Differential Scanning Calorimetry (DSC) and Raman Spectroscopy Study of Poly(dimethylsiloxane)

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ABSTRACT: Poly(dimethylsiloxane) was studied by laser Raman spectroscopy and differential scanning calorimetry. The Si—O—Si skeletal mode at 489 cm^{-1} and the C—Si—C deformation bands at 188 cm^{-1} and 158 cm^{-1} were studied as functions of temperature from ambient to −130°C, and effects of temperature interpreted in accordance with results from thermal analysis. © 1998 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 36: 2805–2810, 1998

Keywords: poly(dimethylsiloxane); DSC; raman spectra; thermal history

INTRODUCTION

High molecular weight siloxane polymers are of great interest and exhibit unique properties. As these properties are related to their molecular structure, spectroscopic studies are important. Several authors have studied the spectroscopic characteristics of organosilicon compounds, and assignments of bands in Infrared and Raman spectra have been reported.[1–20] In particular, the work of Smith and Anderson[6] allows assignment of the vibrational bands of PDMS in a detailed way. In addition, a number of studies have been made of the conformation of the PDMS chain, either theoretically[21,22] or experimentally by using Raman spectroscopy and measuring depolarization ratios.[23–27] X-ray studies on samples at −90°C show that crystalline PDMS has a monoclinic unit cell with the chain in a 3 : 1 helical conformation.[28]

For a detailed interpretation of the vibrational bands the thermal history of the polymer must be known. A number of studies have been made in this area.[29–35] Among them, the most detailed is that of Helmer and Polmanteer,[34] but their work was restricted to high cooling rates from the melt. The effect of stress in promoting crystallization (i.e., raising the melting temperature) has also been noted.[30,34]

In this work our attention was given to the Si—O—Si skeletal deformation band at 489 cm^{-1} and the C—Si—C deformation bands at 188 cm^{-1} and 158 cm^{-1}. There is a clear interest in these bands, as their intensities depend on the temperature and thermal history of the polymer. We have studied the crystallization behavior of the polymer in a more detailed way than heretofore, by applying fast and slow cooling rates, as well as determining melting temperatures and enthalpies of fusion. As will be demonstrated below, these results helped interpretation of the effect of the physical state of the polymer on the vibrational bands under investigation.

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EXPERIMENTAL

Material

Poly(dimethylsiloxane) (PDMS) was obtained as a viscous colorless liquid from Aldrich Chemical Co. (Milwaukee, WI) ($M_n = 119{,}500$).

Differential Scanning Calorimetry

A Perkin–Elmer DSC-4 was used. Known weights (<10 mg) of PDMS were sealed into aluminium pans. The sample was cooled from 0 to −160°C at different cooling rates: −320 K min^{-1} (quenching), −10 K min^{-1} and −2 K min^{-1}. Cooling was followed by heating to 0°C, always at a rate 10 K min^{-1}. Values of the enthalpy of fusion (usually to ±5 J g^{-1}) were obtained from peak areas, and transition points (±1°C) were obtained from the temperature at the maximum or minimum of the peak. The glass transition temperature was obtained as the midpoint. The power and temperature scales of the calorimeter were calibrated against the enthalpy of fusion and melting temperature of indium.

Raman Spectroscopy

Raman scattering at 90° to the incident beam was recorded by means of a Spex Ramalog spectrometer fitted with a 1403 double monochromator, and with a third (1442U) monochromator operated in scanning mode. The light source was a Coherent Innova 90 argon-ion laser operated at 514.5 nm and 200 mW. Typical operating conditions for the frequency ranges under investigation were: bandwidth 1.5 cm^{-1}, scanning increment 0.1 cm^{-1}, integration time 6 s. The frequency scale was calibrated by reference to the 9.6 cm^{-1} and 14.9 cm^{-1} bands in the low-frequency spectrum of L-cystine.

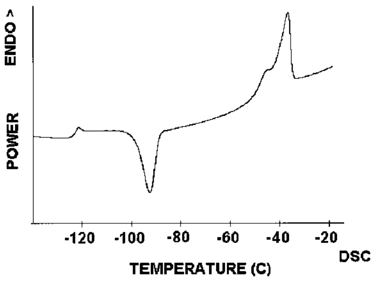

Figure 1. DSC curve (heating rate at 10 K min^{-1}) after quenching the sample to −160°C.

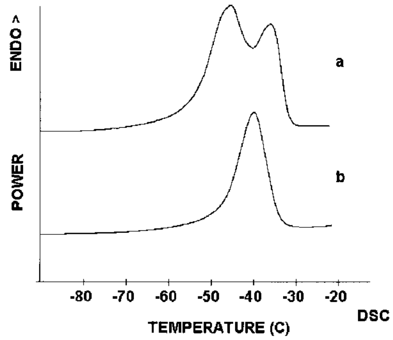

Figure 2. DSC curves (heating rate at 10 K min^{-1}): (a) after cooling at −10 K min^{-1} to −160°C; (b) after cooling at −2 K min^{-1} to −160°C.

Samples were enclosed in capillary tubes and held at a constant temperature (±1°C) in the range −130–25°C, by means of a Harney–Miller cell (available from Spex Industries Inc.). The intensity of a Raman band was observed over a period of time to ensure equilibration of the sample at a given temperature.

RESULTS AND DISCUSSION

Raman spectroscopy was carried out on samples that were quenched from room temperature to −160°C and then heated to various temperatures, as described below. Accordingly, the effect of quenching and subsequent heating was investigated by differential scanning calorimetry.

Differential Scanning Calorimetry

As described in the previous section, three different cooling rates from melt to −160°C were used in studying the thermal behaviour of PDMS. Following these processes, heating at 10 K min^{-1} gave the three DSC curves presented in Figures 1 and 2.

For the sample quenched to −160°C, the DSC curve (Fig. 1) showed a glass transition temperature, T_g, at −124°C, a cold crystallization exotherm at −93°C ($\Delta_{\mathrm{cryst}}H = -19$ J g^{-1}), and a double endotherm corresponding to melting points of −48 and −37°C. There is evidence of melting from −70°C onward, making it difficult to construct a baseline: an approximate value of total $\Delta_{\mathrm{fus}}H$ is 25 J g^{-1}. As this value is higher than

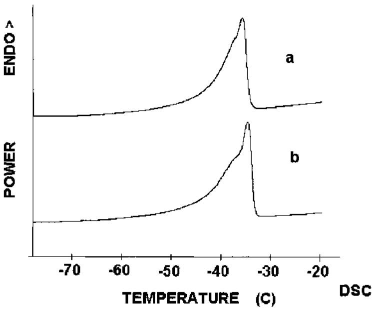

Figure 3. DSC curves (heating rate at 10 K min^{-1}): (a) after quenching from -43°C; (b) after cooling at -10 K min^{-1} from -43°C.

that found for cold crystallization, it can be deduced that a part of the sample crystallized during the fast cooling. Other crystallization processes (see below) gave $\Delta_{\text{fus}}H = 32$ J g^{-1}, consistent with some 20% of realizable crystallinity being achieved during the quench.

A double melting peak has already been referred to by others.[6,30,33,34] For the quenched sample (Fig. 1), the area under the peak at $T_m = -48$°C is much smaller than that under the peak at $T_m = -37$°C. We attribute the minor peak to melting and recrystallization of unstable crystals formed at low temperature during the quench or by cold crystallization. This view was confirmed by subsequent experiments.

Figure 2(a) shows the DSC curve obtained for the sample cooled at -10 K min^{-1}. In this case the peak at $T_m = -47$°C has a larger area than that at -36°C. We suppose that this is due to the formation of more stable crystals on cooling (i.e., compared to quenching) and to their consequent greater stability through the heating process. Finally, the sample cooled at the slowest cooling rate (-2 K min^{-1}) gave the DSC curve shown in Figure 2(b), in which the area of the single peak at $T_m = -40$°C corresponds to $\Delta_{\text{fus}}H = 24$ J g^{-1}, and there is no evidence of melting/recrystallization during heating. However, the melting point was lower than that achieved when recrystallization occurred: -40°C compared with -36 or -37°C.

Further experiments defined conditions for preparing a sample containing predominantly the high-melting form. A controlled cooled (-10 K min^{-1}) sample was heated to -43°C (i.e., 6°C below the target melting point) and quenched before heating to obtain the DSC curve shown in Figure 3(a). The melting point was -35°C and $\Delta_{\text{fus}}H = 30$ J g^{-1}, but some broadening of the peak to low T_m was apparent. The process was repeated, except that after heating to -43°C the sample was cooled at -10 K min^{-1}, in which case the DSC curve [see Fig. 3(b)] contained a peak at -34°C ($\Delta_{\text{fus}}H = 32$ J g^{-1}), with a shoulder at -38°C, indicating a proportion of the $T_m = -40$°C form known to be stable under our DSC conditions. In this case the overall peak area corresponded to $\Delta_{\text{fus}}H = 32$ J g^{-1}, i.e., somewhat higher than that obtained for the sample quenched before heating. The cold crystallization exotherm was absent in both DSC curves (this part of the DSC curve is not shown in Figures 2 and 3.

It is seen that the crystallization of PDMS is strongly temperature dependent. A fast cooling rate (quench) leads to crystallization at low temperatures, and promotes the formation of crystals with low melting points and low enthalpies of fusion that are unstable in DSC under the conditions used. A slow cooling rate (-2 K min^{-1}) leads to crystallization at higher temperatures, and favors the formation of crystals with higher melting points and enthalpies of fusion which are stable in DSC. Annealing, whether during heating of a quenched sample or by partial melting of a quenched sample, leads to the most stable crystals ($T_m = -36$°C, $\Delta_{\text{fus}}H = 32$ J g^{-1}) realized in our experiments. In this process, the unmelted crystals of the high-melting form act as nuclei for the further crystallization in the same form, a process known as self-seeding.

Warrick[30] found that spherulitic growth was favored at fast cooling rates, while aciform growth was favored at slow cooling rates, but these gross changes in morphology could not in themselves change the melting point and extent of crystallinity of the polymer. Most likely the effects found are attributable to changes in chain folding. In this respect it is noted that a similar range of melting points, more than 10 K, has been reported for other melt-crystallized polymers and, via small-angle scattering determination of lamellar thickness, assigned to changes in chain folding; see, for example, the compilation of Illers and Hendus[36] for polyethylene.

Raman Spectroscopy

Raman spectroscopy was carried out on samples that were quenched from room temperature to -160°C and then heated to various temperatures in

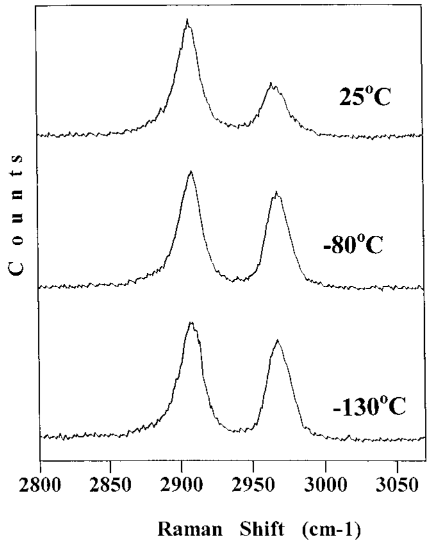

Figure 4. Raman spectra (2800–3100 cm^{-1}) after quenching and raising to: (a) 25°C (rubber); (b) -80°C (semicrystalline); (c) -130°C (glass).

the glassy ($T < -124$°C), semicrystalline ($T < -36$°C), and amorphous ($T > -20$°C) regions. Attention is paid to three regions of the spectrum: high-frequency (2800–3000 cm^{-1}, C—H stretch), and two low-frequency regions: 400–550 cm^{-1}, Si—O—Si skeletal deformation; 100–250 cm^{-1}, C—O—C deformation. Bands sensitive to the state of the polymer were found in all three regions, but the Si—O—Si skeletal deformation band proved most amenable to analysis, as described below.

High-Frequency Region

The high-frequency Raman spectra (up to 3500 cm^{-1}) were similar to those published by Smith and Anderson.[6] The spectra obtained for the polymer in its three physical states, i.e., rubbery, semicrystalline, and glassy, were identical except in the region of C—H stretching, where the peak height intensity ratio of the bands assigned to asymmetric (2968 cm^{-1}) and symmetric (2908 cm^{-1}) stretch changed on going from glass to rubber, as illustrated in Figure 4 and listed in Table I.

Low-Frequency Region

The spectrum of PDMS at room temperature (rubbery state) showed a band at 489 cm^{-1} (band A, see Fig. 5). As the temperature was lowered, this band changed to a doublet with a second band at ca. 466 cm^{-1} (band B). The two bands were assigned as the Si—O—Si stretching mode,[6] with band A assigned to the amorphous fraction and band B assigned to the crystalline fraction of the PDMS.

Table I. Temperature on the Peak Height Intensity Ratio for the Symmetric (2908 cm^{-1}) and Asymmetric (2968 cm^{-1}) C—H Stretch Raman Bands of PDMS

Temperature/°C	Intensity Ratio
25	2.05
0	2.05
−40	1.29
−50	1.25
−80	1.21
−130	1.17

Uncertainty in frequency: ±1 cm^{-1}.

To confirm these assignments, a sample was first quenched to -160°C and then spectra were recorded after heating to six different temperatures. Band component analysis was performed interactively by using GRAMS/32 data analysis software. The bands were described by a Lorentzian–Gaussian product function: an example is given in Figure 6. The results of this analysis are listed in Table II, i.e., the band frequencies and the ratio of band intensities. At 25 and 0°C, where PDMS is rubbery and fully amorphous, only band

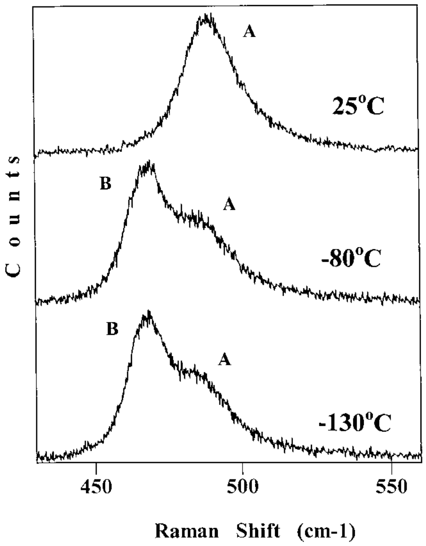

Figure 5. Raman spectra (400–600 cm^{-1}) after quenching and raising to: (a) 25°C; (b) -80°C; (c) -130°C.

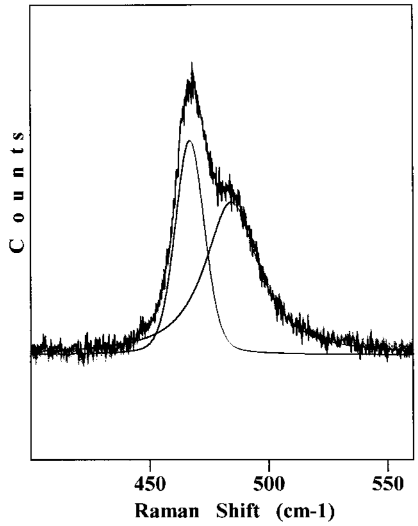

Figure 6. An example of a Lorentzian–Gaussian deconvoluted Raman spectrum (400–550 cm^{-1}) at −130°C.

A is observed at 489 cm^{-1}. At the lower temperatures investigated, crystalline and amorphous parts coexist and the band is seen as a doublet. At −130°C, the polymer exists in major part in its glassy amorphous form and in small part in crystalline form, as discussed in the previous section (DSC), and the peak height intensity ratio, I_A/I_B, is 1.40. At −80°C, the ratio increases to 1.69, as expected, because cold crystallization starts above T_g and is complete above −85°C (see Fig. 1). At −50°C the ratio is reduced to 1.48 as a result of melting, which begins at ca. −70°C. At −40°C the sample is part melted, and the intensity ratio is much lower at 1.21.

Table II. Effect of Temperature on Band Frequencies in the 400–550 cm^{-1} Region of the Raman Spectrum of PDMS: Band A (467 cm^{-1}), Band B (489 cm^{-1}), and the Peak Height Intensity Ratio (I_A/I_B)

Temperature/°C	A (cm^{-1})	B (cm^{-1})	Intensity Ratio
25	489	—	—
0	489	—	—
−40	486	466	1.21
−50	484	465	1.48
−80	486	468	1.69
−130	485	467	1.40

Uncertainty in frequency: ±1 cm^{-1}.

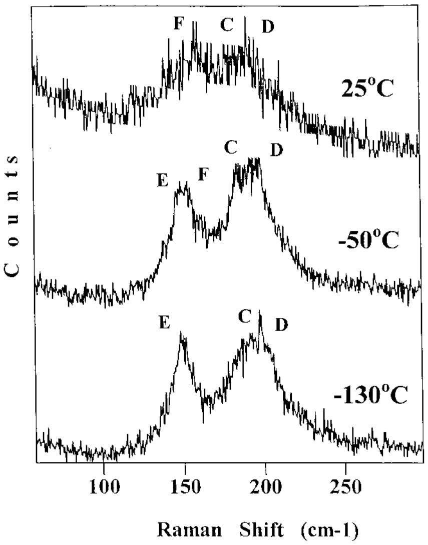

Figure 7. Raman spectra (50–300 cm^{-1}) after quenching and raising to: (a) 25°C; (b) −50°C; (c) −130°C.

The 100–250 cm^{-1} region of the spectrum of PDMS contained a number of bands. Three bands were seen in the spectrum of the samples that was quenched to −160°C and heated to −130°C (Fig. 7), i.e., a composite of two bands centered on 192.5 cm^{-1} (band C) and 197.5 cm^{-1} (band D), and a sharp band at 149.5 cm^{-1} (band E). Following Smith and Anderson,[6] these bands were assigned to C—Si—C deformations. Bands C and D shifted to lower frequencies as the temperature was raised, as indicated in Table III. The frequency of band E was constant (at 149 cm^{-1}) up to the melting point, but split into a doublet at −50°C, i.e. when melting started, due to the appearance of a new band at 152.5 cm^{-1} (band F). Band E was detected only in the spectra of semicrystalline samples ($T < -40$°C). The frequency of band F, assigned to rubbery polymer, increased with temperature up to 25°C (see Table III).

CONCLUSIONS

The conclusions are twofold. (1) The crystallinity of PDMS depends markedly on cooling conditions. It is possible, by carefully thermal treatment, to achieve a high-melting form ($T_m = -36$°C). (2) The Raman spectra of PDMS contain a number of bands that are sensitive to the crystallinity of the sample. Of these, the two Si—O—Si skeletal de-

Table III. Effect of Temperature on Band Frequencies in the 100–250 cm^{-1} Region of the Raman Spectrum of PDMS

Temperature/°C	C/cm^{-1}	D/cm^{-1}	E/cm^{-1}	F/cm^{-1}
25	183	192		159
0	184	193.5		161
−40	185	194	148.5	154
−50	184.2	195	148.5	152.5
−80	188.5	196.5	148.5	
−130	192.5	197.5	149.5	

Uncertainty in frequency: ±0.5 cm^{-1}.

formation bands offer the best prospect of quantitative use via the intensity ratio I_A/I_B.

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