values determined by ^{29}Si NMR values. To achieve similar agreement with the GPC values we had to employ an empirically derived Q-factor ratio of 0.80. The Q-factor ratio of 0.62 which we had used previously in the disiloxanol studies gave GPC molecular weights which differed considerably from the actual molecular weights. Except for the $\bar{M}_n$ values for SF-96(5), both analytical techniques are in good agreement. We conclude that the $\bar{M}_n$ discrepancies noted in the disiloxanol studies are attributable to differential spreading in the GPC by various disiloxanol species.

Experimental Section

NMR Measurements. The ^{29}Si Fourier transform spectra were obtained on a Varian XL-100-15 NMR spectrometer interfaced with a Transform Technology TT1020 high power amplifier operating at 19.86 MHz. All samples were run under proton noise decoupling conditions using deuterated solvents for the internal field frequency controlled lock system. Pulse widths of 45 μsec giving a flip angle of ~60° were used to look at spectral windows of 1000 Hz with 4-sec acquisition times. Spectrometer control was obtained from the system computer (Varian 620i; 16K core) allowing acquisition of 8192 data points, resulting in 4096 output data points in the phase corrected absorption spectra. Samples were doped with about 0.1 M tris(acetylacetonato)chromium to shorten the T_1's by replacing ^{29}Si–^{1}H dipole–dipole (DD) and spin–rotation (SR) relaxation with electron nuclear DD relaxation resulting in T_1's of only a few seconds.[10]

Viscosity Measurements. Bulk viscosities were determined in Cannon-Manning semimicroviscometers in a bath thermostated at 25.0 ± 0.3°C.

Gel Permeation Chromatography Measurements. All samples were analyzed with a Waters Associates GPC 200; chromatograms were run using 0.5 wt % solutions in methylene chloride, injected over a 120-sec period. The GPC columns consisted of five columns in series packed with Styragel, having porosity ranges of 2.5×10^4, 2000–5000, 10^3, 350–700, and 60 Å. The columns were calibrated with standard polystyrene samples (Pressure Chemical Co.) of anionically polymerized polystyrenes and styrene monomer.

The Q factors and Q-factor ratio were calculated as follows. Polystyrene: $Q_{\mathrm{ps}} = 104$ g formula/2.51 Å = 41.5 g formula/Å. Polydimethylsiloxane: $Q_{\mathrm{PDMS}} = 74$ g formula/2.88 Å = 25.75 g formula/Å; $M_{\mathrm{PDMS}} = (25.75/41.5)(M_{\mathrm{ps}}) = 0.62M_{\mathrm{ps}}$.

Materials. All disiloxanols and monodispersed methyl-terminated fluids were provided by Dr. J. Razzano of the Silicone Products Business Department (SPBD), General Electric Co. The 5 cs fluid was General Electric SF-96(5) silicone fluid available from SPBD.

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Raman Spectrum of Crystalline Poly(*trans*-1,4-butadiene)

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ABSTRACT: Raman spectra of mats of poly(*trans*-1,4-butadiene) crystals grown at different temperatures have been obtained at 25°C. Spectra were also taken at temperatures in the 25–78°C region for one preparation and the changes in the Raman spectrum accompanying the transformation from form I to form II are described.

Poly(*trans*-1,4-butadiene) is known to have two crystalline forms; the form stable at room temperature and atmospheric pressure, form I, is reported to have a monoclinic lattice represented by the $P2_1/a$ space group and containing four chains.[1] Form II is stable (at atmospheric pressure) at temperatures between 71°C and the melting temperature; the distance between chains and the repeat distance along the chain is known from x-ray analysis.[2] The x-ray results and potential energy calculations[3] suggest that the polymer chains in form II of PTBD have considerable freedom of motion. In fact, the infrared spectrum found for form II is the same as that for PTBD in the melt or in solution.[4,5] A Raman spectrum for PTBD rubber containing 89% trans units and 9% cis units has been published.[6] A recent Raman study on form I crystals of PTBD has been carried out by Hsu, Moore, and Krimm;[7] in that investigation a normal vibration analysis of crystalline PTBD was also made.

In the present study the Raman spectra for mats of PTBD crystals grown from dilute solution have been obtained. The effects of crystal growth temperature and solvent and of various thermal and mechanical treatments on the spectrum at 25°C have been explored. Raman spectra at temperatures in the 25 to 78°C range have also been recorded and the changes accompanying the form I to form II crystal transition have been observed. These results are presented and discussed below.

Experimental Section

The characteristics of the polymer used in this investigation, PTBD-K, and the methods of crystal preparation have been reported on earlier.[8–13] The results of studies on the amorphous-crystalline content of crystals grown from dilute heptane and toluene solutions are given in Table I.

Raman spectra were obtained with a Spex Ramalog 3 employing an Argon laser. The wavelengths used were 4880 and 5145 Å. Slit widths of 1.7 to 4 cm^{-1} were employed. The crystal mats were

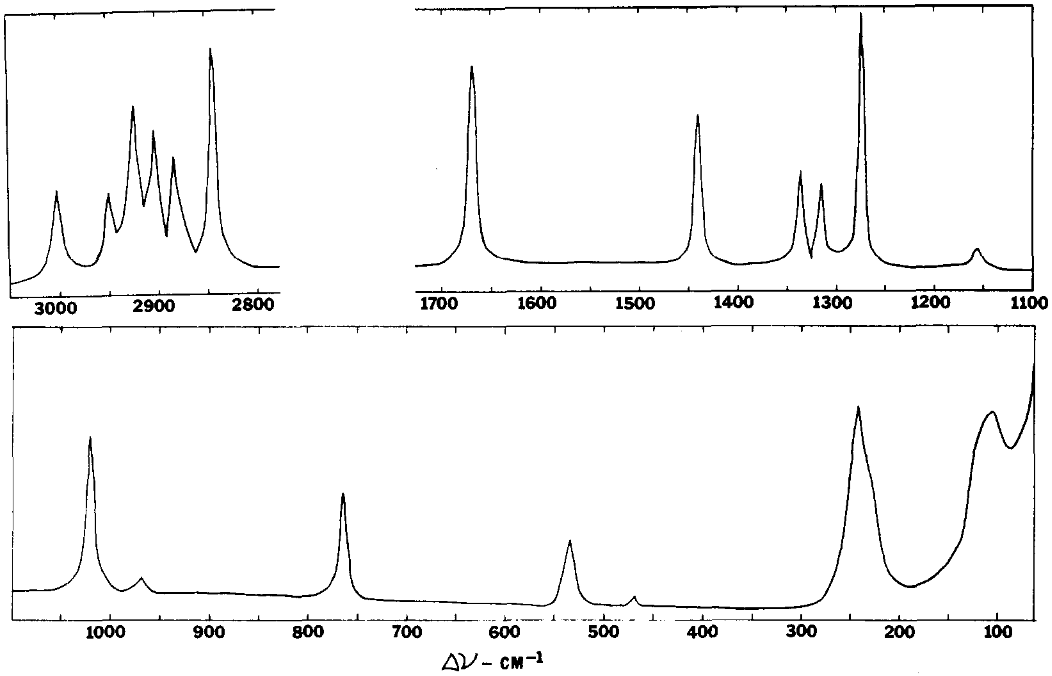

Figure 1. Raman spectra at 25°C for PTBD crystals grown from heptane at 63°C using 5145 Å exciting light.

Table I
Amorphous Fractions for PTBD Crystals

Solvent	Dissolution temp/ precipitation temp	Surface epoxidation[8,9]	Total NMR[13]	Total Ir[10]	Total DSC[12]
Heptane	76°C/63°C	0.14	0.13	0.2	(0.2)
Toluene	50°C/23°C	0.19	0.23	0.5	0.4

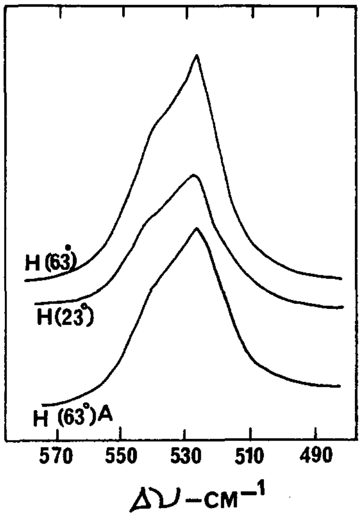

Figure 2. Raman spectra in the 490–570-cm^{-1} region for PTBD crystals grown from heptane at 63°C (H (63°)), crystals grown from heptane at 23°C (H (23°)), and crystals grown from heptane at 63°C and annealed at 80°C for 12 hr (H (63°) A) (4880 Å exciting light used).

mounted on a stainless steel disk held in an Opaque Specimen Platform (No. 1432 M), the angle between the laser beam and the mat surface being 30°; a metal washer was used to ensure a close fit of the mat to the metal disk. The sample was heated by applying heat to the metal disk; the temperature was monitored by a thermistor embedded in the metal disk.

Results

Typical Raman spectra taken at 25°C for a mat of PTBD crystals grown from heptane at 63°C in the frequency ranges of 2800–3150 cm^{-1}, 1100–1750 cm^{-1}, and 50–1100 cm^{-1} are given in Figure 1. A more highly resolved scan for the peak at 534 cm^{-1} is shown in Figure 2 where a higher frequency shoulder is evident. These spectra are in substantial agreement with that of Hsu, Moore, and Krimm[7] taken at 25°C. Spectra at 25°C were also obtained on crystals grown from toluene at 23°C and heptane at the same temperature. The frequencies for the latter two preparations were in agreement within ±2 cm^{-1} with those shown in Figure 1; the 529-cm^{-1} band showed the same complex shape as that recorded for crystals grown from heptane at 63°C (see Figure 2). There are differences in band heights (relative to the height of the 1666-cm^{-1} band, a band which shows little change) between spectra for crystals grown at different temperatures; significant reductions in the relative heights for the bands at 238 (40% reduction), 762, 1131, and 1437 cm^{-1} were found. Raman spectra were also taken for mats of crystals grown at 63°C in heptane (i) after annealing at 80°C for 12 hr, (ii) after pressing at 25000 psi, (iii) after melting and cooling in liquid nitrogen, and (iv) after melting and cooling in the vacuum oven and on a mat of crystals grown from toluene at 23°C and subsequently annealed at 80°C for 12 hr. Again the frequencies were comparable with those given in Figure 1 but difference in relative intensities existed. In all cases the heights of the 238, the 762, and the 1437 cm^{-1} bands (relative to that of the 1666-cm^{-1} band) were lower. However, the 80°C annealed toluene grown crystals and 23°C heptane grown crystals showed relative band heights very close to those of the as prepared toluene grown sample. As can be seen in Figure 2, the complex band shape at 529 cm^{-1} still exists after annealing. The ratio of the height of the 1331 to the 1311-cm^{-1} band, used recently as a measure of order,[7] was found to be 1.2 for crystals grown from heptane at 63°C and ranged from 1.4 to 1.8 for all other samples cited above. This part of the Raman spectrum for those samples is shown in Figure 3. Average values for the frequencies of the bands found are given in Table II.

Spectra for PTBD crystals grown from heptane at 63°C were also obtained at temperatures above 25°C up to 78°C.

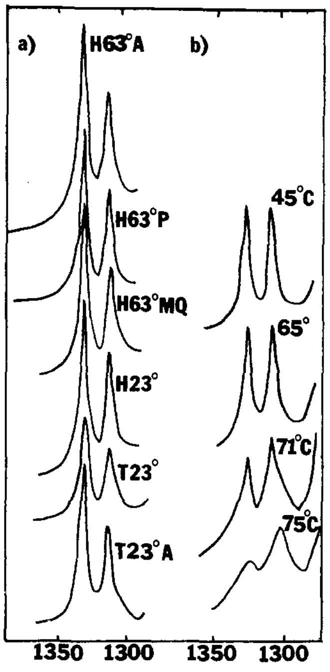

Figure 3. (a) Raman spectra at 25°C in the 1300–1350-cm^{-1} region for PTBD crystals grown from heptane at 63°C. Annealed at 80°C for 12 hr (H 63° A); pressed at 25000 psi (H 63° P), and quenched from the melt in liquid nitrogen (H 63° MQ). For crystals grown from heptane at 23°C (H 23°) and for crystals grown from toluene at 23°C (T 23°C) and for those subsequently annealed at 80°C for 12 hr (T 23° A). (b) Spectra in the 1300–1350-cm^{-1} region taken at various temperatures for crystals grown from heptane at 63°C (4880 Å exciting light used).

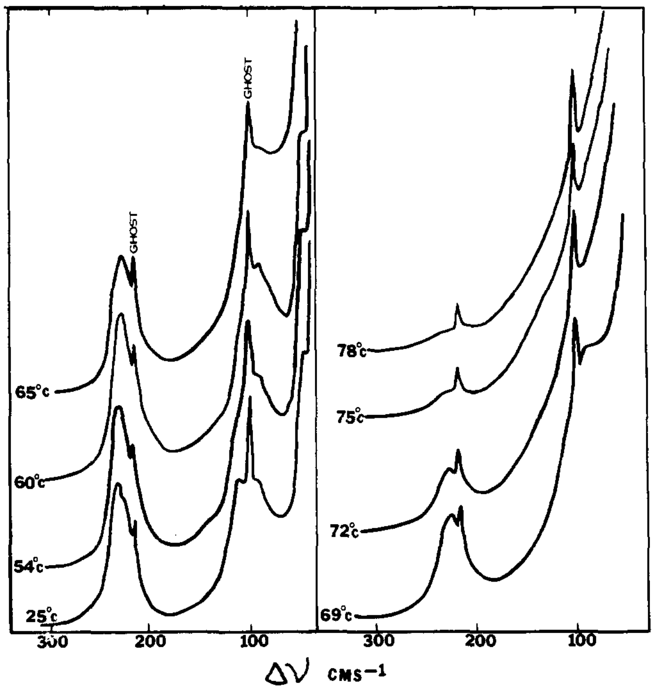

Figure 4. Raman spectra in the 20–60 to 300 cm^{-1} region at various temperatures for PTBD crystals grown from heptane at 63°C (4880 Å exciting light used).

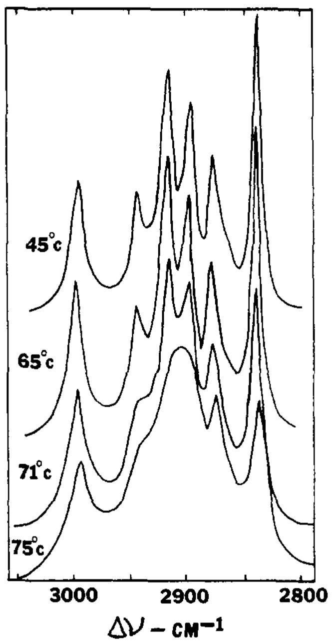

Figure 5. Raman spectra in the 2800–3500-cm^{-1} region at various temperatures for PTBD crystals grown from heptane at 63°C (4880 Å exciting light used).

Table II
Raman Frequencies for Poly(*trans*-1,4-butadiene)

Crystal mat			Rubber[6]	
25°C	69°C	75°C	25°C	Assignment[7]
2999		2999	3003	CH st
2946			2932	CH_2 a. St,
2920		2908		overtones,
2900			2898	combinations
2880		2878	2876	
2838		2840	2846	CH_2 sym st
1666		1665	1664	C=C st, CH i.p. bend, C–C st
1437	1433	1430	1431	CH_2 bend
1331		1337	1324	CH_2 wag, CH_2 twist, CH i.p. bend
1311		1306	1301	CH_2 twist, CH_2 wag, CH i.p. bend
1270		1270	1267	CH_2 wag, CH i.p. bend, C–C st
1152			1124	C–C st, CH_2 rock, CCC′ def
1018	1015	1014	1011	C–C st
967			969	CH_2 rock, C–C st, CCC def, CH o.p. bend
762	771		761	CH o.p. bend, CH_2 rock
529	543		537	CCC′ def, CCC def, CH o.p. bend
238	230		221	C–C tor, C–C st
115				Rotational and translational lattice modes
100				
70	(?)			
47	(?)			

Frequencies for the bands at 69° and/or 75°C are given in Table II and spectra at different temperatures in three frequency regions are given in Figures 3, 4, and 5. The bands at 1437, 1311, 238, and 90–120 cm^{-1} shift to lower frequencies at temperatures above 50–65°C while bands at 762 and 529 cm^{-1} shift to higher frequencies; the bands at 2900, 2930, and 2946 cm^{-1} merge to form a broad band at 2908 cm^{-1} with a high-frequency shoulder. The weak bands at 967 and 1152 cm^{-1} apparently disappear. All the bands below 1166 cm^{-1} decrease in relative height with increasing temperature with the possible exception of the bands at 90–120 cm^{-1}. These bands overlap with a low-frequency continuum which is found to increase in intensity above 60°C (see Figure 4).

Also included in Table II are the relevant frequencies of

Cornell and Koenig[6] for a PTBD rubber containing 89% trans units and the vibration assignments of Hsu, Moore, and Krimm.[7]

Discussion

In the paper of Hsu, Moore, and Krimm[7] the higher-frequency part of the 529-cm^{-1} band was given a noncrystalline assignment; this assignment was partially based on a sharpening of this band upon annealing at an unspecified temperature. In the present work annealing at 80°C is not found to sharpen this band nor do crystal mats with two- to threefold differences in amorphous content show significant variations in this band. A second indication of increased crystallinity cited by Hsu et al.[7] was an increase in the 1331/1311 height ratio. However, in the present work this ratio is not found to be sensitive only to crystallinity changes.

The transformation of form I to II taking place at 71°C brings about significant changes in the $=CH-CH_2-$ torsion angle.[2] This change is expected to cause a shift in some of the Raman bands, particularly those at low frequencies. The analysis of Hsu et al.[7] correctly predicts the direction of this frequency shift of the bands at 1018, 762, 529, and 238 cm^{-1} found experimentally, as given in Table I. The lattice vibration bands at 90–120 cm^{-1} are expected to shift to lower frequencies with an increase in temperature, as observed in this work in the 25°C to 69°C range and by Hsu et al.[7] with measurements at −160°C and room temperature. The disappearance of the bands at 967 and 1152 cm^{-1} at higher temperatures appears to be consistent with the chain analysis.[7] X-ray diffraction results[2] and energy calculations[3] for form II suggest that rotation about C–C bonds is taking place and this should lead to the disappearance of such bands as well as the disappearance of the band at 238 cm^{-1}, due principally to C–C torsion, and the lattice vibration bands at 90–120 cm^{-1}. An increase in Raman scattering intensity, observed in the 20–200-cm^{-1} frequency region at temperatures above 60°C, accompanies the form I to II transition. This apparently is a manifestation of the various conformations made available to the PTBD chain molecules in form II. The changes taking place in the CH_2 stretching, overtone, and combination band region at higher frequencies (see Table I) are probably due to shifts in one or more of the lower-frequency bands which contribute to this region. A similar effect was observed in these laboratories earlier for the infrared bands in the $-CH$ and $-CH_2$ stretching region.

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Dielectric Study of Chain Motion of Poly(*p*-chlorostyrene) in Dilute Solution

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ABSTRACT: Dielectric relaxation measurements were carried out on dilute solutions of poly(*p*-chlorostyrene) in benzene, toluene, ethyl benzene, and dioxane in the frequency range of 1–150 MHz. An asymmetrical loss curve was observed for each solution. The relaxation time τ_m could be described by $\tau_m = 8.0 \times 10^{-9}\eta_0 \exp(E/RT)$ (sec), where η_0 is solvent viscosity in units of poise and E has a value of 2.9 kcal/mol. The dielectric loss could be attributed to a local conformational transition in the chain backbone. If the transition is assumed to be that of the crankshaft, a reasonable value of the number of monomer units between the two collinear bonds, which turned out to be 1–4, was obtained by employing the Kramers rate constant for the transition and the three-state model.

Dielectric behavior of polymers having dipoles rigidly and perpendicularly attached to the chain backbone in dilute solution is a subject of considerable interest, since the relaxation phenomenon of such dipoles is directly connected with the backbone motion.

It was previously reported that such polymers in dilute solution generally exhibit a dielectric dispersion in a rather high-frequency region (10^6–10^{10} Hz) and have relaxation times which do not depend on the molecular weight of the polymer.[1-5] Although the dispersion is undoubtedly attributable to the backbone motion associated with a conformational transition,[3,7] it is still unclear what kind of conformational transition gives rise to the dispersion; an understanding of the magnitude of the relaxation time is not established. The relaxation time is of particular interest in connection with the rate constant for the conformational transition.

In our previous paper[5] it was reported that (1) the relaxation time of some vinyl polymers in dilute solution is approximately proportional to solvent viscosity and (2) the apparent activation energy for the relaxation process, ΔH_A, is related to that for the solvent viscosity, ΔH_η, by the ex-