Notes

A Study of the Phase Transitions in Cyclic Poly(dimethylsiloxane) by Raman Spectroscopy and Thermal Analysis

Stephen J. Clarson*

Department of Materials Science and Engineering and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0012

John F. Rabolt*

IBM Almaden Research Center,
San Jose, California 95120-6099

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Introduction

Many of the technological applications of poly(dimethylsiloxane), $-[(CH_3)_2SiO]_y-$ (PDMS), result from both its low- and high-temperature properties being superior to many of the commercial organic polymers.[1-3] The low intermolecular interactions and the high flexibility of the polymer skeletal backbone result in PDMS having a particularly low glass transition temperature T_g (150 K) and the polymer being significantly above its melting point at room temperature. Thus varying the molar mass of linear PDMS gives fluids covering a wide range of viscosity, and the availability of a variety of methods for chemically cross-linking the siloxane chains, either through direct methods or through organic substituents, gives highly elastomeric materials.

It has been shown previously that high molar mass linear PDMS materials are highly crystalline and do not show a glass transition when they are cooled at rates of less than about 1 K min^{-1}.[4] When high molar mass cyclic or linear PDMS is quenched or rapidly cooled to below T_g, four thermal transitions are typically observed in the measured DSC thermogram upon reheating to room temperature. These correspond to T_g, an exothermic cold crystallization, and two endothermic melting peaks.[5,6] Multiple endothermic peaks are frequently observed for a variety of polymeric materials that have been studied by differential scanning calorimetry (DSC).[7] Three possible causes of this phenomenon could be (i) differences in crystallite size distribution, (ii) melting–recrystallization of the original crystallites and their subsequent melting, and (iii) different crystalline forms of the polymer. In DSC studies of PDMS model networks, however, only one crystalline melting peak was observed, suggesting that the junction points may inhibit the melting–recrystallization of the original crystallites and that this is therefore the likely source of the double endothermic melting peaks commonly observed for linear PDMS.[6,8] This is also consistent with the fact that only one type of crystal structure has been reported for linear PDMS,[9] which is monoclinic, with a helix conformation and having six structural units per primitive cell. The measured crystallographic parameters are a = 13.0 Å, b = 8.3 Å (helix axis), c = 7.75 Å, and $\beta = 60°$.[9,10] These data give a theoretical density of fully crystallized PDMS of ρ = 1.07 cm^{-3}. Recent results from solid-state NMR studies have led Tonelli and co-workers[11] to question the assigned crystal structure of PDMS and suggest an alternative extended helical structure with 35–40° rotations away from the trans conformation about each of the backbone bonds. Further interest in the crystallization behavior of PDMS has arisen from the fact that no mesophase transitions have been observed for this polymer, whereas the other symmetrically disubstituted polysiloxanes—poly(diethylsiloxane),[12-18] poly(di-*n*-propylsiloxane),[19,20] poly(di-*n*-butylsiloxane),[21] and poly(diphenylsiloxane)[22]—have all been reported to exhibit mesophases.

Friedrich and Rabolt have reported detailed Raman scattering studies of linear PDMS at 296 and 6 K.[12] The spectra at these temperatures were seen to be quite similar in all regions except for those bands near 490 cm^{-1}. This band has been assigned to the symmetric Si–O stretching vibration ν_s(Si–O). The changes observed in the Raman spectrum at 6 K have been attributed to the semicrystalline nature of the material, with ν_s(Si–O) in the amorphous region being assigned to the peak at 486 cm^{-1} and that at 466 cm^{-1} being the corresponding crystalline component. Little change was observed in the bandwidth of either the 486- or 466-cm^{-1} Raman peaks until the polymer was considerably above T_g. The collapse onto one Raman band having the same frequency and bandwidth then occurred in the −60 to −40 °C temperature range, which corresponds to the crystalline melting range of linear PDMS.

Pure low molar mass cyclic and linear dimethylsiloxanes form molecular crystals. Cyclic dimethylsiloxane sharp fractions having number-average numbers of skeletal bonds n_n in the range $24 \le n_n \le 79$ showed only a glass transition when investigated over the temperature range 103–298 K.[6] The fact that such materials are completely amorphous presumably results from these medium-size rings not being able to be incorporated into the polymer lamellar structures, whereas the PDMS rings with $84 \le n_n$ clearly form the same polymer crystals as high molar mass linear PDMS.[6]

Investigations of the mobility of fluorescent probes within such materials at subambient temperatures have been carried out previously[23] to investigate conformational mobility in cyclic PDMS melts. In order to confirm the noncrystallization of these cyclics found in the studies described above, an investigation of the low-temperature Raman spectra is reported here.

Experimental Section

The cyclic PDMS samples were prepared and characterized by methods described previously.[6] The differential scanning calorimetry (DSC) measurements were carried out using a Mettler TA 3000 Series DSC 30 differential scanning calorimeter connected to a Mettler TC 10 TA microprocessor. In order to ensure a consistent thermal history for each of the samples, the following conditions were employed. The DSC cell containing the sample was rapidly cooled to 103 K at a rate of 49 K min^{-1}. It was then held at 103 K for 3 min to allow the system to attain thermal equilibrium. The cell was then heated to 298 K at a rate of 10 K min^{-1}. All the exothermal and endothermal events over the temperature range scanned were recorded by the microprocessor.

The Raman spectra of the cyclic PDMS samples were obtained with a Spectra Physics 165-08 argon ion laser operating at

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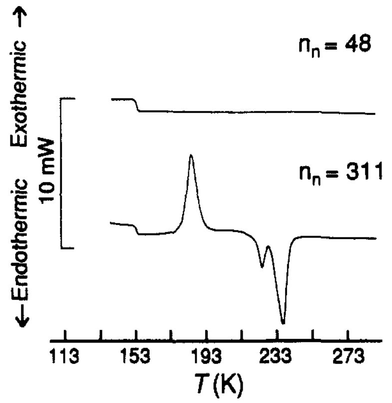

Figure 1. DSC thermograms of cyclic PDMS.

Table I. Number-Average Number of Skeletal Bonds (n_n), Number-Average Molar Mass (M_n), Polydispersity Index (M_w/M_n), and Thermal Transitions of the Cyclic PDMS Samples

n_n	M_n	M_w/M_n	T_g/K	T_{m1}/K	T_{m2}/K
48	1730	1.02	151.9		
311	11530	1.05	150.1	224.5	238.2

wavelengths of either 488.0 or 514.5 nm with a power level of 100 mW. Light scattered at 90° to the incident laser direction was collected and focused into a Jobin-Yvon Ramanor HG2S double monochromator equipped with standard photon counting electronics. Data from multiple scans were collected and averaged with a Nicolet data system.

The low-temperature data were obtained using a Harney-Miller cell through which was passed helium gas that had been cooled in a liquid-nitrogen heat exchanger. The cooling gas was in conjunction with a cartridge heater and a platinum resistor to adjust the temperature to within ±1 °C using an electronic feedback system designed by IBM (San Jose, CA) laboratories.

It should be noted that changes in Raman intensities simply due to the temperature dependence of the Raman scattering cross sections were calculated to be approximately 3% at $\nu = 480$ cm^{-1} and to be negligible at 1456 cm^{-1}. Hence, any band intensity variations outside this range can be attributed solely to changes in conformational structure.

Results and Discussion

The DSC thermograms of the cyclic PDMS fractions are shown in Figure 1, and their thermal characteristics are presented in Table I. The 311 bond cyclic showed four thermal transitions as have been described above. The 48 bond cyclic, however, showed only a glass transition. The thermogram shown is for the heating cycle following a quenching to below T_g; however, different thermal histories did not reveal any detectable crystallization for this sample.

The Raman spectra of the 311 and 48 bond cyclics are shown in Figures 2 and 3, respectively. The Raman spectrum in Figure 2 clearly shows a splitting of the band near 490 cm^{-1} into two peaks upon cooling for the cyclic PDMS fraction with 311 skeletal bonds. The appearance of the second intense component at 470 cm^{-1} is clearly indicative of conformational order as shown previously for high molar mass linear PDMS.[12] Additional evidence for crystallization comes from a consideration of the bandwidths shown in Figure 2. In the top spectrum of cyclic PDMS ($n_n = 311$) in the amorphous state above T_g the bands are broad, reflecting the broad distribution of conformers present at 273 K. In the low-temperature Raman spectrum it is clear that the bandwidths narrow dramatically. In fact most bands exhibit at least a factor of 2 decrease in their fullwidth at half-peak-height. Many bands, like that at 710 cm^{-1} attributable to the Si–CH$_3$ stretching vibration, are observed to increase their peak intensity significantly. Both the peak intensity increases and bandwidth decreases are indicative of a narrowing of the conformational distribution as would occur by confining PDMS chains to a lattice. By contrast, as seen in Figure 3 the Raman spectra for the $n_n = 48$ cyclic PDMS changes little with decreasing temperature and certainly does not exhibit the bandwidth and peak intensity changes observed for the $n_n = 311$ sample. Hence, one can conclude that the former does not crystallize perhaps due to the steric constraints imposed by the connective "loops" upon the relatively short segments of PDMS for the $n_n = 48$ sample, which would have to be accommodated in the crystalline regions.

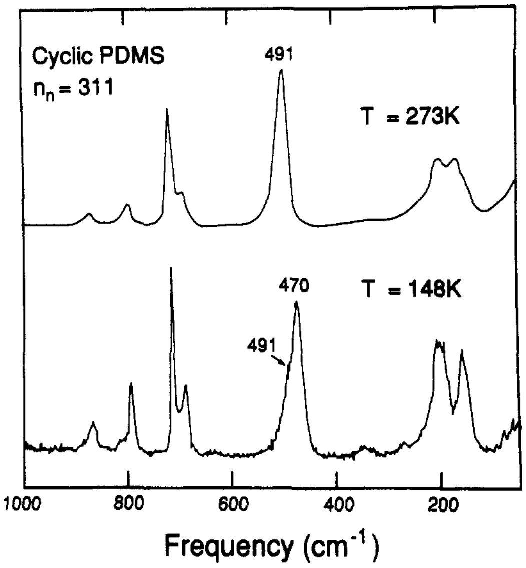

Figure 2. Raman spectra of high molar mass cyclic PDMS ($n_n = 311$) obtained at 298 and 148 K.

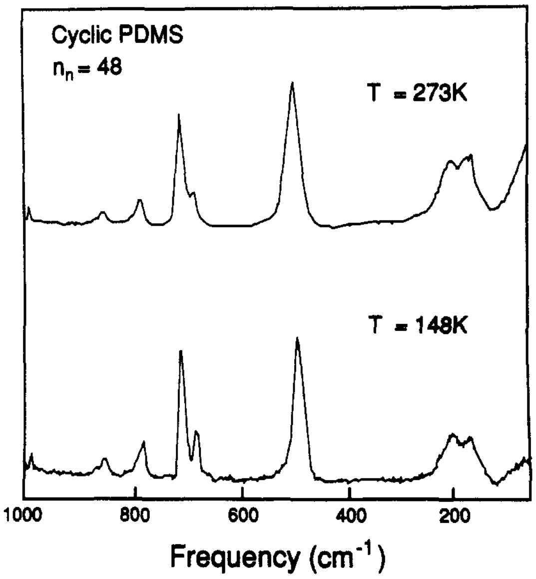

Figure 3. Raman spectra of cyclic PDMS ($n_n = 48$) obtained at 298 and 148 K.

The DSC and Raman data are therefore consistent in showing the noncrystallization of the PDMS cyclic with 48 skeletal bonds. The results also confirm the previous spectral assignments[12] of the Raman bands of the crystalline and amorphous regions for PDMS.

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