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Effects of dangling chains on some dynamic mechanical properties of model poly(dimethylsiloxane) networks

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Summary

Elastomeric networks of polydimethylsiloxane (PDMS)) prepared previously for studying the effects of dangling chains on equilibrium elastomeric properties are now studied with regard to their dynamic mechanical properties. These model irregular networks had been prepared by end-linking divinyl-terminated PDMS chains having a number-average molecular weight of 11.3 x 10^3 g mol^{-1}. The tetrafunctional end-linking agent present was used in varying amounts smaller than that corresponding to stoichiometric balance between its active hydrogen atoms and the chain vinyl groups. The resulting networks were studied from -135 to -28 ^{o}C using a Rheovibron DDV III Viscoelastometer. The glass transition temperature T_g was found to be generally insensitive to the concentration of dangling chains, over the range 0 to 41.1 wt %. The intensity of the tan δ relaxation, however, decreased significantly with increase in concentration over most of this range, suggesting the dangling chains facilitated crystallization. At the highest concentration, tan δ begins to increase, however, presumably because the inherent energy-dissipating ability of the dangling chains finally predominates.

Introduction

Preparing elastomeric networks by end linking functionally-terminated chains has several advantages,[1-7] one of which is the possibility of preparing networks with known numbers of dangling-chain irregularities.[8,9] This can be done by using unbalanced stoichiometry; the larger the excess of chain ends over functional groups on the end-linking agent, the larger the number of dangling chains. Their average molecular weight is, of course, the same as that of the elastically-effective chains, i. e., those attached at both ends to different junctions in the network.

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Since such dangling chains are elastically ineffective and represent structural irregularities, they tend to diminish the moduli and ultimate properties of the network.[8] Relatively little, however, is known about their effects on the glass transition temperature T_g of the network and its dynamic mechanical properties in general.

The present investigation was carried out to provide some information on this issue. It represents an extension of two previous studies. The first used networks of end-linked poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$] to document the effect of dangling-chain irregularites on equilibrium mechanical properties, in particular the ultimate strength and maximum extensibility.[8] The second involved dynamic mechanical properties of PDMS networks, but the irregularities in this case were the very short chains in networks having a strongly bimodal distribution of network chain lengths.[10] Of particular interest now is the determination of values of T_g and viscoelastic losses for the same dangling-chain PDMS networks studied previously,[8] and to interpret the results in the light of the corresponding results obtained on bimodal PDMS networks.[10]

Some Experimental Details

The model irregular networks of PDMS employed were the same as those used in the previous study of equilibrium mechanical properties.[8] In brief, they had been prepared by end-linking divinyl-terminated PDMS chains having a number-average molecular weight of 11.3 x 10^3 g mol^{-1}. The tetrafunctional end-linking agent used had the structure $Si[OSi(CH_3)_2H]_4$, and was present in varying amounts smaller than that corresponding to stoichiometric balance between its active hydrogen atoms and the chain vinyl groups. The end-linking catalyst was chloroplatinic acid and was present in amount of 2 - 4 ppm, and the reaction was carried out as described elsewhere.[11,12]

The relative numbers of dangling chains in these predominantly tetrafunctional networks were directly determined by iodometric titration for unreacted vinyl groups.[11,12] The six samples available for investigation had values of the wt % dangling chains of 0.0, 4.7, 23.5, 29.4, 36.2, and 41.1.[8]

The dynamic mechanical measurements were made using a Rheovibron DDV III Viscoelastometer over a temperature range of -135 to approximately -28 ^{o}C, at an average heating rate of approximately 1 ^{o}C/min.

A separate experiment involved two portions of the network containing 0.0 % dangling chains. One portion was extended to an elongation $a = L/L_0$ of 1.9, and then cooled to - 60 ^{o}C, which is well below its melting point of approximately -40 °C.[13] The deforming force was then removed and the sample cooled further to -140 °C for the start of viscoelastic measurements. The other portion was cooled directly to -140 °C, without any deformation.

Results and Discussion

The results were presented in terms of tan δ = E"/E', where E" is the loss modulus and E' the storage modulus.[14] The results 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 weight percent of dangling chains, gave approximately the same glass transition temperature, -112 to -118 °C. This is clearly consistent with the previous observation that T_g was found to be independent of cross-link density.[8] It appears, therefore, that increasing the constraints by increase in cross-link density, or decreasing them by in effect detaching some chains from cross links does not significantly change the overall mobility of the chains in these networks to an appreciable degree.

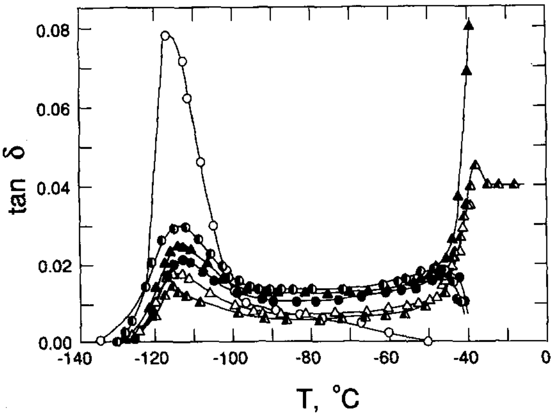

Fig. 1 - Temperature dependence of the dynamic mechanical loss tangent for the PDMS networks, measured at 11.0 Hz. The values of the wt % dangling chains present are 0.0 (○), 4.7 (◐), 23.5 (●), 29.4 (△), 36.2 (▲), and 41.1 (▲).

The area under a tan δ vs. temperature curves is a measure of the fraction of repeat units available for the cooperative molecular motions involved in the dynamic mechanical loss process.[14] The present networks show a significant decrease in this area with increase in the concentration of dangling chains over most of the range investigated. This is shown in Figure 2, as

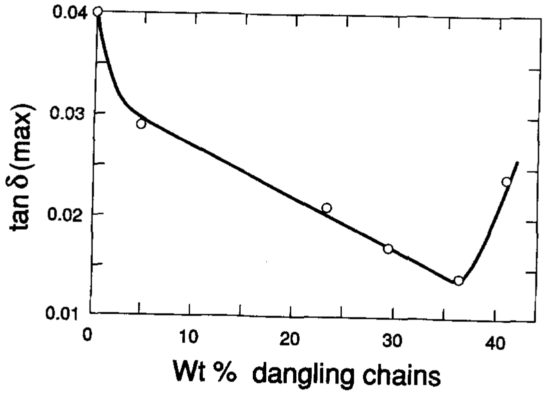

Fig. 2 - Dependence of the intensity of the tan δ peak on the wt % dangling chains present in the PDMS networks.

gauged by the maximum value of tan δ. There is seen to be a strong initial decease in this height, followed by a linear decrease up to a concentration of approximately 36 weight percent dangling chains. This suggests that the primary effect of the dangling chains is to increase the crystallinity in the network, presumably because of their increased mobility. In effect, the incorporation of repeat units into crystallites prevents them from prticipating in dynamic loss processes. The observed decreases in tan δ(max) are larger than could be expected on the basis of the crystallites containing only dangling chains, indicating the cooperative participation of some of the elastically-effective chains as well.

The present results parallel those found for bimodal PDMS networks.[10] Specifically, incorporating very long chains in a short-chain network also caused a initial large drop in tan δ(max), followed by an approximately linear decrease upon increase in their concentration. This was attributed in part to the long chains increasing the mobility of the short chains, thus increasing their tendency to crystallize.

As shown in Figure 2, the highest concentration of dangling chains causes tan δ to begin to increase. This is presumably because the inherent energy-dissipating ability of the dangling chains finally predominates over their ability to facilitate crystallization.

Some relevant information was obtained from the separate experiment carried out on the PDMS network which had been stretched before cooling to the starting temperature of the experiment. This sample should be more highly crystalline than the unstretched reference sample because of the strain-induced crystallization.[7,15,16] It was found to have a value of tan δ(max) of 0.34, which is significantly below the value 0.40 exhibited by the reference sample. This change is in the direction supporting crystallization decreasing the magnitude of the viscoelastic losses in these networks.

There is some related work in which 10 and 15 % unattached PDMS chains were trapped within PDMS networks.[5] The relaxations of these unattached chains were found to be slower within the network environment than in uncross-linked polymer by one or two orders of magnitude. A similar difference in the relaxations of unattached chains in cross-linked and uncross-linked environments was observed for polybutadiene,[17] and for styrene-butadiene-styrene copolymers.[18] These results suggest that in a network the cross links, and possibly entanglements, represent topological constraints which severely restrict the motions of such unattached chains.

The present PDMS networks differ from those with unattached chains[5] in two important respects. The dangling chains are attached to the network structure at one end, which should further constrain them, at least in the vicinity of these cross links. Also, the dangling chains had effectively the same molecular weight as the elastically-effective chains, whereas in the other networks the unattached chains were much larger than the elastically-effective ones.[5] The degree of entrapment is therefore expected to be smaller in the case of the dangling chains than it is in the case of the unattached chains. The decreased participation of the dangling chains in the relaxation processes is therefore more likely a result of the contributions of the dangling chains to increases in crystallinity, than to restrictions of chain motions arising from network topology.

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References

(1) Mark, J. E.; Llorente, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 632.

(2) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *72*, 2282.

(3) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *73*, 1439.

(4) Gottlieb, M.; Macosko, C.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039.

(5) Granick, S.; Pedersen, S.; Nelb, G. W.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1745.

(6) Miller, D. R.; Macosko, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2441.

(7) Mark, J. E.; Erman, B. *Rubberlike Elasticity. A Molecular Primer*, Wiley-Interscience: New York, 1988.

(8) Andrady, A. L.; Llorente, M. A.; Sharaf, M. A.; Rahalkar, R. R.; Mark, J. E.; Sullivan, J. L.; Yu, C. U.; Falender, J. R. *J. Appl. Polym. Sci.* **1981**, *26*, 1829.

(9) Jiang, C.-Y.; Mark, J. E. *Preprints, Div. Polym. Chem., Inc.* **1983**, *24(2)*, 92.

(10) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *Polym. Bulletin* **1991**, *26*, 357.
(11) Llorente, M. A.; Mark, J. E. *Macromolecules* **1980**, *13*, 681.
(12) Llorente, M. A.; Andrady, A. L.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2263.
(13) *Handbook of Polymer Science*; Brandrup, J.; Immergut, E., Ed.; Wiley: New York, 1975.
(14) Ferry, J. D. *Viscoelastic Properties of Polymers;* 3rd ed.; Wiley: New York, 1980.
(15) Levin, V. Y.; Solonimski, G. L.; Andrianov, K. A.; Zhdanov, A. A.; Godovski, Y. A.; Papkov, V. S.; Lyubavskaya, A. Y. *Polym. Sci., U. S. S. R.* **1963**, *15*, 256.
(16) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: 1975.
(17) Nelb, G. W.; Pedersen, S.; Taylor, C. R.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 645.
(18) Kan, H.-C.; Ferry, J. D.; Fetters, L. J. *Macromolecules* **1980**, *13*, 1687.

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