An Investigation of the Properties of Non-Gaussian Poly(dimethylsiloxane) Model Networks in the Swollen State

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ABSTRACT: Tetrafunctional poly(dimethylsiloxane) (PDMS) networks having unimodal and bimodal distributions of chain lengths between junction points were swollen by using the first three members of the linear phenylmethylsiloxane $Me_3SiO[PhMeSiO]_ySiMe_3$ homologous series. The diluents were of low volatility, and the volume fractions of the polymer, v_{2m}, at equilibrium swelling for both the unimodal and bimodal PDMS elastomers were found to increase with increasing molar mass of the linear phenylmethylsiloxanes. The swelling behavior of the networks was interpreted by using the Flory–Rehner theory of equilibrium swelling—which gave interaction parameters χ_1 in the range $0.063 \leqslant \chi_1 \leqslant 0.438$. Uniaxial extension investigations of the bimodal networks in the unswollen and swollen states show characteristic non-Gaussian behavior—in particular large increases in modulus at high extensions, due to limited chain extensibility of the short network chains. The modulus values of the bimodal elastomers were found to decrease as a function of v_{2m}—and hence the molar mass of the phenylmethylsiloxane diluents—for the bimodal elastomer containing 90.4 mol % short chains (440 g mol^{-1}). These findings may be contrasted with a PDMS bimodal elastomer containing 93.4 mol % short chains (880 g mol^{-1}), where the modulus was found to increase upon swelling with the first member of the linear phenylmethylsiloxane series. The results of this study therefore demonstrate that the quantity of short network chains is a key parameter in determining whether or not this interesting—and possibly technologically useful—phenomenon is observed for non-Gaussian elastomeric materials.

Introduction

The end-linking of functionally terminated polymer chains, instead of randomly joining chain segments, has proved to be extremely useful for synthesizing model elastomeric networks, which are materials prepared in a way that provides reliable independent information on their molecular structures.[1,2] A novel extension of this approach is to prepare bimodal model networks in which short poly(dimethylsiloxane) (PDMS) chains are mixed with relatively long PDMS chains prior to carrying out the end-linking reaction.[3-5] Such unfilled bimodal networks have unusual elastomeric properties, in particular large increases in modulus at high elongations. This behavior has been demonstrated to be intramolecular in origin and results from the limited extensibility of the short network chains.[6,7]

This investigation was prompted by the observation that the modulus of bimodal elastomers may be increased by swelling with suitable dilutents.[8,9] Furthermore, the upturn in modulus at high elongations for the bimodal networks is present even in the swollen state[8,9]—thus strongly supporting the intramolecular interpretation of this unusual phenomenon. It is the purpose of this publication to report (a) the changes in the modulus observed in the stress–strain isotherms for bimodal PDMS elastomers upon swelling with the first three members of the linear phenylmethylsiloxane homologous series and (b) the equilibrium swelling characteristics of unimodal and bimodal PDMS model networks and the thermodynamic interaction of phenylmethylsiloxanes and dimethylsiloxanes as interpreted by using the Flory–Rehner theory for equilibrium swelling.

Experimental Section

The linear phenylmethylsiloxanes $Me_3SiO[PhMeSiO]_ySiMe_3$ (MP_yM) used in this study were synthesized by methods reported in detail previously.[10-12] The materials were separated from a mixture of the linear homologous series by vacuum fractional distillation and characterized by using gas–liquid chromatography, high-performance liquid chromatography, mass spectrometry, and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.

The unimodal network was prepared by end-linking hydroxyl-terminated linear PDMS having a molar mass, M_n, of 21 300 g mol^{-1} with an exact stoichiometric amount of tetraethylorthosilicate (TEOS) (Fischer Scientific). The bimodal networks were prepared by tetrafunctionally end-linking a mixture of PDMS long chains (M_n = 21 300 g mol^{-1}) and PDMS short chains (M_n = 440 or 880 g mol^{-1}) with an exact stoichiometric amount of TEOS. The catalyst used was stannous 2-ethylhexanoate (Sigma Chemical Co.), and the materials were cross-linked under a dry nitrogen atmosphere by using procedures described previously.[5,13] After cross-linking, the elastomers were thoroughly extracted by using toluene to remove the small quantities (<3 wt %) of soluble material that they contained. The networks were then deswollen with toluene/methanol mixtures and finally methanol, before drying to constant weight.

A portion of the network to be studied was swollen to its equilibrium value[14] at 298 K by immersing the material in the respective diluent before the stress–strain measurements. The volume fraction of polymer, v_{2m}, at equilibrium swelling was determined in each case. The uniaxial stress–strain measurements were made on both the unswollen and swollen networks

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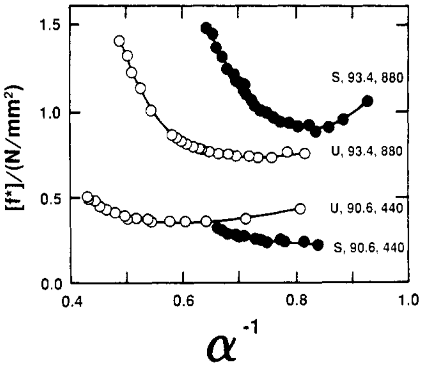

Figure 1. Stress–strain isotherms at 298 K for poly(dimethylsiloxane) bimodal networks in the unswollen (U) and swollen (S) states. The diluent used was the linear phenylmethylsiloxane oligomer MPM and each curve is labeled with the mole percentage and molar mass of the short chains present in the network.

at 298 K in the usual manner.[15] The elastomeric quantity of primary interest was the reduced stress or modulus, as defined by[15,16]

$$[f^*] = f v_{2m}^{1/3} / A^*(\alpha - \alpha^{-2}) \tag{1}$$

where f is the elastic force, A^* is the cross-sectional area in the unstretched, unswollen sample, and $\alpha = L/L_i$ (where L and L_i are the stretched and unstretched lengths, respectively). Each measurement was made to the rupture point of the elastomer.

Results and Discussion

The effect of swelling on the stress–strain behavior of bimodal PDMS model networks with the first member of the linear phenylmethylsiloxanes MPM is shown in Figure 1. The representation shown is based upon the Mooney–Rivlin equation[16]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{2}$$

where $2C_1$ and $2C_2$ are constants, and thus reduced stress or modulus is plotted against reciprocal elongation. For the bimodal network having 90.6 mol % short chains of molar mass 440 g mol^{-1} the modulus is seen to be decreased upon swelling, as is characteristically observed for elastomers having unimodal distributions of chain lengths between junction points in the swollen state.[14-16] This is contrasted with a PDMS bimodal elastomer containing 93.4 mol % short chains of molar mass 880 g mol^{-1}, where it is clearly seen that there is an increase in the modulus upon swelling. Such findings demonstrate that the quantity of short network chains is a key parameter in determining the mechanical characteristics of these non-Gaussian elastomers. The stress–strain isotherms for the bimodal elastomer containing 90.6 mol % short chains (440 g mol^{-1}) swollen with the first three members of the linear phenylmethylsiloxane homologous series—MPM, MP$_2$M, and MP$_3$M, respectively—are shown in Figure 2. The decreases in modulus along the series of the linear phenylmethylsiloxanes can be correlated with the fact that the volume fraction of polymer, v_{2m}, at equilibrium swelling at 298 K increases with the molar masses of the diluents (see Table I). In all cases the elongation at rupture α_r for the bimodal elastomers are lower for the swollen networks as expected.[15] The results corrected for dilation as follows

$$\alpha_{r,u} = \alpha_{r,s} v_{2m}^{-1/3} \tag{3}$$

where the subscripts u and s represent the unswollen and swollen states, respectively, are presented in Table II.

Table I shows that the volume fraction of polymer at equilibrium swelling, v_{2m}, for a unimodal PDMS elastomer (molar mass between cross-links, M_c = 21 300 g mol^{-1}) increases with increasing molar mass of the linear phenylmethylsiloxane diluent M_d. The decrease in swelling (increase in v_{2m}) with increasing M_d may be interpreted in terms of the Flory–Rehner equation for equilibrium swelling[19,20]

$$\chi_1 = -\frac{(\rho_p V_1/M_c)(v_{2m}^{1/3} - (^1/_2)v_{2m}) + \ln(1 - v_{2m}) + v_{2m}}{v_{2m}^2} \tag{4}$$

where ρ_p = 0.970 g cm^{-3} is the density of the PDMS network,[21] $V_1 = M_d/\rho_d$ is the molar volume of the phenylmethylsiloxane diluent, and χ_1 is the Flory–Huggins thermodynamic interaction parameter for the network–diluent system.[14] As we are comparing the interactions between the networks and diluents of a homologous series, the χ_1 parameters presented in Table I have been normalized by dividing by the degree of polymerization of the diluent so that they pertain to the interaction per repeat unit rather than the interaction per molecule.[22] The χ_1 parameters for both the unimodal and bimodal

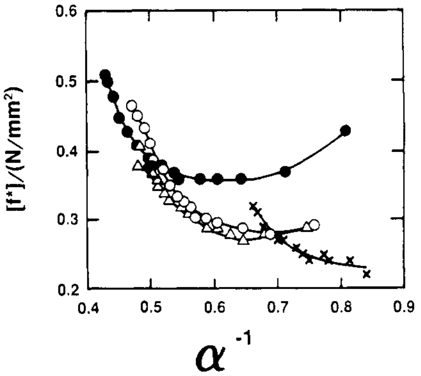

Figure 2. Stress–strain isotherms at 298 K for a poly(dimethylsiloxane) bimodal model network containing 21 300 g mol^{-1} chains with 90.6 mol % short chains of molar mass 440 g mol^{-1}. The isotherms were measured in the unswollen state (●) and upon swelling with the linear oligomeric phenylmethylsiloxane diluents MPM (×), MP$_2$M (△), and MP$_3$M (○), respectively.

Table I
Properties of the PPMS Diluents, Volume Fraction of Polymer, v_{2m}, for Unimodal and Bimodal PDMS Elastomers at Equilibrium Swelling at 298 K and the Corresponding Flory–Huggins Parameters χ_1

			unimodal[a]			bimodal[b]		
diluent	M_d	ρ_d	v_{2m}	χ_1[c]	χ_1[d]	v_{2m}	χ_1[c]	χ_1[d]
MPM	298.6	0.9098[e]	0.182	0.356	0.249	0.344	0.063	0.044
MP$_2$M	434.8	0.9763[f]	0.620	0.438	0.307	0.649	0.357	0.250
MP$_3$M	571.0	1.0120[f]	0.718	0.345	0.242	0.758	0.313	0.219

[a] Molar mass between cross-links, M_c = 21 300 g mol^{-1}. [b] Containing 90.6 mol % short chains of M_n = 440 g mol^{-1}. [c] Calculated by using the Flory–Rehner theory for equilibrium swelling. [d] Calculated by using eq 8 (see text). [e] Reference 9. [f] Reference 18.

Table II
Number-Average Molar Mass of the Linear PDMS Precursor Short Chains (M_n), Mole Percent of Short Chains, and Elongation at Rupture ($\alpha_{r,s}$) for the Bimodal PDMS Networks in the Swollen State

			$\alpha_{r,s}$	
M_n, g mol^{-1}	mol % of short chains	diluent	exptl	theory[a]
880	93.4	MPM	1.622	1.538
440	90.6	MPM	1.533	1.709
440	90.6	MP$_2$M	2.110	2.112
440	90.6	MP$_3$M	2.127	2.224

[a] Calculated by using eq 3.

Table III
Number-Average Molar Masses of the Linear PDMS Precursor Chains (M_n), Mole Percent of Short Chains in the Networks, Average Molar Masses between Cross-Links (M_c), Volume Fraction of Polymer (v_{2m}) at Equilibrium Swelling with MPM at 298 K and the Corresponding Flory–Huggins Interaction Parameters χ_1

M_n, g mol^{-1}						
long chains	short chains	mol % of short chains	M_c, g mol^{-1}	v_{2m}	$\chi_1{}^a$	$\chi_1{}^b$
21 300		0	21300	0.182	0.356	0.249
21 300	440	90.6	2400	0.344	0.063	0.044
21 300	880	60.0	9050	0.230	0.263	0.184
21 300	880	70.0	7010	0.250	0.236	0.165
21 300	880	93.4	2230	0.390	0.183	0.128

[a] Calculated by using the Flory–Rehner theory for equilibrium swelling. [b] Calculated by using eq 8 (see text).

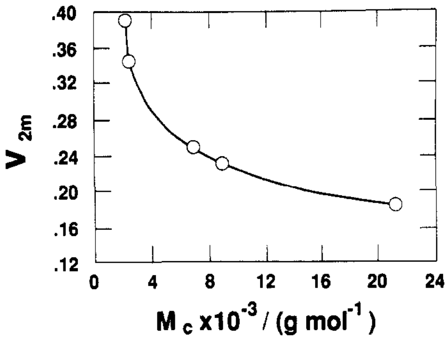

Figure 3. Volume fraction of polymer at equilibrium swelling v_{2m} plotted against average molar mass between cross-links M_c for the bimodal and unimodal PDMS elastomers swollen with MPM at 298 K.

PDMS networks are shown in columns 5 and 7 of Table I, respectively. The values were all found to be in the range $0.063 \leqslant \chi_1 \leqslant 0.438$.

The characteristics of unimodal PDMS and a variety of bimodal PDMS elastomers upon swelling with MPM are shown in Table III. The volume fraction of polymer at equilibrium swelling v_{2m} is seen to increase as the average molar mass between cross-links, M_c decreases as expected[15] (see Figure 3). For all the networks studied ($2230 < M_c < 21\ 300$ g mol^{-1}) a least-squares fit through the equilibrium swelling data gives

$$\chi_1 = 0.182 + 0.221 v_{2m} \qquad (5)$$

at 298 K. When considering only the elastomers with $7010 < M_c < 21\ 300$ g mol^{-1}—which, despite the bimodal networks containing short chains, have average molar masses between cross-links M_c typical of Gaussian networks[15,16]—one then obtains

$$\chi_1 = 0.250 + 0.195 v_{2m} \qquad (6)$$

The interaction parameters χ_1 in both cases, therefore, show quite a strong dependence on v_{2m}. Brotzman and Eichinger[23,24] have inferred from vapor sorption studies of PDMS that there may be large differences between interaction parameters for junctions and network chains. The Flory–Huggins interaction parameters for cross-linked networks, χ_c, may then be represented as[24]

$$\chi_c v_{2m} = \chi_j v_{2j} + \chi_u v_{2u} \qquad (7)$$

where the contributions from the junctions and chain units are denoted by the subscripts j and u, repectively. As the networks described in the present investigation have quite high junction densities, future studies of the swelling behaviour of such systems using a wide variety of solvents would be of interest to test this hypothesis. A detailed interpretation of the experimental results using the Flory–Rehner theory requires the assumption of an affine nature for the junction point deformations. Recently, Stein[25] has used a front factor F_φ along with the Flory–Erman theory[26,27] to account for the departure from the affine model of deformation. This gives

$$M_c = \frac{F_\varphi \rho_p V_1 [(2v_{2m}/\phi) - v_{2m}{}^{1/3}]}{\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}{}^2} \qquad (8)$$

PDMS unimodal and bimodal networks with molar masses between cross-links in the range $770 < M_c < 22\ 500$ g mol^{-1} were then swollen with benzene and toluene, respectively, at 298 K. From these results, Stein[25] obtained an average value, F_4, of 0.70 for the tetrafunctional PDMS networks ($\phi = 4$), thus indicating significant departure from the affine deformation assumed in the Flory–Rehner theory.[19,20] Using this approach, the χ_1 parameters obtained from the Flory–Rehner theory were corrected to allow for deviations from affine behavior. The values are presented in columns 6 and 9 of Table I and column 7 of Table III, respectively. The concentration dependence relationships for χ_1, corresponding to eq 4 and 5, are then

$$\chi_1 = 0.127 + 0.155 v_{2m} \qquad (9)$$

and

$$\chi_1 = 0.174 + 0.136 v_{2m} \qquad (10)$$

respectively.

It is clear from the results of the present study that the mechanical and swelling behavior of the bimodal PDMS networks are non-Gaussian due to the limited chain extensibility of the short network chains.[3,4,8,9] Recently some theory has been developed for interpreting the intramolecular non-Gaussian nature of short network chains in bimodal elastomers.[6,7,28] There is, however, a need for new theory addressing the apportioning of the strain between the long and short chains within such network structures as a function of elongation. This, in turn, may provide a detailed understanding of the mechanical, swelling, and stress-optical characteristics of elastomeric materials having controlled network chain length distributions between cross-links, as illustrated by the present study.

In the context of this investigation, it is worth noting that high molar mass linear PPMS and linear PDMS are incompatible at 298 K[17] and that a more detailed thermodynamic treatment of the PDMS/PPMS system will be reported later.[29] Further studies of bimodal PDMS networks are also in progress.

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Sorption Properties of Methylene Chloride in Isotactic Polypropylene

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ABSTRACT: The sorption curves of methylene chloride vapor in different samples of isotactic polypropyllene were analyzed at 25 °C to investigate the effect of different parameters on the sorption mode. The investigated parameters were (a) molecular weight and molecular weight distribution, (b) aging, and (c) drawing to high draw ratio. The sorption isotherms were analyzed using some of the established isotherm equations derived on the basis of various sorption models. The Flory–Huggins interaction parameter, χ, derived for the different samples, shows that methylene chloride is a poor solvent for isotactic polypropylene (iPP). An attempt to correlate clustering of solvent molecules with the lowering of the upper T_g of iPP was performed.

Introduction

The study of the interactions between solvent systems and organic polymers in the solid state can help clarify many particulars about polymer structure.[1–5]

In the last years the equilibrium sorption and the diffusion of organic penetrants have been more and more frequently used to study the basic aspects of the polymer structure. In particular, the "mode of sorption", that is the manner by which penetrant molecules are sorbed within the polymer matrix, depends principally on the polymer chain segmental mobility, and this, in turn, can be affected by the presence of the penetrant, causing a change in the mode of sorption. The sorption modes of interest are random dispersion of free penetrant molecules, localization of penetrant molecules at specific polymer groups, and penetrant–penetrant molecule cluster formation. Each of these sorption modes is related to the particular structural and morphological situation of the polymer chains.

In the case of isotactic polypropylene (iPP), the molecular weight as well as the thermal and mechanical treatments greatly influences the transport properties, and there are many unsolved problems in the evaluation of the experimental data.[6–8]

The purpose of this work is to elucidate some properties and structural aspects of iPP through the study of the sorption modes of methylene chloride vapor in films of different molecular weight submitted to different treatments.

Table I
Density (g/cm³), Amorphous Fraction, α_a, Interaction Parameter, χ, and Upper T_g Calculated from Eq 4, for the Different Samples

sample	density	α_a	χ	T_g^u, °C
A	0.9020	0.40	1.48	45
B	0.9050	0.36	1.46	45
C	0.9034	0.38	1.66	
D	0.9017	0.40	1.44	52

Experimental Section

Isotactic polypropylene of M_w = 307 000 and M_n = 15 600 was a product of RAPRA (Shrewsbury, Great Britain).

Films of this sample were obtained by heating pellets at 200 °C, pressing them into the film shape with a thickness 0.02 cm (sample A) and 0.005 cm (sample B), and cooling the melt quickly to 100–110 °C and then slowly to room temperature. Sample A was tested 2 mo after the preparation, sample B, after 16 mo.

A different film, quenched at 0 °C, was drawn at 110 °C up to a draw ratio of 15 and cooled to room temperature before being unhooked from the testing device (sample C).

A fourth sample (sample D) was obtained with the same procedure as sample A starting from pellets of iPP of M_w = 630 000 and M_n = 190 000 supplied by Himont, Italy.

Density measurements were obtained by floating the samples in a mixture of 1,2-diethoxyethanol and 2-ethoxyethane.

In Table I the samples and the corresponding densities are

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