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Some evidence on pore sizes in poly(dimethylsiloxane) elastomers having unimodal, bimodal, or trimodal distributions of network chain lengths

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SUMMARY

Unimodal, bimodal, and trimodal networks were prepared by end linking functionally-terminated chains of poly(dimethylsiloxane). The resulting materials were characterized using a "thermoporometric" technique in which freezing points or melting points are determined for solvent absorbed into the network stuctures. The extent to which the normal melting point is suppressed depends on how much the solvent is constrained within the network pores. Several well-defined melting points were observed for some of the multimodal networks, which is consistent with their unusual distributions of network chain lengths.

Key words: Model elastomers, bimodal networks, poly(dimethyl-siloxane), differential scanning calorimetry, melting point depression, network chain-length distributions, pore sizes.

INTRODUCTION

One way to improve the mechanical properties of an elastomer is to prepare it so that it has a *bimodal* distribution of network chain lengths.[1-17] This can be done by end linking very short functionally-terminated polymer chains to some of the much longer ones that are normally associated with rubberlike elasticity.[18,19] This type of model network can also be used to obtain a better molecular understanding of rubberlike elasticity, particularly with regard to limited chain extensibility and strain-induced crystallization.

The purpose of the present investigation was to attempt to obtain direct evidence on the existence of unusual pore size distributions in networks that have multimodal distributions of network chain lengths. To this end, unimodal, bimodal, and trimodal networks of poly(dimethylsiloxane) (PDMS) $[\text{—Si(CH}_3)_2\text{O—}]_x$ were prepared by end linking hydroxyl-terminated PDMS chains of various lengths. In spite of their very different distributions, they were prepared so to have essentially the same *average* molecular weight M_c between cross links. The experimental method employed was "thermoporometry", in which freezing points or melting points are determined for solvent absorbed into the network stuctures. The extent to which the normal melting point is suppressed depends on how much the solvent is constrained within the network pores.

It has long been known that small particles, however formed, have significantly decreased melting temperatures.[20] The goal of thermoporometry is

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*Present address: Department of Chemistry, Helwan University, Cairo, Egypt thus to probe pore sizes by determining melting points and their distribution for solvents constrained in porous media. The clearest application involves media that are hard, such as controlled-pore glasses[21,22] silica alcogels,[23] and carbon black,[24] molecular dynamics simulations of melting under these conditions have been carried out.[25] The situation in softer, miscible media such as swollen polymer gels,[26-39] is less well understood[38,39] in that the more mobile constraints in these systems could also function by other mechanisms, for example by suppressing the nucleation process. Finally, regions of short chains would not only give rise to small pores, but would also give increased polymer concentrations that could give larger melting point depressions in the usual manner.[18]

In this semi-quantitative study, it was hoped that the these networks would have sufficiently peculiar distributions of pore sizes for swelling solvents to exhibit a a number of distinguishable melting points.

THEORY

The dependence of the free enthalpy on surface area causes the solid-liquid (sl) phase transition in small volumes to occur at temperatures T_{sl} below the freezing point $T_{sl,o}$ of the corresponding macroscopic liquid phase.[37] Volumes of importance in this regard are thought to be generally in the range of 3 - 300 nm.[30]

The relationship between the freezing point depression ΔT and a characteristic dimension of the solvent crystal D_k, is given by[37]

$$\Delta T = zT_{sl,o}S_{sl}/l_oD_k\, r \qquad (1)$$

where z is the structure factor of the solvent crystal (4 for cubic crystal), S_{sl} the interfacial tension between the crystal and its melt, l_o the specific heat of melting of the crystal, and r its density. The same considerations apply, of course, to melting points, which have the advantage of not being complicated by supercooling effects generally present in freezing processes.[38]

SOME EXPERIMENTAL DETAILS

Preparation of Samples

The three polymers employed, "short chains I," "short chains II," and "long chains," were all dihydroxyl-terminated PDMS chains, and had number-average molecular weights M_n of 417, 2,760 and 18,000 g mol^{-1}, respectively.[16] These three components were mixed in various proportions to give the compositions listed in Table 1. The network samples were given designations which refer to the mole percentages of the two types of short PDMS chains employed in the reactions. For example, the composition 54, 38 refers to the trimodal network that contains 54, 38, and 8 mol % of the three types of PDMS chains having molecular weight 417, 2,756, and 18,000 g mol^{-1}, respectively. The only exception was the network designated 0, 0, which is a unimodal PDMS network having M_n = 4,200 g mol^{-1} (a molecular weight chosen to facilitate comparisons with bimodal and trimodal networks having a similar average value of M_n). The compositions were chosen to give two groups, each having comparable values of

Table1. Sample Compositions and Estimated Pore Radii[a] in nm

Composition	2nd Peak	3rd Peak	4th Peak	5th Peak	6th Peak
0, 100[b]	-	-	-	24.1	-
87, 0[c]	-	-	20.1	-	-
54, 38[d]	-	12.8	-	-	-
22, 75[d]	-	-	-	22.7	-
0, 0[b]	-	-	-	-	35.0
78, 0[c]	-	-	19.4	-	-
45, 38[d]	4.56	-	-	-	47.9
13, 75[d]	-	8.74	15.9	-	-

[a] The first peak is not reported since it corresponds to the melting point of the pure benzene on the surface of the sample. [b] Unimodal samples. [c] Bimodal samples. [d] Trimodal samples.

M_c. Specifically, the samples were grouped so that the ones described in the first four columns of the Table have values of M_c of approximately 2.7 x 10^3 g mol^{-1}, and the last four approximately 4.2 x 10^3 g mol^{-1}.

The samples were carefully dried for several days in order to remove all traces of extraneous hydroxyl groups (e.g. from water), which might otherwise compete with those on the PDMS chains during the end-linking process. The crosslinking agent, tetraethylorthosilicate, $[Si(OC_2H_5)_4]$, was present in the amount required to give exact stoichiometric balance between its ethoxy groups and the hydroxyl end groups in the PDMS mixture. The catalyst, stannous-2-ethylhexanoate was present in amounts corresponding to 1.0 - 1.2 % by weight of polymer.

The thoroughly mixed ingredients were poured into glass molds and the reaction was allowed to proceed at room temperature for two days in the usual manner.[40] After the first day, the partially crosslinked sheets were removed from the molds and turned over in order to facilitate removal of ethanol, which appears as a by-product. Values of the molecular weight M_c between cross links in the resulting networks, were taken to be the corresponding values of M_n.[5]

Each sheet thus prepared was extracted with toluene at room temperature for one week, in order to remove the catalyst as well as any non-crosslinked polymer. The networks were then carefully deswollen in a series of toluene and methanol mixtures of increasing methanol content. The amount of material thus removed was found to be approximately 4 % of the total weight of polymer.

Differential Scanning Calorimetry

The networks were swollen to equilibrium in benzene for the calorimetry measurements, which were carried out in a Perkin-Elmer differential scanning calorimeter (DSC 7). The DSC sample containers were large-volume, stainless-steel pans (Perkin-Elmer #0319-0218) sealed with O-rings to prevent liquid loss, as described elsewhere.[38] The elastomeric sample and the liquid benzene were weighed separately into the pre-weighed sample pans. After the heating part of the cycle, the samples were reweighed to determine whether the pans had been sealed properly. In most cases, the reweighed sample pans were within 0.1 mg of their original weights. (Some very small weight losses were observed and were attributed to the diffusion of the benzene through the rubber O-ring; they were considered inconsequential).

A cooling rate of 25 °C/min was used to reach the starting temperature of -40 °C. The heating scans were then allowed to proceed at 5 °C/min to obtain melting curves, and were concluded at 50 °C. Values of the melting point depression ΔT obtained on heating were calculated using the temperatures of the heat-flow maxima in the DSC scans.

RESULTS AND DISCUSSION

The thermal behavior of the pure benzene showed a sharp, single peak corresponding to a melting point at 8.26 °C.[16] Figures 1 through 4 present the

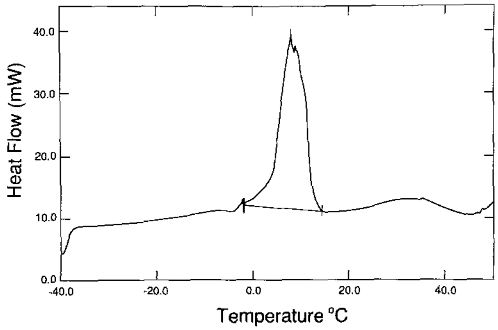

Fig. 1. Typical DSC scan, for the unimodal PDMS sample having M_c = 4.2 x 10^3 g mol^{-1}, and the composition 0, 0 (see text).

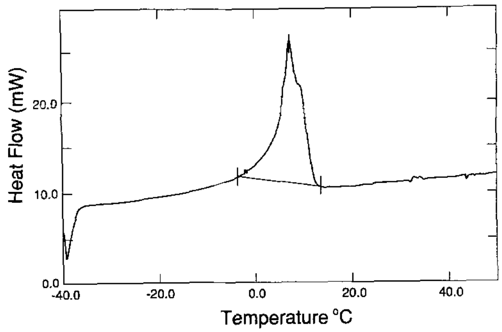

Fig. 2. Typical DSC scan, for the bimodal PDMS sample having M_c = 4.2 x 10^3 g mol^{-1}, and the composition 78, 0 (see text).

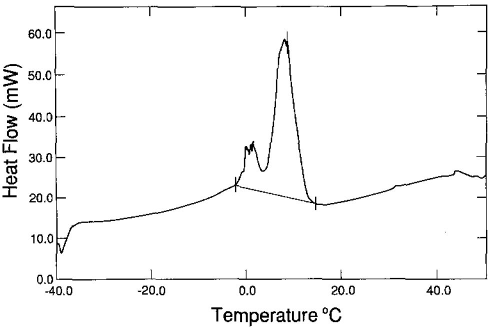

Fig. 3. Typical DSC scan, for the trimodal PDMS sample having $M_C = 4.2 \times 10^3$ g mol^{-1}, and the composition 45, 38 (see text).

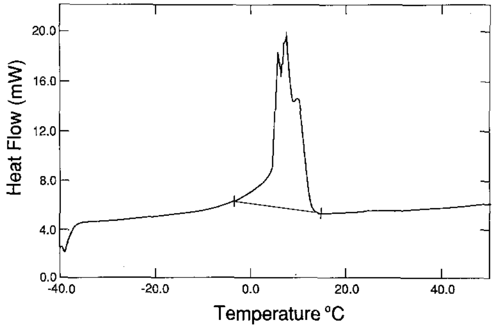

Fig. 4. Typical DSC scan, for the trimodal PDMS sample having $M_C = 4.2 \times 10^3$ g mol^{-1}, and the composition 13, 75 (see text).

results for the $M_C = 4.2 \times 10^3$ g mol^{-1} networks having unimodal, bimodal, and two trimodal distributions. Similar results were obtained for the networks having $M_C = 2.7 \times 10^3$ g mol^{-1}.[16] There were found to be multiple melting peaks, particularly in the case of the networks having the larger value of M_C. This may be due to the fact that some single peaks may contain several non-resolved contributions. (Crystals of very similar size would presumably melt within a close range of temperatures, thus giving rise to one strong peak). The effect may be most pronounced in the case of the networks with the smaller value of M_C since the corresponding crystal sizes would be much smaller in this group of networks.

The most important qualitative conclusion from these results is that there are indeed significantly different melting points exhibited by the benzene diluent. The different melting points are possibly due to crystals which have different sizes, a possiblility that could be checked by X-ray diffraction measurements. If confirmed, the variation in sizes would be due to their growth within different-sized pores in the PDMS networks. This is perhaps to be expected, particularly for the networks with trimodal distributions of network chain lengths.

Because of the complex nature of these network structures, it is very difficult to make the analysis more quantitative. It may be useful, however, to estimate some values of the pore dimension D_k from Equation for the pore radius r as a function of the melting point depression ΔT. This equation can be simplified to $r = 35.0/\Delta T$ for r in nm, using the following parameters for benzene:[37] $z = 4$, $T_{sl,o} = 278.65$ K (standard literature value), $s_{sl} = 4.0 \times 10^{-3}$ J m^{-2}, $r = 1.01$ g cm^{-3}, and $l_o = 126.1$ J g^{-1}.

Table1 shows values of the pore radius thus estimated for some of the peaks. The values are similar to those estimated for the single peaks observed for unimodal networks of PDMS, natural rubber, *cis*-1,4-polybutadiene, and copolymers of these components, using benzene, cyclohexane, and 1,4-dioxane as solvents.[37] They seem reasonable for the the chain lengths involved, and may be interpretable in more quantitative terms using a suitable model for the relevant network structures.

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