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Some dynamic mechanical properties of unimodal and bimodal networks of poly(dimethylsiloxane)

A. L. Andrady*, M. A. Llorente, and J. E. Mark**

Department of Chemistry and the Polymer Research Center, University of Cincinnati,
Cincinnati, OH 45221-0172, USA

Summary

Elastomeric networks of polydimethylsiloxane prepared by end-linking chains having molecular weights in the range 18,500 to 220 g mol^{-1} were studied from -128 to 50°C using a Rheovibron DDV III Viscoelastometer. In the case of the unimodal networks, the glass transition temperature T_g was generally insensitive to degree of cross-linking. The intensity of the tan δ relaxation, however, increased by over an order of magnitude over the range of cross-link densities investigated. Bimodal networks prepared from mixtures of relatively long and very short PDMS chains also had values of T_g which were insensitive to degree of cross-linking. Finally, as expected, the intensities of the tan δ peak for the bimodal networks could not be explained on the basis of simple additivity of contributions from the relatively long and the very short network chains.

Key words: Model networks, bimodal networks, dynamic mechanical properties, poly(dimethylsiloxane).

Introduction

Unlike the case of linear polymers, there have been relatively few experimental studies on dynamic mechanical behavior and particularly on glass transition phenomenon in crosslinked systems. Such studies have, in the past, been conducted using randomly crosslinked networks.[1-3] These networks typically exhibit a variety of network defects and suffer the disadvantage that network parameters such as M_c, the average network chain length, cannot be directly, unambiguously determined. Network defects, particularly plasticization by free chains trapped within the network structure and dangling chains, will undoubtedly influence the glass transition temperature T_g of such systems. In any event, experimental difficulties in characterizing network geometry and average chain length are severe handicaps in the molecular interpretation of such data on networks.

The present work involves the use of model networks of poly(dimethylsiloxane), PDMS, to study the effect of crosslinking upon dynamic mechanical properties of networks. Use of model networks[4-6] has the advantage of not only providing relatively defect-free networks of homogeneous junction functionality, but also allows accurate estimates of M_c to be made. If required, even the network chain-length distribution may be controlled by the experimenter.

Use of such well-defined and characterized network systems will, it is hoped, allow the dynamic mechanical properties to be interpreted directly as a function of actual M_c rather than an indirect measure of it based on mechanical properties, as has often been done in the past.[1-2] In

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*Permanent address: Research Triangle Institute, P. O. Box 12194, Research Triangle Park, NC 27709, USA

**Permanent address: Departamento de Quimica Fisica, Universidad a Distancia, E-28040 Madrid, Spain any event, lack of information on network structure and average network chain-length has been a severe handicap in the molecular interpretation of elastomeric data on cross-linked polymers.

Some Experimental Details

The methods of preparation of the model networks of PDMS have been described elsewhere.[7] Six networks having M_c values of 220, 660, 1,100, 4,000, 11,300 and 18,500 g mol^{-1} were prepared. Preparation of bimodal networks using prepolymer of M_n = 1,100 and M_n = 18,500 g mol^{-1} was also carried out, as described elsewhere.[5,6] The dynamic mechanical measurements were made on rapidly-cooled samples using a Rheovibron DDV III Viscoelastometer over a temperature range of -128°C to approximately 50°C, at an average heating rate of approximately 1°C/min. Included in this range are the glass transition temperature (normally near -125°C) and the melting poiint (normally near - 45°C). The T_g of liquid prepolymer was measured using a support of glass-fiber paper.

Results and Discussion

The results obtained are presented in Figure 1. All networks tested gave sharp well-defined α-transition peaks. The glass transition temperature was taken as the temperature corresponding to a maximum in tan δ (or loss modulus E"). The networks, in spite of having widely different crosslink densities, gave about the same glass transition temperature, T_g. This is in agreement with previous results on PDMS,[8] and is in contrast to the linear decrease in T_g with $1/M_c$ reported for model networks of polyglycols.[9] This could be due to the very different chemical

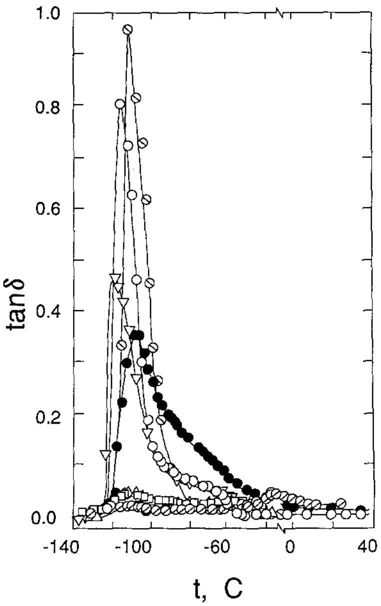

Fig. 1 - Temperature dependence of the dynamicl mechanical loss tangent for unimodal networks, measured at 11 Hz. The values of 10^{-3} M_c are 0.220 (●), 0.660 (⦸), 1.10 (tetra-functional) (○), 1.10 (trifunctional) (▽), 4.00 (△), 11.3 (□), and 18.5 (⊘).

structures of the cross links and the network chains in the latter case.[9,10] The results on the unimodal networks are summarized in Table I, and those on the bimodal networks in Table II.

This lack of dependence of T_g on crosslink density is a result of the extreme flexibility of the PDMS chains. In most polymers, crosslinking introduces severe constraints on the mobility of

Table I - Results on Unimodal Networks[a]

Network Designation	M_c (g mol^{-1})	T_g (°C)[b]	tan δ (max)[b]	Area Under E" Curve (dynes °C cm^{-2})	Estimated Fraction of Amorphous Polymer[c]
1	18,500	-113	0.015	0.396	0.062
2	11,300[a]	-114	0.040	2.030	0.318
3	4,000	-114	0.046	1.850	0.289
4	1,100	-117	0.800	2.030	0.318
5	660	-116	0.950	5.830	0.914
6	220	-116	0.355	6.380	1.000

[a] Networks prepared using vinyl-terminated polymer.

[b] Measurements carried out at 11 Hz.

[c] Estimated using equation (1), assuming network #6 to be fully amorphous.

Table II - Results on Bimodal Networks

Network Designation	Mol % Short Chains	Weight % Short Chains	$10^{-3}M_c$ (g mol^{-1})	T_g (°C)	tan δ (max)
1	98.0	74.4	1.45	-115	0.114
2	95.0	53.4	1.95	-115	0.043
3	77.0	16.6	5.10	-116	0.022
4[a]	0.	0.	18.50	-113	0.015
5[b]	100.0	100.0	1.10	-117	0.800

[a] Data on unimodal M_c = 18,500 network.

[b] Data on unimodal M_c = 1,100 network.

the chains, making it more difficult for the chains to participate in the cooperative chain movements associated with the glass-rubber transition.[11] Consequently, the glass transition can be achieved only at temperatures greater than that for the uncross-linked polymer. In PDMS, crosslinking, while introducing some constraints, fails to reduce the overall mobility of the system by an appreciable degree.[8] Therefore, the T_g of the networks remains about the same, since main-chain flexibility overrides the constraining effect of the crosslinks.[8] However, the very low molecular weight polymer (such as that having M_n = 220 g mol^{-1}) showed an increase in its T_g by 9°C when crosslinked.

A second mechanism which tends to increase the T_g of a polymer because of crosslinking is the "copolymer effect".[12] The crosslinking agent adds on to the main polymer system modifying it into a "copolymer" (of the polymer and crosslinking agent), thus changing its inherent T_g.[11] However, the cross-link structure in these model PDMS networks is similar to the structural chemistry of main chains. Therefore, no appreciable contribution from this effect is expected.

This lack of effect of crosslinking upon molecular dynamics in the network, as evidenced by the present data, is confirmed by data on gas transport. It has been shown that the rate of gas permeation in PDMS networks is unaffected by crosslinking,[13] unlike the case of other networks.[14,15]

The area under the loss modulus curve (i.e. E" versus temperature) is a measure of the fraction of repeat units available for the cooperative molecular motions involved in the dynamic mechanical loss process. In amorphous networks, increasing the crosslink density results in a progressively larger fraction of repeat units being restrained and made unavailable for the loss process. Consequently, the intensity of the tan δ peak and area under the E" curve would decrease with increase in crosslinking.

However, the present networks show an increase in the area under E" curve as crosslink density increases. This is interpreted as a result of the crosslinks decreasing the percent crystallinity of the polymer,[8] freeing up large fractions of repeat units (formerly locked into crystallites) to participate in the dynamic loss process. The contributions from these repeat units more than offset the loss of those units at or near the new crosslink points and of restricted mobility. Similar increases in either the tan δ (max) values or the area under the E" curve, A_e, with increasing crosslink density has been observed with other systems.[15]

PDMS is a readily crystallizable polymer because of its symmetric structure and high chain flexibility. Maximum rates of crystallization have been observed at relatively low crosslink densities and high uniaxial extensions. As the area under the E" curve gives a measure of the amorphous fraction free to participate in the loss process, and since the contribution of crystallites (and their neighboring repeat units) to the loss process is negligible, the dynamic mechanical data may be used to estimate the completely unconstrained amorphous fraction in the network from

$$A_e = (A_e)_u f \tag{1}$$

where $(A_e)_u$ is the area under the E" curve for a completely amorphous network and f the fraction of unconstrained repeat units. It is seen that at or above an M_c value of 1,100, more than half the repeat units are unable to undergo the molecular motions which are responsible for the loss process.

Several bimodal networks (M_c = 18,500 and M_c = 1100 g mol^{-1}) were tested to determine the effect of mixing chains on the dynamic mechanical properties. The results are given in Table II. Again, T_g values were independent of crosslink density and were comparable to those obtained for unimodal networks. However, the tan δ (max) values observed were much lower than might be expected on an additive basis, from data on unimodal networks. This is shown in Table II and Figure 2. For instance, addition of 2 mol percent (25.6% by wt.) of long (M_c = 18,500) chains to the M_c = 1,100 network caused its tan δ (max) to be decreased by more than 85 percent! Even on a weight fraction basis, the predicted decrease should not have been more than 25 percent. These results suggest a role played by the long chain component in promoting crystallinity in the rigidly crosslinked network by affording additional mobility to the shorter network chains (M_c = 1,100 g mol^{-1}).

The frequency dependence of the α-transition peak was studied for two of the networks (M_c = 660 and M_c = 18,500 g mol^{-1}). The average value for the activation energy obtained on this basis was 22 kcal mol^{-1}, in good agreement with previous determinations.

Conclusions

In model networks of PDMS, T_g was found to be independent of the cross-link density in the range of degrees of cross linking studied. However, the fraction of polymer chains available for the dynamic mechanical loss process increases with increasing cross-link density due to a drastic reduction in crystallinity with cross linking. In bimodal networks, the effect of incorporating the long-chain component is to increase the overall degree of crystallinity. This is apparently brought about by (a) the inherently higher degree of crystallinity in long-chain molecules containing relatively long sequences of repeat units uninterrupted by junction points, and (b) promoting crystallinity involving the short-chain fraction, presumably as a result of increased segmental mobility afforded to short chains in a bimodal network.

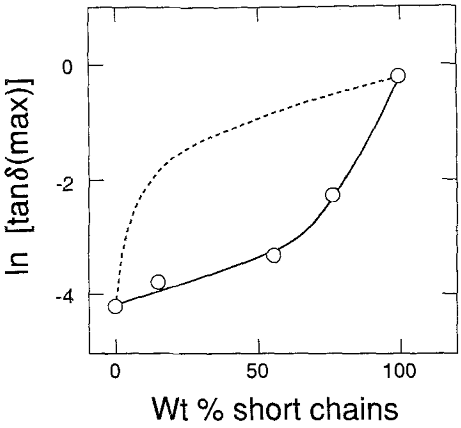

Fig. 2 - Dependence of the intensity of the tan δ peak on the composition of bimodal networks composed of long chains (18,500 g mol^{-1}) and short chains (1,100 g mol^{-1}). The dashed line shows the results calculated on the basis of weight fractions.

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