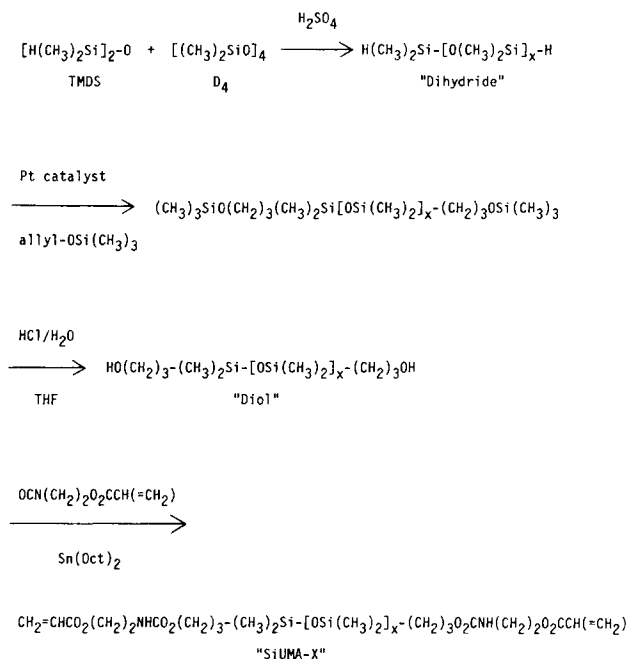
$$\text{[H(CH}_3)_2\text{Si]}_2\text{-O} \quad + \quad \text{[(CH}_3)_2\text{SiO]}_4 \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \text{H(CH}_3)_2\text{Si-[O(CH}_3)_2\text{Si]}_x\text{-H}$$

TMDS $\qquad$ D_4 $\qquad\qquad$ "Dihydride"

$$\xrightarrow[\text{allyl-OSi(CH}_3)_3]{\text{Pt catalyst}} \quad \text{(CH}_3)_3\text{SiO(CH}_2)_3\text{(CH}_3)_2\text{Si[OSi(CH}_3)_2]}_x\text{-(CH}_2)_3\text{OSi(CH}_3)_3$$

$$\xrightarrow[\text{THF}]{\text{HCl/H}_2\text{O}} \quad \text{HO(CH}_2)_3\text{-(CH}_3)_2\text{Si-[OSi(CH}_3)_2]}_x\text{-(CH}_2)_3\text{OH}$$

$\qquad\qquad$ "Diol"

$$\xrightarrow[\text{Sn(Oct)}_2]{\text{OCN(CH}_2)_2\text{O}_2\text{CCH(=CH}_2)}$$

$$\text{CH}_2\text{=CHCO}_2\text{(CH}_2)_2\text{NHCO}_2\text{(CH}_2)_3\text{-(CH}_3)_2\text{Si-[OSi(CH}_3)_2]}_x\text{-(CH}_2)_3\text{O}_2\text{CNH(CH}_2)_2\text{O}_2\text{CCH(=CH}_2)$$

"SiUMA-X"

Fig. 1. Synthesis of silicone urethane methacrylate (SiUMA) oligomers.

Preparation of Poly(dimethylsiloxane) with Terminal Hydride Groups (Step 1)

A mixture of 122.4 g octamethylcyclotetrasiloxane, 13.4 g tetramethyld-isiloxane, 0.7 g activated charcoal powder, and 0.07 g concentrated sulfuric acid was agitated and heated at 65°C for 24 h. The mixture was then filtered and the filtrate subjected to a reduced pressure of about 0.2 torr while heating at 70° C for 48 h on a rotary evaporator. The resulting colorless liquid was a linear poly(dimethylsiloxane) that had a number-average molecular weight of about 1650 and terminal silicon hydride groups as determined by nuclear magnetic resonance (NMR) spectroscopy.

Preparation of Silicone Diol (Step 2)

Into a suitable reaction vessel equipped with stirrer, thermometer, and apparatus for maintaining an inert atmosphere was placed 142 g (0.086 mol) of the above-prepared silicone hydride, 26.6 g (0.2 mol) of allyloxytri-methylsilane, and 130 ml toluene. The mixture was stirred under dry nitrogen, and an oil bath at 60°C was placed about the vessel. When the temperature of the contents of the vessel reached 40°C, there was added 2 drops of a solution in divinyltetramethyldisiloxane of a platinum complex, the solution containing 26% by weight of platinum (the catalyst solution was prepared in accordance with example 1 of U.S. Patent No. 3,775,452). An exothermic reaction occurred, raising the temperature of the mixture to over 80° C over 10–15 min. The temperature then slowly dropped to 60° C where it was held for an additional 2 h. Volatile material was then removed from the reaction mixture by vacuum distillation leaving as residue the silicone with terminal trimethylsiloxypropyl groups.

A mixture of 149 g of the above-prepared protected alcohol, 300 ml tetrahydrofuran, and 300 ml 0.1 N hydrochloric acid was stirred vigorously at about 25°C for 5 h. The reaction mixture was extracted with hexane. After removal of volatile material by vacuum distillation, a residue of silicone diol was obtained.

Preparation of SiUMA (Step 3)

A mixture of 138 g of the above-prepared silicone diol, 24.3 g of 2-isocyanatoethyl methacrylate (IEM), and 10 drops of stannous octoate was stirred under nitrogen and heated at 60°C for 24 h. During the reaction period, the presence of the isocyanate group, as indicated by a 2260 cm^{-1} peak, was monitored by infrared spectroscopy. On observing the disappearance of the isocyanate peak, about 1 g increments of IEM were added until the isocyanate peak persisted, when 10 ml tetrahydrofuran and 0.1 ml water were added and the mixture stirred for an additional hour. Infrared spectroscopy confirmed the absence of the isocyanate group. The reaction mixture was then decolorized by adding 150 ml hexane and 1.5 g decolorizing carbon and stirring for 5 h or more. On filtration and vacuum distillation of volatiles, linear poly(dimethylsiloxane) with terminal 3-[2-(methacryloyloxy)ethylcarbamoyloxy]propyl groups (SiUMA) was obtained.

This compound was stored for about 3 days at 0°C. A white solid precipitated and was identified as $N,N,'$,2-tris(methacryloyloxyethyl)-imidocarbonic diamide. This solid was removed by vacuum filtration before using the SiUMA for polymerizations.

Molecular Weight Determinations

By adjusting the amounts of octamethylcyclotetrasiloxane in step 1, SiUMA compounds were obtained with the desired number of silicon atoms per average chain. The molecular weight of the synthetic intermediates and products was monitored in several ways. The hydride-terminal silicones could be treated with alcoholic base and the liberated hydrogen measured volumetrically. This technique is very useful and reproducible but somewhat tedious and not applicable to the other chemical species. Porton NMR has been used routinely as an end-group analysis technique with some success. Both chemical and NMR analyses yield number-average molecular weight values. Figure 2 shows a comparison between the molecular weight of silicone hydride, measured by the chemical "titration," and the molecular weight of all silicones in the synthetic scheme, measured by NMR. The agreement is quite good.

Another method of molecular weight measurement is gel permeation chromatography (GPC). Polystyrene standards were used for calibration. Figure 3 shows a comparison of NMR and GPC results for the SiUMA compounds only. Note the wide dispersion of GPC results, depending on which detector was used. For these systems, the refractive index detector appeared to give the best agreement with NMR.
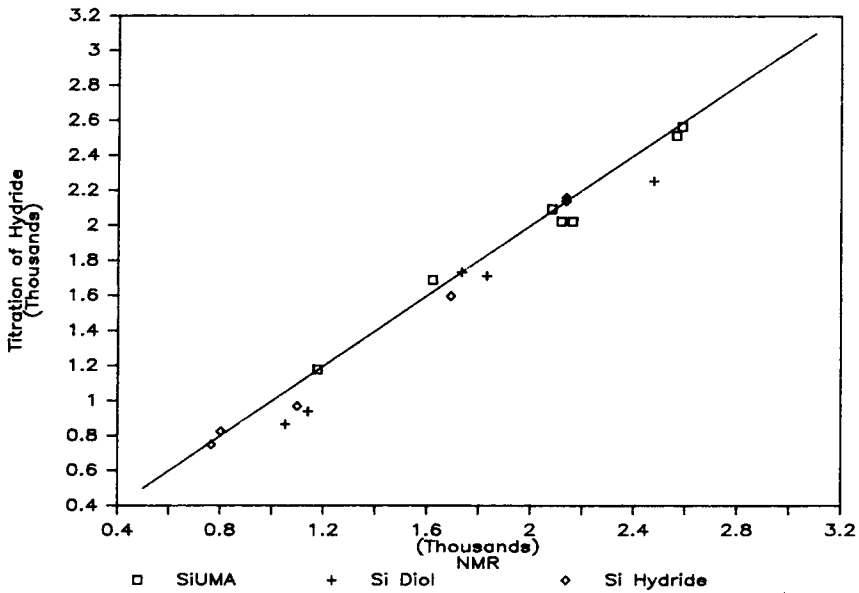
WILLIAMS

Molecular Weight Analyses

Fig. 2. Comparison of molecular weight determinations by titration of hydride-terminated polysiloxanes and by NMR of synthetic intermediates.

Copolymer Preparations by Photopolymerization

In a typical procedure, a mixture of 30 parts by weight of SiUMA, 57 parts of methyl methacrylate, 10 parts of 2-hydroxyethyl methacrylate, 3 parts of ethylene dimethacrylate and 0.5 parts of a photoinitiator (e.g.,
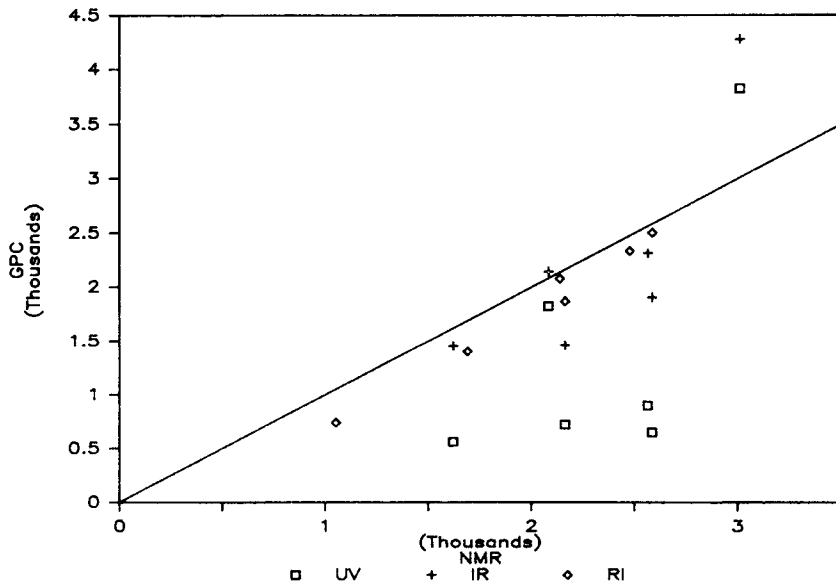
Molecular Weight Analyses

Fig. 3. Comparison of molecular weight determinations by NMR and by GPC with various detectors.

2-hydroxy-2-methyl-1-phenyl-1-propanone, Darocure 1173, E. Merck and Co.), was freeze-thaw degassed *in vacuo* three times to give a clear colorless solution. A portion of this solution was injected with a syringe into a 125 × 125 mm mold made by assembling a 300-μ spacer (actually two thicknesses of vinyl electrical tape) between two glass plates with a release liner of 62.5 μ thick poly(ethylene terephthalate) attached to each inner glass surface. The spacer also had small channels at the top to permit loading and to allow the escape of bubbles. The filled mold was exposed to the radiation of a medium-pressure ultraviolet lamp. The solution polymerized to an optically clear transparent sheet that was readily removed from the mold and the liner sheets. All physical property measurements were performed on polymer sheets cured in this way. This polymer was cryogenically ground and was shown by solid-state NMR analysis (modified Varian XL200) to contain less than 5% unreacted double bonds (close to the detection limit for the instrument).

Morphological Analyses of Block Copolymers

Differential scanning calorimetry (DSC) was performed with a Mettler TA3000, scanning from −170°C to +250°C at 20°C/p min. The instrument was calibrated with an indium standard above ambient temperature. A low-temperature "calibration" was obtained by measuring the T_g of Dow Corning 360 Medical Fluid, a methyl terminated polydimethylsiloxane (PDMS) with molecular weight of 1900, as determined by silicon NMR. The observed T_g was −123°C,[8] determined as the midpoint of the inflection in the heat flow versus temperature curve. Dynamic mechanical analysis (DMA) was performed with a DuPont Model 1090/981.DMA instrument, scanning at 5°C/min. Permeability measurements were performed on an "Ox-Tran 100 Twin" with Model DL 200 "Datalogger" (both from Modern Controls, Minneapolis, Minn.) using 95% relative humidity at 35°C. Transmission electron microscopy (TEM) was performed on samples sectioned to 0.1μm with a Reichert OMU3 microtome and viewed with a JEOL 100 CX Analytical Electron Microscope. The samples were exposed to hydrazine vapor for 1 h (to react with ester groups) and then to osmium tetroxide overnight before viewing. Scanning electron microscopy (SEM) was performed with a Model ISI-60 SEM on samples fractured while immersed in liquid nitrogen.

RESULTS AND DISCUSSION

Extensive use was made of differential scanning calorimetry for the morphological investigations. Figure 4 shows the change in T_g of the monomeric SiUMA compounds and their homopolymers. Note the steady decrease in T_g with increasing chain length of the siloxane. Figure 5 shows the DSC scans for SiUMA-22 and its homopolymer. Note the easily detectable T_g at about −105°C for both samples. Note also that this T_g is significantly higher than that of the Dow Corning 360 fluid. It is suggested that the chains in the SiUMA molecules are so short that their motion is significantly restricted by the higher T_g end groups, both in the monomer and in the polymer. The apparent lack of crystallinity is also ascribed to the shortness of the chains.

Yilgor et al.[9], have reported T_g values for a series of aminopropyl-ter-

Tg of SiUMA Monomers
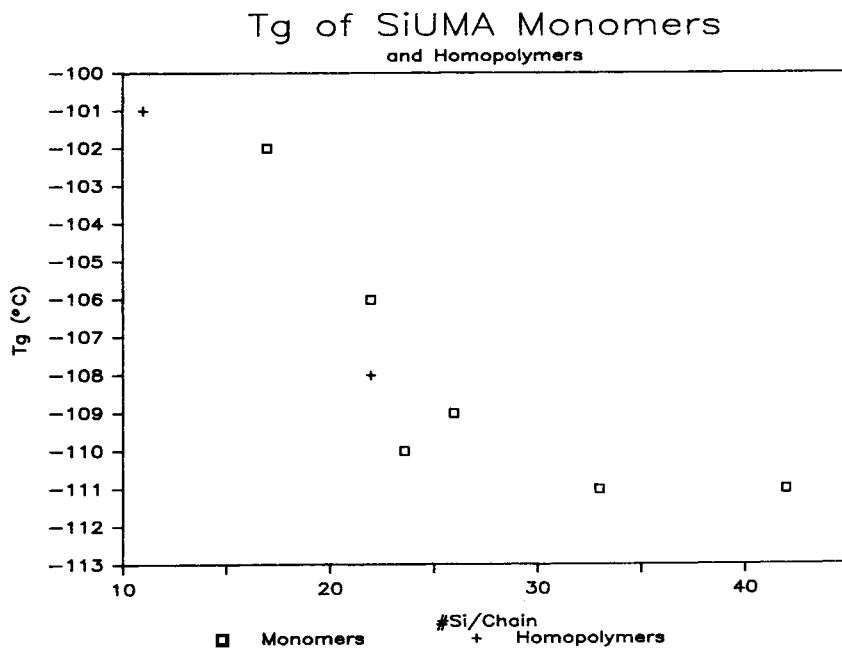### and Homopolymers

Fig. 4. T_g of SiUMA monomers and homopolymers by DSC.
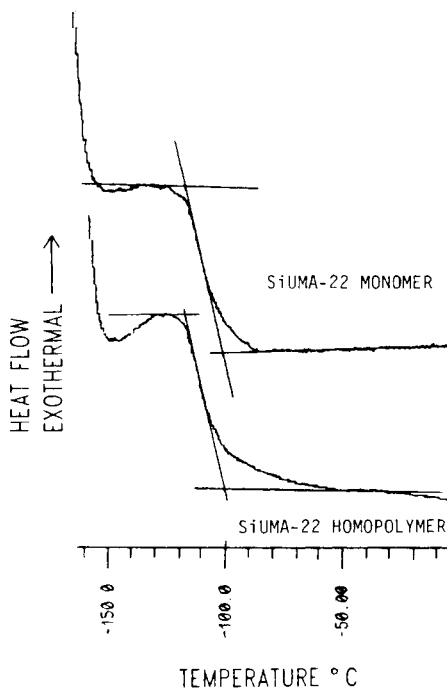

Fig. 5.   Low-temperature DSC curves of SiUMA-22 monomer and homopolymer.

minated PDMS compounds of similar chain lengths. Their values are 10–17°C lower than those observed in this work. It is possible that the urethane-acrylate end groups in this work have a T_g higher than for the aminopropyl groups and raise the PDMS T_g by an anchoring effect. It is interesting that the incorporation of either the acrylic-terminated or the aminopropyl-terminated[9] oligomers into a polymer matrix has very little effect on their T_g values.

Figure 6 shows the curves for three samples. The acrylate-only sample contained the nonsilicone components of the "typical" formulation (Table I) in the same ratios. The other two samples contained all the components, with SiUMA having 22 or 29 Si per chain. Note the presence of two well-defined T_g in the SiUMA-29 curve, a well-defined upper, but indistinct lower T_g in the SiUMA-22 curve, and only the upper T_g in the acrylate-only curve. The lower T_g was more distinct in several other curves for SiUMA-22 copolymers. Note also that the upper T_g for all three curves in Figure 6 are about the same. This congruency might be explained by the fact that these copolymers are essentially "ladder"-type networks, with the silicone chains acting as rungs connecting relatively pure poly(methacrylate) chains. This situation is to be contrasted with alternating block copolymers studied by McGrath,[10] in which the T_g of the hard block is depressed by phase mixing.

A large number of SiUMA copolymers were prepared with varying levels of SiUMA, MMA, and added ethylene dimethacrylate (EDMA) cross-linker. The T_g were measured by DSC on photocured film samples. The results of these determinations are presented in Figures 7 and 8. The following conclusions can be drawn from the data: (1). For SiAc copolymers with SiUMA of at least 20 silicon atoms, there are clearly two T_g, indicating a well-established phase-separated morphology. (2). Given the variability of the data, there is no significant change in T_g of the siloxane phase with either
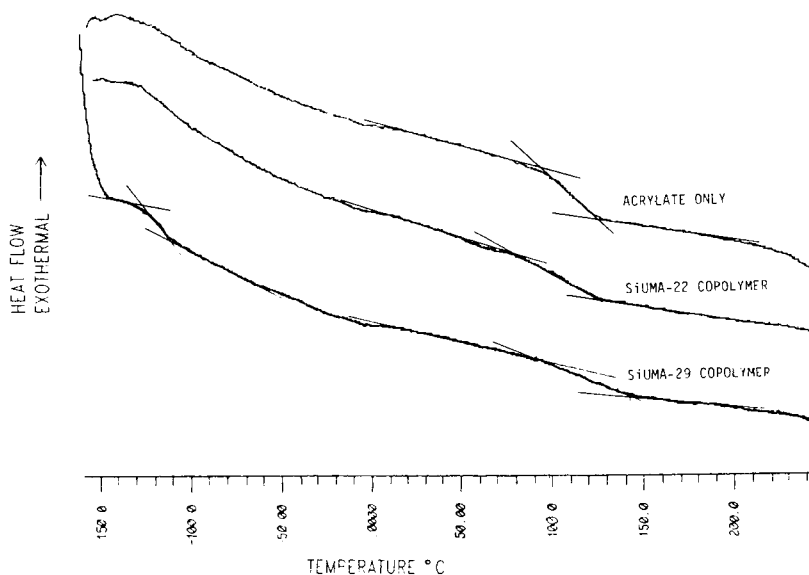

Fig. 6.   DSC curves of typical SiAc copolymers.

TABLE I

% SiUMA	PO_2 (Barrer)[a]
10	5,3
20	41, 6, 29
32.5	21, 19
40	5, 5, 55
50	93, 58
60	118, 142
70	191

[a] Barrer $= 10^{-11}$ (ml O_2 $\times$ cm)/(cm^2 $\times$ s $\times$ mm Hg).

chain length or cross-linking level for these copolymers. The relatively indistinct lower T_g for the copolymers with shorter SiUMA chain lengths probably obscure T_g differences that are evident in Figure 4. (3). There does seem to be a trend of the upper T_g to higher temperature with increased amount of cross-linker and with increased siloxane chain length. This trend may be due both to decreased chain mobility with increased cross-linking and to increased phase separation with the longer SiUMA chains. Again, these copolymers show different properties than alternating block copolymers in which the polysiloxane chain length has a large effect on the T_g of the hard block.[10] The data scatter in the present work requires that these interpretations remain somewhat tentative for the present.

Figures 9 and 10 show the results of measuring the T_g on several samples of differing SiUMA content and molecular weight. From these data it can be concluded that there is no effect of chain length or siloxane content on the lower T_g, but the upper T_g is lowered at the higher siloxane contents. This may be due to an increased proportion of mixed acrylate phase in
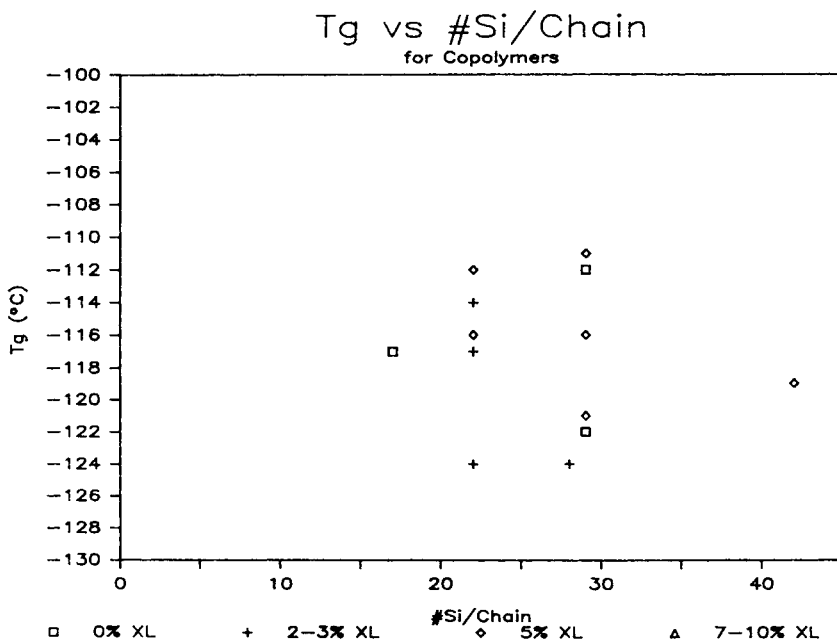

Fig. 7. Low-temperature T_g of SiUMA copolymers versus SiUMA chain length.

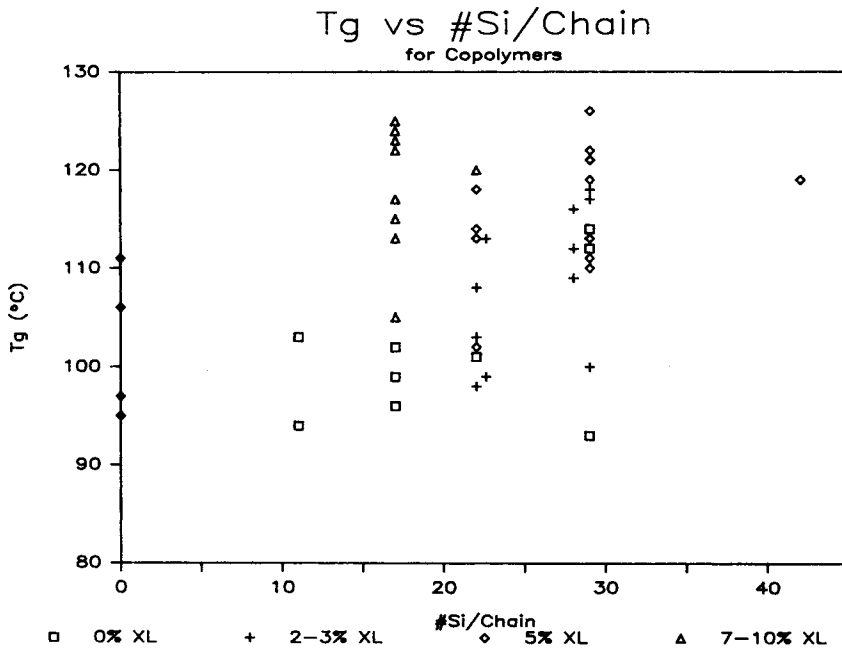## Tg vs #Si/Chain
for Copolymers

Fig. 8.   High-temperature T_g of SiUMA copolymers versus SiUMA chain length.

which the more flexible propylene-urethane-ethylene methacrylate ends of the siloxanes mix with the more rigid MMA and EDMA units.

DMA was used sparingly to study these copolymers. Figure 11 shows superimposed tan δ curves from three samples, similar to Figure 6. The
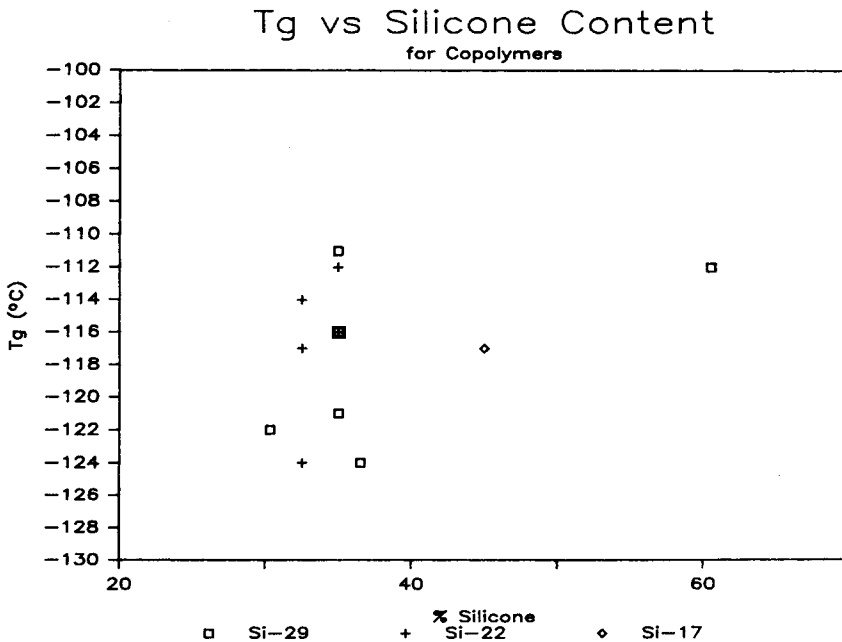
Tg vs Silicone Content
for Copolymers

Fig. 9.   Low-temperature T_g of SiUMA copolymers versus silicone content.

Tg vs Silicone Content
for Copolymers
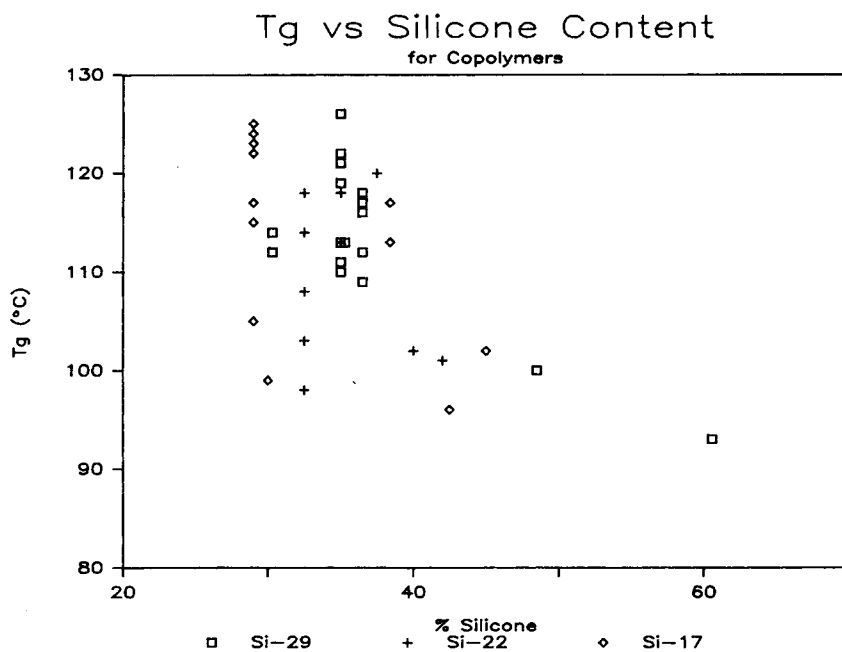
Fig. 10.   High-temperature T_g of SiUMA copolymers versus silicone content.

low T_g peaks for the SiAc polymers are different sizes because there was no normalization for sample dimensions. Note that the acrylate-only curve shows an upper tan δ peak, and thus (presumably) a T_g, at a *lower* temperature than either silicone-containing copolymer. No simple explanation for this phenomenon is readily apparent. A peak for the secondary meth-
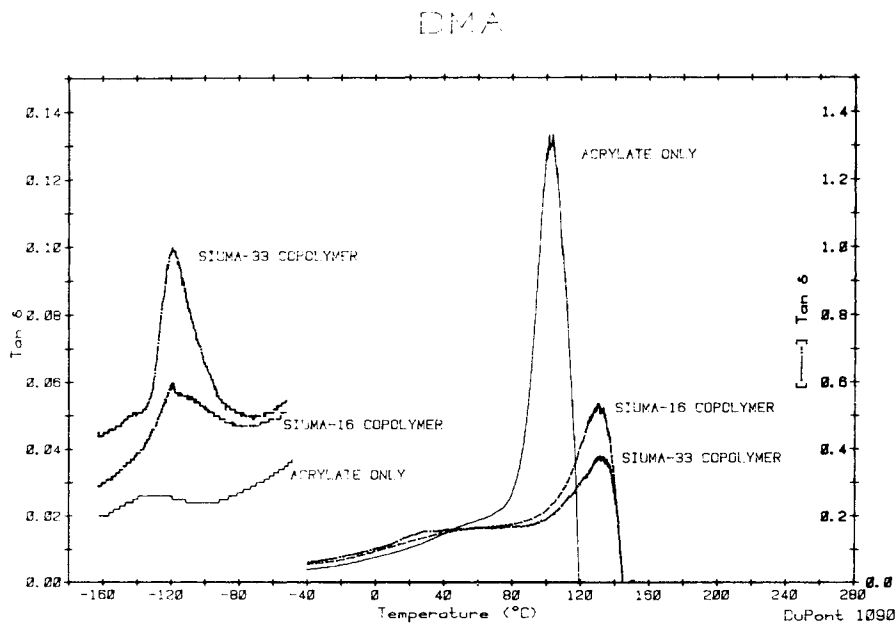

Fig. 11.   DMA curves (tan δ) for typical SiAc copolymers.

acrylate transition was observed at ~55 to −60°C, but it is not shown on Figure 11 for the sake of clarity. Note that the lower T_g of these copolymers is measured at about −120°C with the DMA, as opposed to about −105°C with the DSC. A major contributing factor to this apparent discrepancy is the different speeds of the two tests (5°C/min for DMA and 20°C/min for DSC).

Another physical property that might shed light on the morphology of these materials is tensile strength. Figure 12 shows how tensile strength varies with siloxane chain length and with added cross-linking. As might be expected, increasing siloxane chain length decreases strength, and added cross-linker increases strength. Unfortunately, these tensile strength data do not allow distinguishing between a phase-mixed and a phase-separated morphology.

Oxygen permeability is a way to probe morphology in copolymers in which the two phases are expected to have greatly different permeabilities.[11] Figure 13 shows likely morphologies for the present series of copolymers. At low silicone content the morphology can be viewed as in Figure 13a, with the silicone-rich phase dispersed in an acrylate matrix. If P_i and f_i are the permeability and volume fraction of phase i, if phase a is silicone poor and phase b is silicone rich, if $P_b >> P_a$, and if the silicone-rich phase is dispersed, the overall permeability can be approximated by eq. (1)[11]:

$$P = P_a \frac{1 + 2f_b}{1 - f_b} \tag{1}$$

A plot of P versus f_b will be nearly a straight line at low f_b, with more curvature at high f_b.

Tensile Strength
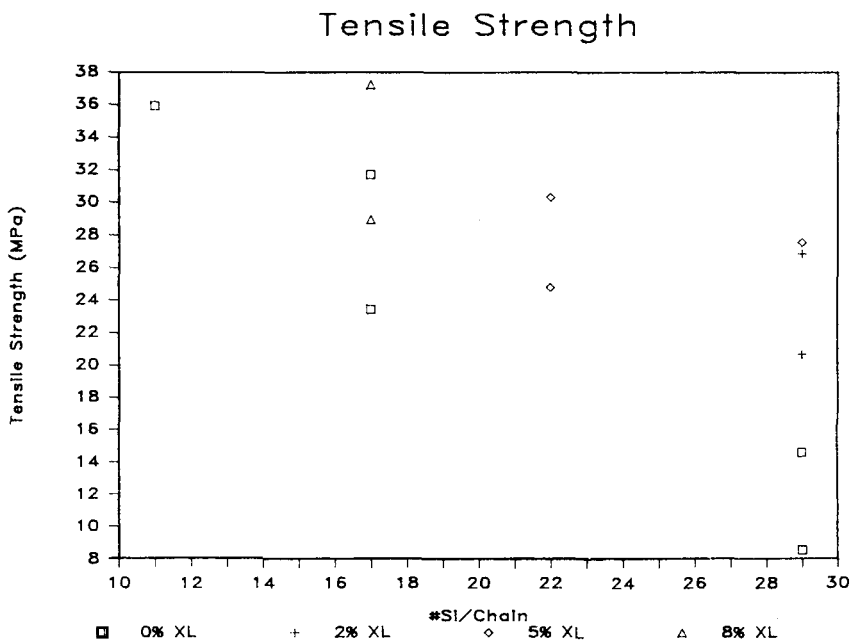

Fig. 12.   Tensile strength of SiUMA copolymers versus SiUMA chain length.
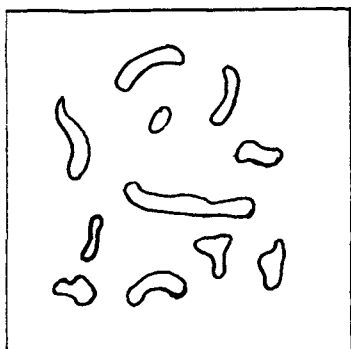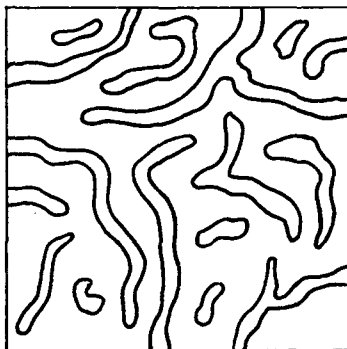
Figure 13a   Figure 13b

Fig. 13.   Possible morphologies of SiUMA copolymers.

However, at intermediate silicone content, Figure 13b shows a more prob-
ably morphology: cocontinuous siloxane and acrylic phases. The permea-
bility of the cocontinuous morphology can be approximated by eq. (2)
(neglecting the tortuosity of the phase structure).[11]

$$P = P_a f_a + P_b f_b \qquad (2)$$

If $P_b >> P_a$, then a plot of P versus f_b will be a straight line of slope P_b.
At high silicone level, a phase inversion probably occurs back to the mor-
phology of Figure 13a, with the acrylic phase now dispersed in a silicone
matrix. For a dispersed acrylic phase the permeability can be described by
eq. (3) ($P_b >> P_a$).

$$P = P_b \frac{2f_b}{3 - f_b} \qquad (3)$$

A plot of permeability versus f_b here will give nearly a straight line at high
f_b. The mathematical description of permeability in the transition between
the morphology of Fig. 13a (silicone dispersed) and Fig. 13b is very complex
and difficult to predict, but this transition should occur somewhere in the
30–60% silicone range.
   A series of copolymers was prepared with the compositions shown in Table
I (SiUMA-22 was used). The oxygen permeabilities of these materials were
measured with a MOCON tester, using 95% relative humidity at 35°C. The
data are graphed in Figure 14, along with curves for eqs. (1) through (3).
Note that weight fraction was used instead of volume fraction, but the
densities of the various components of these copolymers are nearly equal.
The permeability of the pure silicone phase was assumed to be 500 Barrer,
based on results reported in the literature for pure poly(dimethylsiloxane).[12]
The curve for eq. (2) was offset to reflect the hypothesized change in mor-
phology at about 40% silicone; that is, a significant contribution of a con-
tinuous silicone phase does not start until near that concentration.
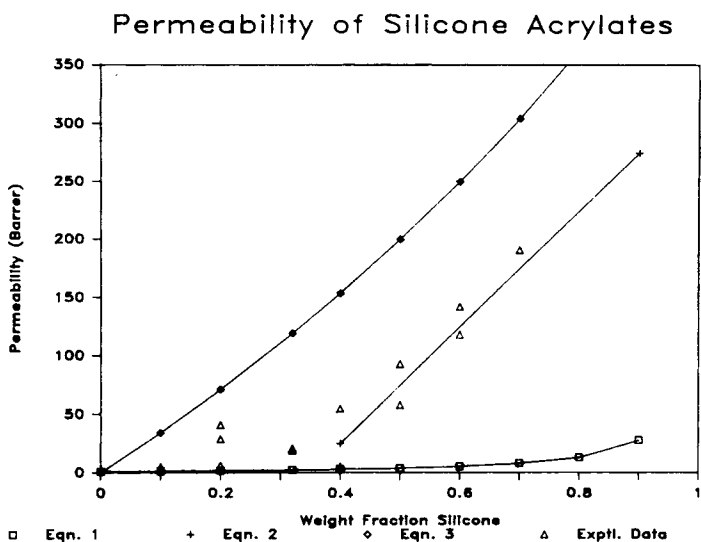
Permeability of Silicone Acrylates

Fig. 14.   Permeability of SiUMA copolymers versus silicone content.

The results actually follow quite nicely the behavior predicted by eqs. (1) and (2), with a rather pronounced break in slope at about 40% SiUMA. Because of the scatter of the data, it is impossible to tell anything definite about the behavior of the experimental curve in the vicinity of the break. The scatter of the data is difficult to explain with any certainty. All permeability measurements are extraordinarily sensitive to changes in operator, instrument, and sample. The uncensored data are presented here in the spirit of honesty. The basic conclusions about morphology are unaffected by the observed experimental error. Suffice to say that these materials apparently exist as phase-separated systems and that there is a change in morphology from discontinuous to continuous siloxane phase structure at about the 40% siloxane level.[13]

Small-angle x-ray scattering (SAXS) has been widely used to study domain size in multiphase copolymer systems.[14] In the present case, dispersed silicone-rich domains should have a higher average electron density than the surrounding acrylic matrix and scattering should result. Two samples were investigated at the University of Minnesota x-ray analysis laboratory: a SiUMA-22 copolymer and the corresponding acrylate-only polymer, which was used as a standard. Figure 15 shows the scattering curves for the two samples, and it is obvious that there are scattering bodies in the SiAc copolymer not present in the acrylate only sample.

The data were analyzed using a Guinier plot (Fig. 15) and Guinier's approximation to obtain an apparent equivalent spherical diameter of 184 Å. This analysis assumes a dilute dispersion of monodisperse spheres, which is probably not true with this system. Polydispersity of the starting SiUMA is evident from the mode of synthesis and from GPC data, and siloxane-rich phases should also be polydisperse. This size polydisperisty is indicated (but not proven) by the curvature of the Guinier plot in Figure 15. Further,
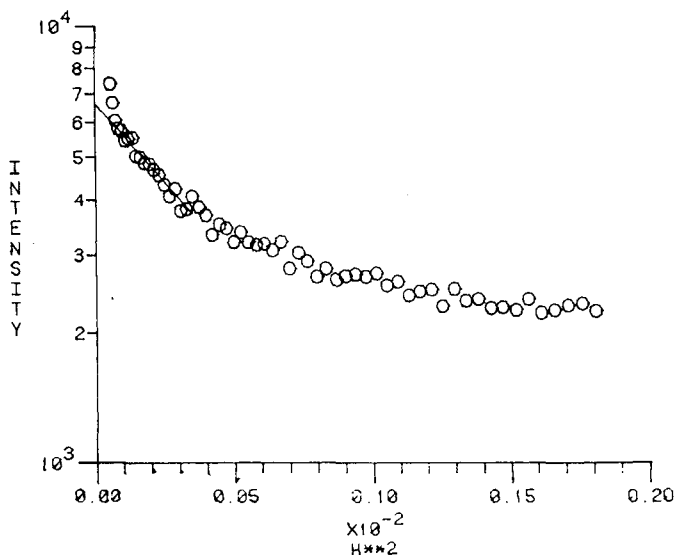
Fig. 15.   Guinier plot for SiUMA-22 copolymer.

because a fully extended SiUMA-22 chain is only 62 Å, the shape of these siloxane-rich domains must not be spherical but in fact is in some other shape, such as rods, disks, or "snakes." Unfortunately, proven mathematical models are not available to analyze SAXS data for other than a spherical discrete-phase morphology. Other investigators[10] have reported nominal diameters (by SAXS) of 100–200 Å for PDMS phases in block copolymers in which the PDMS blocks had M_n 5–10 × 10^3.

Attempts were made to visualize these domains directly by various microscopic techniques. Optical microscopoy was unable to resolve any microstructure, indicating a small size to the particles. Transmission electron microscopy has often been used in studies of this kind[10], but was unsuccessful in distinguishing electron-rich siloxane domains in these SiAc systems. One contributing factor to the TEM failure is probably the minimum 1000 Å sample thickness obtainable by the microtome available. Because these samples are all somewhat cross-linked because of the bifunctionality of the SiUMA, solvent deposition of very thin films was not possible.

Scanning electron microscopy was somewhat successful. Samples of SiAc copolymers were frozen in liquid nitrogen and then fractured. SEM imaging of the fractured surfaces showed irregular surfaces studded with "bumps" of (presumably) siloxane-rich domains. These bumps had a range of sizes corresponding roughly to the relative SiUMA chain lengths, as shown in Table II. From these results we might conclude the domains are spherical with diameters approximately equal to the dimensions in Table II.

Unfortunately, the conclusion that the domains are spherical is not necessarily valid. McGrath et al.[10,15], have shown that, in polycarbonate-polydimethylsiloxane block copolymers (polymers that display cocontinuous, spongelike phases by TEM), SEM of surfaces shows bumps, ridges and jagged peaks. The bumps seen in our samples are obviously too large to be domains made of individual siloxane chains. Thus, the exact shape of the dispersed phase in these systems is still unknown.

TABLE II
SiUMA-X

X	Weight %	SEM particle size (Å)
11	31.75	300–600
22	32.5	300–600
29	31.75	300–1500

CONCLUSIONS

From DSC data it is clear that these SiAC copolymers with a siloxane chain of more than 10 silicon atoms possess a two-phase morphology. Each phase exhibits a T_g that is close to that of the pure separate phase, either SiUMA homopolymer of acrylate only. In some samples with siloxane chains of as few as 11 silicons, a lower T_g was detectable, but that may be due to a high-molecular-weight fraction of the polydisperse SiUMA. All samples showed an upper T_g near the acrylate-only value. That this upper T_g is not displaced very much indicates that there is significant phase separation even with the lower molecular weight siloxanes.

This two-phase model is confirmed by data from DMA, permeability, SAXS, and SEM analysis. The most plausible model that fits the data envisions the siloxane-rich domains as a discontinuous, dispersed phase at low siloxane content, changing to a continuous phase at about the 40% weight fraction level. The dispersed siloxane domains are probably not spherical.

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