Effects of Phenyl Substituents on the Mechanical and Swelling Properties of Poly(dimethylsiloxane) Networks

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Introduction

Networks of poly(dimethylsiloxane), PDMS, are often used as model elastomers to test theories of rubber elasticity and swelling of polymer networks.[1−5] PDMS is chosen as an experimental approximation to an ideal elastic chain because of its highly flexible siloxane backbone and small methyl side groups.[6] It is also of interest to study networks with more complex chemical structure, however. Variables such as chain stiffness, side-group size, and the chemical nature of the backbone affect chain packing and can play a role in the elasticity of networks.[7] A good approach to eliciting information about the effects of chemical structure is to study slight structural variations of PDMS networks. By substituting various structural elements in PDMS networks, the effects of these changes on the elasticity can be inferred by comparison to pure PDMS elastomers for which a large amount of data is available.

We investigate in this study the properties of siloxane networks with 15% diphenylsiloxane structural units and 85% dimethylsiloxane units (denoted as 15/85 copolymer). Our goal here is to note the effects of the bulky substituents on network elasticity and swelling in a good solvent. In this system, two factors might be predicted to alter the mechanical properties. First, since the large side groups should restrict the number of conformations an individual chain can take, the stiffness of the individual chain is expected to increase. Second, recent calculations have demonstrated the importance of attractive interactions between pairs of phenyl groups in methylphenylsiloxane chains.[8] Such a coupling between two phenyl groups on different strands, if it were present in the 15/85 copolymer, might increase the effective cross-link density in a network. To study these effects, we synthesized networks of this copolymer by end-linking using a hydrosilylation reaction to achieve well-defined structures.

Intrinsic viscosity measurements were performed on the precursor chains to obtain information on the interaction parameter with toluene using a Stockmayer−Fixman analysis.[9] These measurements also allowed for the calculation of the plateau modulus and the entanglement molecular weight in the melt using the correlations of Fetters et al.[10,11] After the extraction of the soluble fraction, mechanical measurements to obtain elastic moduli of the dry networks and measurements of the extent of equilibrium swelling in toluene were performed. The power law relation between the dry modulus and the equilibrium swelling was determined and compared to that for PDMS networks and to recent theoretical predictions.[12] The results were analyzed also in the context of the Flory−Rehner model[13] with a markedly different conclusion regarding the suitability of this model for the diphenyl-substituted PDMS copolymer networks as compared to its suitability for the pure PDMS networks.

Experimental Section

Materials. Polymer precursors were purchased from Gelest, Inc. (catalog no. PDV-1631) and United Chemicals, Inc. (catalog nos. PS-782 and PS-785). All polymers were α,ω-vinyl-endcapped, linear chains containing nominally 14−16 mol % diphenylsiloxane units and 84−86 mol % dimethylsiloxane units. These raw precursors were analyzed by gel permeation chromatography and found to contain oligomeric impurities. The polydispersity, excluding the oligomers, was about 2.0 for all of the samples. The precursors were repeatedly washed in refluxing methanol to remove most of the oligomers. The washed samples were then fractionated using toluene as a good solvent and methanol as a poor solvent. Starting concentration for the fractionations was 1.0 wt % in toluene. The fractionation removed any residual impurities and reduced the polydispersity. Approximately 10 wt % of the original polymer was precipitated with each fraction. Toluene and methanol were obtained from Mallinckrodt (HPLC grade). *cis*-Dichlorobis(diethyl sulfide)platinum(II) was obtained from Strem Chemicals, Inc. Tetrakis(dimethylsiloxy)silane was obtained from Gelest, Inc. These materials were used as received.

Precursor Characterization. The phenyl content of several of the fractions was measured by ^{1}H NMR on a spectrometer operating at 200 MHz. The relative ratio of phenyl to methyl protons was determined and was converted to a percentage phenyl substituents by multiplying by $^3/_5$. All samples contained 15 mol % phenyl substituents within experimental errors. The polymers were assumed to be random copolymers. The 2.0 polydispersity and oligomeric impurities in the original materials indicate that the polymerization may have occurred under conditions permitting extensive chain-transfer reactions. This type of polymerization leads to chain-scrambling processes that would likely result in a random copolymer.[14] Furthermore, PDMS chains and the 15/85 copolymer chains are almost totally immiscible—an indication that the diphenyl substituents are fairly randomly distributed along the chains.

Polymer fractions were analyzed by gel permeation chromatography (GPC) in order to determine the number-average and weight-average molecular weights, both of which were required for our study. The GPC consisted of a Waters model 6000A solvent delivery system, two Waters Styragel columns (models HR-3 and HR-4), and a Waters model R401 refractive index detector. All samples were run at 21 °C with toluene as the solvent at a flow rate of 1.0 cm^3/min. Calibration was conducted with polystyrene standards from Scientific Polymer Products, Inc. Polystyrene-equivalent molecular weights are reported throughout this study.

Viscometry. Intrinsic viscosities of the fractionated samples were measured using a Cannon Ubbelohde viscometer (capillary size 50) and an automatic timer. The viscometry experiments were conducted in dilute toluene solutions with polymer concentrations no higher than 1.0 g/dL. The viscometer was immersed in a constant-temperature water bath maintained at 25.0 ± 0.2 °C during measurements.

Network Preparation and Characterization. The networks were prepared by end-linking the vinyl-endcapped precursors in the melt with the tetrafunctional cross-linker tetrakis(dimethylsiloxy)silane (A_4). The catalyst *cis*-dichlorobis(diethyl sulfide)platinum(II) was prepared in toluene solution at a concentration of 0.0023 g of catalyst/1.0 mL of toluene. A 20.0 μL aliquot of the catalyst solution was added per gram of polymer. The hydrosilylation cross-linking reaction was carried out under air at 35 °C.

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The amount of A_4 added was not stoichiometrically equivalent to the vinyl content of the precursor, in part due to the presence of some side reactions in this system.[15] To obtain networks with the highest possible modulus for a given precursor, an excess of A_4 is required to compensate for loss of Si−H groups in the side reactions. The ratio of Si−H to vinyl used was denoted r and is defined by

$$r = \frac{4(\text{moles of } A_4)}{2(\text{moles of polymer})} \tag{1}$$

The optimum value, r_{opt}, for a given polymer sample was determined by trial and error. r_{opt} was taken as the ratio yielding a network with the highest modulus and lowest degree of equilibrium swelling.[5] r_{opt} for this polymer was between 1.2 and 1.6 for most of the samples studied. The name given to a network contains the recipe for its synthesis. For example, PS-785-II-1.89 was made from polymer PS-785, fraction II, with an Si−H to vinyl ratio of $r = 1.89$.

The networks were cast into rectangular, 1.25 mm thick films by curing in a glass mold. The mold was left open on one side, exposing the thin edge of the sample, so gaseous byproducts could escape during curing. To prevent gas bubbles from forming in the network, the reaction mixture was placed under vacuum for the first few minutes of curing. The films were then cured at 35 °C for 3 days under air. Samples were punched out of the film using a rectangular steel “cookie cutter” device. In this manner, samples with smooth surfaces and very regular dimensions could be obtained for mechanical measurements.

Networks were swollen in toluene in order to remove any impurities or unattached chains (soluble fraction). The networks were swollen for at least 3 days, and the solvent was replaced with fresh toluene every day. Networks were deswollen by progressively adding methanol to the toluene over a period of several days. The networks were dried first in the air and then in a vacuum oven at 60 °C for 12 h. The soluble fraction was computed as the weight fraction of soluble material removed during swelling. The swelling ratio was computed from the relationship

$$Q = \left(1 + \frac{M_s - M_{\text{ext}}}{M_{\text{ext}}}\left(\frac{\rho_2}{\rho_1}\right)\right) \tag{2}$$

where Q is the swelling ratio, M_s is the swollen mass (of the network and solvent combined), M_{ext} is the dry weight of the network after extraction, and ρ_1 and ρ_2 are the densities of solvent and polymer, respectively.

A Perkin-Elmer DMA 7e was used to measure the elastic modulus, E, of the networks in extension. The elastic modulus was measured at a strain of approximately 1% and was converted to the equilibrium shear modulus, G_e, through the relationship $E = 3G_e$. The cross-sectional area was assumed not to change appreciably under the small strains studied. The validity of this method was checked by testing PDMS samples of known G_e which had been previously studied in oscillatory shear. The values of G_e calculated from E were within a few percent of those found in shear.

Results and Discussion

Table 1. GPC and Viscometric Data for the Copolymer Chains

polymer	fraction	M_w	M_w/M_n	[n], dL/g
PS 785	I	181 000	1.26	0.529
	II	122 000	1.21	0.368
	III	82 000	1.18	0.288
	IV	64 000	1.16	0.227
	V	49 000	1.14	0.203
PDV-1631	III	35 000	1.27	0.160
	E	18 000	1.14	0.098

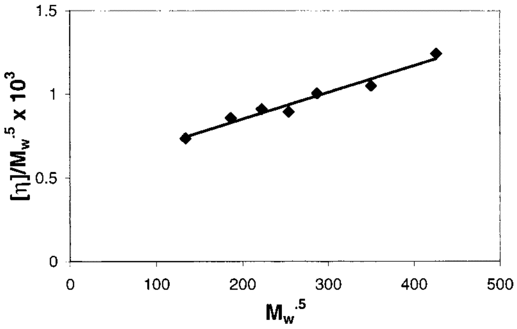

Figure 1. Stockmayer−Fixman plot of viscometry data from copolymer fractions.

Viscometry. Intrinsic viscosities were determined for seven copolymer fractions having M_w/M_n less than 1.30. Intrinsic viscosities and GPC molecular weights are listed in Table 1. Intrinsic viscosities and weight-average molecular weights from GPC were plotted according to the method of Stockmayer and Fixman[9] (Figure 1). The line in Figure 1 represents a least-squares fit to the data. The slope of the plot was used to determine a polymer−toluene interaction parameter χ_0 at near zero polymer concentration. χ_0 was determined from the relationship

$$\text{slope} = 0.51\Phi_0\left(\frac{v_2^{\,2}}{v_1 N_A}\right)(1 - 2\chi_0) \tag{3}$$

where Φ_0 is a “universal” viscosity constant taken to have a value of 2.5×10^{23} mol^{-1} in this work;[16,17] v_2 is the specific volume of the polymer, which was measured to be 0.9606 cm^3/g; v_1 is the molar volume of toluene, 106.5 cm^3/mol; and N_A is Avogadro’s number. Using eq 7, χ_0 for the copolymer in toluene has a value of 0.456, which is very close to the measured value of 0.458 for PDMS in toluene.[18] The intercept of this plot yields the parameter K_θ, which has a value of 5.30×10^{-4} (dL/g)(g/mol)$^{-0.5}$. For comparison, a value of 7.94×10^{-4} (dL/g)(g/mol)$^{-0.5}$ has been previously reported for PDMS in toluene.[18] The plateau modulus and entanglement molecular weight of the copolymer can be estimated from K_θ by the method of Fetters et al.[10] The estimated plateau modulus can be found at 298 K from the semiempirical relationship

$$G_N^{\;0} = [3.68 \times 10^5 \text{MPa cm}^9 \text{ mol}^{-1} \text{ dL}^{-2}] K_\theta^{\;2} \rho^3 \tag{4}$$

where ρ is the density of the polymer in the melt at 298 K, 1.041 g/cm^3. The value of G_N^0 obtained for the copolymer is about 1.17×10^5 Pa, whereas G_N^0 of PDMS is calculated to be 2.0×10^5 Pa. The molecular weight between entanglements is obtained from the relation

$$M_e = [5.39 \times 10^{-3} \text{ dL}^2 \text{ cm}^{-6}] K_\theta^{\;-2} \rho^{-2} \tag{5}$$

M_e of the copolymer is estimated to be 18 000 g/mol, as opposed to 9600 g/mol for PDMS.[11] The empirical correlations obtained by Fetters et al. allow also for the calculation of two parameters that ensue from the concept of entanglement formation in a polymer; these are the tube diameter d_t and the packing length p. At 298 K, one obtains $d_t \approx 70$ Å and $p \approx 4.0$ Å for PDMS,[11] whereas for the 15/85 copolymer, these values are

Table 2. Swelling and Dry Modulus of Networks

network	precursor M_n (g/mol)	M_w/M_n	w_{sol} (%)	ϕ_2(toluene)	G_e/RT (mol/m^3)
PS-782-III-1.36	14 500	1.27	0.9	0.205	103.6
PS-782-I-1.50	18 400	1.50	1.4	0.201	101.8
PDV-1631-D-1.51	21 900	1.19	3.8	0.143	56.2
PDV-1631-DD-1.51	25 200	1.15	3.4	0.149	59.8
PDV-1631-AA-1.44	48 200	1.35	2.9	0.136	49.9
PS-785-II-1.89	100 900	1.21	7.1	0.093	24.5

estimated to be 84 and 4.9 Å, respectively, from the correlations[11]

$$d_t = [0.537\ \text{Å}\ \text{dL}^{2/3}\,\text{cm}^{-3}\,\text{mol}^{1/3}]K_\theta^{-2}\rho^{-1} \tag{6}$$

and

$$d_t = 17.68p \tag{7}$$

The random presence of 15 mol % diphenyl−Si units in the PDMS causes a stiffening in the chain and an increase (~20%) in the average values of the tube diameter and packing length. This increase causes in turn a very substantial increase (drop) in the value of the molecular weight between entanglements (plateau modulus). This result does not support a coupling between two parallel phenyl groups on different chains that would lead to an increase in the plateau modulus.

The viscometry results show that the interaction parameter at infinite dilution of the polymer chains with toluene (as measured by χ_0) is not appreciably affected by the addition of 15% phenyl groups. The thermodynamic interaction with an aromatic solvent is not necessarily improved by the inclusion of aromatic groups on the chains. In fact, high polymers consisting of only diphenylsiloxane units are insoluble in toluene at room temperature and only dissolve in high boiling solvents above 150 °C.[19] Viscometry data (through the value of K_θ) also show that these chains have a larger free volume than PDMS due to the bulky phenyl groups, which is reflected in the larger tube diameter and packing length. This increase in the chain volume leads to entropic effects which are likely responsible for changes in the swelling behavior, an issue which will be addressed later.

Viscometry results were also used to find the parameters K and a of the Mark−Houwink relation between M_w and the intrinsic viscosity:

$$[\eta] = KM_w^{a} \tag{8}$$

Since the polydispersities of the samples were quite low, M_w was taken to be a good estimate of M_v. The best fit to the data is

$$[\eta]\ (\text{g/dL}) = 9.33 \times 10^{-5} M_w^{0.71} \tag{9}$$

By comparison, the exponent a for PDMS/toluene is 0.68,[18] indicating that toluene is a solvent of approximately equal quality for PDMS and the 15/85 copolymer, an issue to be discussed again below.

Equilibrium Swelling and Modulus Measurements. Soluble fractions, equilibrium swelling results in toluene, and moduli of dry samples measured at 25 °C are summarized in Table 2. The networks listed are at or near the optimum value of the parameter "r".

The soluble fractions of the networks are an indicator of the degree of perfection of the end-linked structure. The lowest soluble fractions were obtained from network synthesized from the lowest molecular weight commercial precursors (PS-782). These networks might have had the highest percentage of vinyl end functionalization in their precursors. The fractions prepared from PDV-1631 and PS-785 had progressively worse vinyl functionalization by this logic. The PS-782 networks can be regarded as "model" with the smallest fraction of pendent structures, whereas the others are best termed "slightly imperfect". The last network with a soluble fraction of 7.1% is an example of quite an imperfect network.

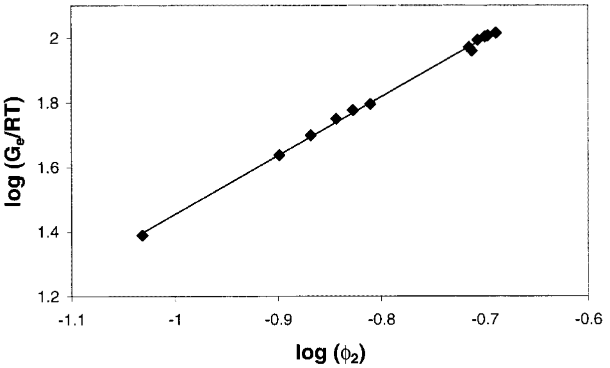

Figure 2. Dependence of the modulus, G_e/RT, on the polymer volume fraction at equilibrium swelling, ϕ_2. The slope of the best fit line is 1.82.

A wide range of values for the modulus of dry extracted samples was obtained. Although the number of data points listed in Table 2 is limited, the trend is very similar to the previously extensive results on model PDMS networks.[5] In particular, the modulus of networks from low molecular weight precursors, $G_e/RT \approx$ 100 mol/m^3, corresponds to an average elastic strand of 9000. This is well below the precursor molecular weights of 15K and 18K and demonstrates the influence of chain interpenetration. Furthermore, as one goes beyond precursor molecular weights equivalent to twice the predicted melt entanglement molecular weight of 18K, one observes a value of G_e around the plateau value estimated to be equivalent to 50 mol/m^3. This value should essentially be maintained for optimal end-linked networks (few pendent chain defects) prepared from higher molecular weight precursors as demonstrated by the previous work on PDMS networks[5] and by molecular dynamic simulation.[20] The fact that the modulus of the 100K precursor network falls well below the melt plateau modulus is another indirect indication of the imperfectness of this network.[5]

Some surprising results appear, however, when we consider the data from the swelling measurements in conjunction with the modulus data. Figure 2 is a plot of log(G_e/RT) versus log ϕ_2 for the copolymer networks. Here, ϕ_2 denotes the polymer volume fraction at equilibrium swelling and is equal to Q^{-1}. Such a correlation is independent of the architecture of the networks (whether perfect or not),[5,12] and several data points in addition to those of Table 2 have been added to obtain a more accurate correlation. The scaling law between ϕ_2 and G_e/RT was determined to be

$$G_e/RT \sim \phi_2^{1.82} \tag{10}$$

or

$$G_e/RT \sim Q^{-1.82} \tag{11}$$

The exponent in eq 11 is in reasonable agreement with the value of $-5/3$ predicted by the theory of Obukhov et al.[12] for the swelling of networks in good solvents. This is also the limit arrived at by the Flory–Rehner model in the limit of large extent of swelling.[21] However, to achieve this limit in the Flory model, ϕ_2 should be well below 0.1 and log ϕ_2 less than -1. All the data in Figure 2 (with one exception, see also Table 2) are above $\phi_2 = 0.1$. In this range of ϕ_2, the Flory–Rehner model predicts an approximate scaling power for G_e versus ϕ_2 close to 2.2 that has been observed experimentally for PDMS networks.[22] The Flory–Rehner model thus seems to have worked adequately for the PDMS networks when the dry modulus, the polymer volume fraction at equilibrium swelling, and the χ parameter as a function of concentration are all independently measured.[5] The model fails dramatically, however, for the 15/85 random copolymer networks.

Another way to observe the failure of the Flory–Rehner model is to extract from it values of χ for the copolymer networks–toluene system. These values are not known independently for this system except at infinite dilution from the intrinsic viscosity measurements reported here. Values for the modulus of dry networks of the copolymer and the corresponding equilibrium volume fractions in toluene are inserted into the Flory–Rehner model to obtain values of $\chi(\phi_2)$. The two versions of the model are[13,21]

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2^{\,2} = v_1\left(\frac{G_e}{RT}\right)\left[\frac{\phi_2}{2}-\phi_2^{\,1/3}\right] \tag{12}$$

for what has been called the affine model of swelling, and

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2^{\,2} = -v_1\left(\frac{G_e}{RT}\right)\phi_2^{\,1/3} \tag{13}$$

for the phantom model of swelling. In the above equations, v_1 is the molar volume of the solvent taken to be 106.5 cm^3/mol for toluene. Both equations were applied to the data to extract the values of χ shown in Figure 3.

In the case of PDMS, a previous study[5] demonstrated that the interaction parameters calculated from swelling experiments agreed quite well with independent measurements in solution obtained from osmometry.[23] Furthermore, extrapolation of the swelling data to zero concentration yields a χ_0 parameter which agrees with viscometry measurements of dilute solutions of PDMS chains.[5,19] In contrast, the results for the copolymer networks are quite different. Both affine and phantom models yield interaction parameters that are inconsistent with that obtained by viscometry ($\chi_0 = 0.456$). Extrapolation of χ vs ϕ_2 data to zero concentration in Figure 3 yields χ_0 parameters of 0.369 for the affine model and 0.365 for the phantom model. These low values of χ_0 are a consequence of the much larger swelling of the copolymer networks compared to PDMS networks with the same modulus. For example, a PDMS network with a modulus G_e/RT of about 100 mol/m^3 has an equilibrium swelling corresponding to $\phi_2 = 0.264$[5] whereas a 15/85 copolymer network of the same modulus (Table 2) has an equilibrium $\phi_2 = 0.20$. One reason for the discrepancy between Flory–Rehner's prediction of the interaction parameter and the intrinsic viscosity value of this parameter in this case may be the increased free volume of the chains (compared to PDMS) mentioned previously. The mixing term (the left-hand side of eqs 12 and 13) does not account for differences in such entropic effects which may also be reflected in differences in volume changes upon mixing. Thus, the inaccurate calculation of the mixing term could lead to an artificially low value for χ_0.

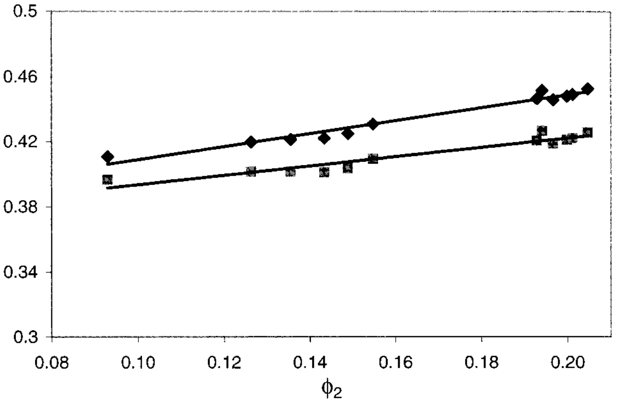

Figure 3. Values of the interaction parameter, χ, as a function of ϕ_2 extracted from the Flory–Rehner model: (◆) based on the affine model, eq 12, or (■) based on the phantom model, eq 13.

In light of this discussion, the interaction parameter determined from the Flory–Rehner model should, in general, not be the same as that obtained from solution measurements. Other authors have noted similar discrepancies between χ(network) and χ(solution) for such systems as poly(vinyl alcohol)/water[24] and natural rubber/various solvents.[25] Discrepancies between measured network and solution thermodynamic properties in the poly(vinyl acetate)/(toluene or acetone) systems have been previously attributed to the observation that the mixing free energy in a network is not necessarily the same as that of a corresponding solution.[26] In any case, the mixing term for a network taken to be the same as for a solution of the same concentration in the Flory–Rehner model must be understood to be an approximation which can lead to a value of χ inconsistent with that obtained from solutions.

Assuming the additivity of the elastic free energy and the free energy of mixing, the most likely reason for the success of the Flory–Rehner model for pure PDMS networks is a fortuitous cancellation of errors. The elastic energy of swelling is calculated on the basis of affine deformation at the scale of the elastic strand and the free energy of solvent mixing in the network is assumed to be that of a polymer solution at the same concentration. Both of these assumptions have been challenged.[27–29]

Summary

Networks have been prepared from a (15% diphenyl, 85% dimethyl)siloxane random copolymer using hydrosilylation end-linking. Intrinsic viscosity measurements performed on precursor chains indicate indirectly that the presence of the phenyl substituents lowers the plateau modulus and increases the entanglement molecular weight (relative to PDMS). The copolymer also has a greater tube diameter and packing length in the melt. Networks with a narrow distribution of molecular weights between cross-links were prepared. Most of the networks considered here have low soluble fractions and thus have a minimum amount of pendent defects. Swelling of the networks in a good solvent (toluene) was conducted to remove the soluble fraction and to find the equilibrium swelling ratio. Moduli of the extracted networks were determined by mechanical measurements in the dry state. The power law between modulus and equilibrium swelling in a good solvent is found to be quite close to recent scaling predictions. The swelling and modulus data were also examined in the context of the Flory–Rehner model. In contrast to the case for PDMS, the value of the copolymer–toluene interaction parameter at low concentration determined from viscometric analysis of the precursor chains cannot be reconciled with the value extracted from the Flory–Rehner analysis.

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