High-Resolution NMR Spectra of Solid Poly(dimethylsiloxane) Gums, Silicone Resins, and Incompatible Resin/Gum Blends

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ABSTRACT: High-resolution ^{13}C and ^{29}Si NMR spectra have been obtained on solid poly(dimethylsiloxane) gum, poly(dimethylsiloxane-*co*-diphenylsiloxane) gum, silicone resin, and the solid resin/gum blends. Relaxation times and nuclear Overhauser enhancement factors (NOEF) have been determined and indicate substantial segmental motion of the solid polymers at ambient temperature. The ^{29}Si resin NOEF approaches -1 and requires that the NOE be suppressed to observe absorption spectra. Spectral line widths have been determined as a function of temperature. The gum and resin ^{29}Si absorptions are distinct, and the two different temperatures at which these resonances collapse were determined for 60/40, 50/50, and 33/67 blends of resin and gum. The line widths have been correlated with the glass transition temperatures and rheological data of the same samples.

Introduction

High-resolution carbon-13 NMR spectra can be obtained directly on the solid forms of elastomeric and partially crystalline polymers.[1-5] These high-resolution spectra are obtained without magic angle spinning (MAS), cross polarization (CP), or high-power spin decoupling. Indeed, CP MAS spectra on some organosilicon resins do not show the elastomeric dimethylsiloxy groups,[6] because they are too mobile to cross polarize efficiently.[7]

It appears known that high-resolution silicon spectra can be obtained directly on silicone elastomers,[6,8] but no examples have been published in the literature. However, very narrow (350 Hz) wide-line proton spectra have been observed.[9,10] We have obtained high-resolution silicon and carbon spectra on solid siloxane gums and blends of gums and resins. It is not possible to distinguish the gum and resin methyls from the carbon spectrum due to peak overlap. However, the line widths in the high-resolution silicon spectra of these solid elastomers are comparable to line widths observed in high-resolution carbon spectra of elastomeric polymers, and separate absorptions are observable for the resin and gum silicons.

Axelson and Mandelkern, using ^{13}C NMR, observed that the temperature, T_c, at which the backbone carbon resonances become too broad to resolve occurs 30–60 °C above the glass transition temperature, T_g, for nine different polymers.[1] Boyer et al. showed that the T_c/T_g ratio was 1.21 ± 0.05 in these nine samples.[11] Mandelkern has discussed this ratio further in terms of the correlation-time–temperature relations of several polymers and the Williams–Landel–Ferry relation.[12,13] From the variable-temperature silicon NMR spectra of the resin/siloxane gum blends studied in this paper, it was possible to obtain two different temperatures, one for the collapse of the gum dimethylsilyl resonance and one for the collapse of the resin trimethylsilyl. These variable-temperature spectra have been correlated with the glass transition temperatures and rheological data of the same samples.[14,15] The ^{29}Si NMR data confirm that these resin/gum blends are two-phase incompatible blends.

Results

Samples. High-resolution ^{29}Si and ^{13}C NMR spectra were obtained on solid elastomers, on resin/gum blends, and on blends of resins and silicone fluids. The elastomers studied were a poly(dimethylsiloxane) gum (PDMS) and a poly(dimethylsiloxane-*co*-diphenylsiloxane) gum (PDMDPS).[14,15] The ^{29}Si high-resolution spectrum of PDMS in $CDCl_3$ showed a singlet at -22.4 ppm. End-group absorptions were not observable, but a sharp weak peak at -19.6 ppm attributable to cyclic tetramer was observed at the 6% level.[16] High-resolution spectra of PDMDPS showed major absorptions at -21.2, -22.2, and -49.3 ppm, assigned to $-OSiMe_2O$ α to $SiPh_2$, $OSiMe_2O$, and $OSiPh_2O$, respectively.[17] A dimethylsiloxane:diphenylsiloxane ratio of 86:14 was determined from integration of the proton spectrum obtained on a sample in $CDCl_3$. The NMR spectra of solid PDMS and PDMDPS are similar to the solution spectra except that the absorptions are broadened from about 2–5 Hz in solution to 15–60 Hz in the bulk phase (top spectra in Figures 1 and 2).

The resin used in these studies is a typical MQ resin containing approximately equal numbers of trimethylsilyl groups (M, $Me_3SiO_{0.5}$, δ +9.3) and quaternary silicons (Q, $Si(O_{0.5})_4$, δ -108). A spectrum of the resin in solution indicated the M:Q ratio was 41:59. Solution spectra of similar resins have been reported in the literature.[18] Spectra were also obtained on a silanol-terminated PDMS fluid (Silanol) and on a trimethylsilyl end-capped fluid (DC-200). The $HOMe_2Si-$ and Me_3SiO- end-group absorptions in the fluids are observed at -12.1 and +6.5 ppm. The six blends studied in detail were 60/40, 50/50, and 33/67 (w/w) blends of resin with PDMS and PDMDPS. ^{29}Si spectra of PDMS, PDMDPS, resin, and the blends as a function of temperature are shown in Figures 1–3. In addition, ambient-temperature ^{29}Si spectra of 50/50 and 90/10 blends of resin with the Silanol and the DC-200 fluid were obtained (Figure 4). The spectral region shown (-70 to +60 ppm) does not include the quaternary silicons in the resin which were obscured by a large background peak from silicon in the NMR tube and the probe.

Resin/Silicone Fluid Blends. A broad ^{29}Si peak centered near the trimethylsilyl absorption is observed with a line width (at 22 °C) of 850 Hz for the pure resin (Figure 3). However, spectra of 50/50 blends of resin and silicone fluids show sharp resin peaks (width about 100 Hz, Figure 4). These materials are very viscous and clear. When the concentration of resin in the blend is increased to 90:10, the samples are glassy powders and their NMR spectra show very large line widths for both the silicone fluid and resin components.

^{29}Si Relative Peak Intensities. Determination of quantitative relative intensities require obtaining nuclear Overhauser effect (NOE) suppressed spectra with a recycle time in excess of 4 times the relaxation time, T_1. Consequently, T_1 was determined for the pure gums, resin, and the 50/50 blends at +22 °C using the standard $180°-\tau-90°$

Table I
Relaxation Times (T_1) and NOEF at +22 °C for Siloxane Gums and Silicone Resin

	$T_1(^{29}Si)$			$T_1(^{13}C)$				
	gum		resin	gum				
sample	$SiMe_2$	$SiPh_2$	$SiMe_3$	Me	ipso	ortho	meta	para
PDMS	31			3.2				
PDMDPS	19	35		2.7	3.4	0.8	0.7	0.14
resin			15					
50/50 resin/PDMS	28			4[a]				
50/50 resin/PDMDPS	15	20	13	2.3	*b*	0.4	0.5	*b*
	NOEF(^{29}Si)			NOEF(^{13}C)				
PDMS	−1.5			1.7				
PDMDPS	−1.5	−1.4		1.5	0.7	2.0	1.8	1.5
resin			−0.8					
50/50 resin/PDMS	−1.4		−1.0	1.4				
50/50 resin/PDMDPS	−1.5	−1.7	−1.0					

[a] Inaccurate due to overlap of broad resin peak with methyl gum peak. [b] Not resolved.

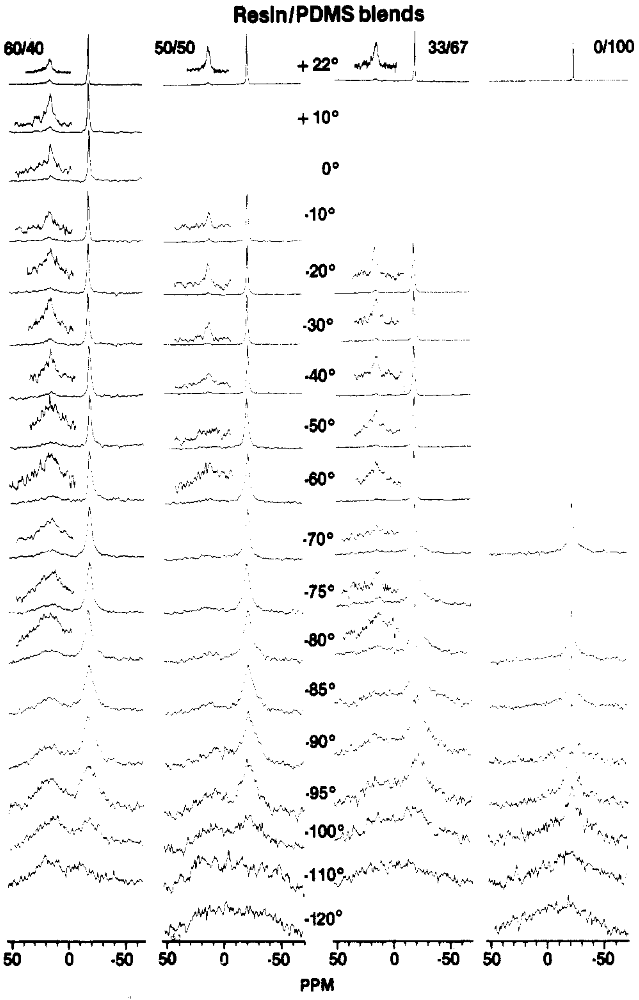


Figure 1. ^{29}Si variable-temperature spectra of resin/PDMS blends. The spectra are plotted at different vertical gain. Each spectrum was obtained by time-averaging 40 transients in 7 min.

Table II
Chemical Shifts for Gums, Resin, and 50:50 Blends

	^{29}Si		^{13}C				
	$SiMe_2$	$SiPh_2$	Me	ipso	ortho	meta	para
PDMS	−22.4		1.7				
PDMDPS	−22.4[a]	−49.3	1.5	136.3	134.7	128.0	130.3
resin	+9.3[b]		2[b]				
Silanol	−22.4	−12.1[c]					
fluid	−22.4	+6.5[d]					
50/50 resin/Me gum	−22.4		1.7				
50/50 resin/Ph gum	−21.4	−49.3	1.6	*e*	134.8	128.2	*e*

[a] $SiMe_2$ α to $SiPh_2$ at −21.4. [b] $SiMe_3$ of resin. [c] $SiMe_2OH$ absorption of Silanol. [d] $SiMe_3$ absorption of fluid. [e] Not resolved.

Table III
Relative Peak Intensities for ^{29}Si Spectra

	obsd			calcd[a]		
	gum		resin	gum		resin
sample	$SiMe_2$	$SiPh_2$	$SiMe_3$	$SiMe_2$	$SiPh_2$	$SiMe_3$
60/40 resin/PDMS	70		30	59		41
50/50 resin/PDMS	87		13	69		31
33/67 resin/PDMS	86		14	82		18
60/40 resin/PDMDPS	63	6	32	47	8	46
50/50 resin PDMDPS	63	10	28	55	9	36
33/67 resin/PDMDPS	71	10	19	67	11	22
50/50 resin/Silanol	67	7[b]	26	62	7	31
90/10 resin/Silanol	15	2[b]	83	18	2	80
50/50 resin/fluid	74	2[c]	24	67	2	31
90/10 resin/fluid	27		73	19	1	80

[a] Based on 86:14 ratio of $SiMe_2$:$SiPh_2$ in PDMDPS and 41:59 M:Q ratio in resin. [b] $SiMe_2OH$ absorption of Silanol. [c] $SiMe_3$ absorption of fluid.

pulse[19] sequence and are reported in Table I. The ^{29}Si chemical shifts are given in Table II.

Theoretical intensities for the blends were calculated based on the blend ratio using the analysis of the individual components given above and are compared to the observed intensity ratios at +22 °C in Table III. The accuracy of the integrals is poor because of the difficulty of adjusting the phase precisely on the broad resin absorption relative to the sharp gum absorption. There is reasonably good agreement between the calculated and observed peak areas for the viscous fluids *and* for the solid gums. Since all the silyl resonances of the fluid should be observable, these data indicate that most of the silicons from the broad resin peak are observable in the spectra of the blends of *both* the resin/silicone fluids and gums at +22 °C.

Nuclear Overhauser Effect. In order to optimize the sensitivity of the variable-temperature spectra, the nuclear Overhauser enhancement factors[20] (NOEF) were also determined at ambient temperature and are reported in Table I. The observed NOEF of −1 for the resin peak in the spectra of the solid MQ resin and the resin/gum blends results in nulling of the resin signal if a continuous proton

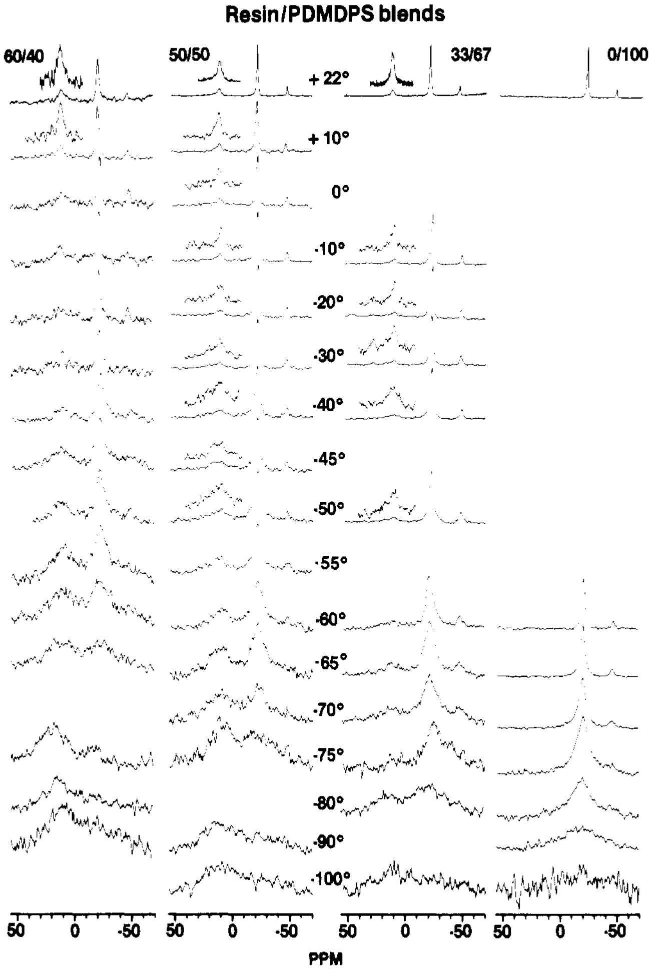


Figure 2. ^{29}Si variable-temperature spectra of resin/PDMDPS blends. The spectra are plotted at different vertical gain.

noise decoupled spectrum is obtained. Since the $^3J_{\mathrm{SiH}}$ is under 10 Hz,[18] the broadening due to coupling is insignificant compared to the line width in ^{29}Si spectra of solid elastomers. Variable-temperature spectra were obtained undecoupled to avoid unnecessary radio-frequency heating of the sample.

Carbon Spectra. ^{13}C chemical shifts are given in Table II. At +22 °C the pure resin shows a broad absorption with a 200-Hz width and the same chemical shift as the gum dimethylsilyl absorption. Spin–lattice relaxation times (T_1) and NOEFs for the carbon absorptions are measurements at ambient temperature and are given in Table I. The carbon NOEF is close to the theoretical maximum (2.0) for all carbons except the quaternary ipso carbon. Since this carbon has no adjacent protons, other relaxation mechanisms such as chemical shift anisotropy and spin rotation interactions can contribute significantly to the relaxation and reduce the NOEF. The relatively rapid segmental motion of the polymer chain determines T_1 while the slower modes of segmental motion contribute to T_2, which is determined from the line width in these spectra from $T_2 = 1/\Delta\nu_{1/2}$. Correlation times for these motions range between 10^{-5} and 10^{-9} s.[21] The short carbon relaxation times, nearly full NOEF, and narrow absorptions indicate rapid internal motions due to segmental motion along the polymer chain. Neither the methyl nor the phenyl groups are in the polymer backbone. Methyl and phenyl rotation will increase both T_1 and the NOEF compared to similar carbons in a polymer backbone. Thus it is not surprising that the aromatic T_1 values in PDMDPS are 2–4 times those found in poly(ethylene oxide), polyethylene, polyisoprene, polyisobutylene, or poly(tetramethylene terephthalate-*co*-tetramethyleneoxy terephthalate) (Hytrel).[3,5,22-24] Relaxation times for the methyl are fairly long due to the known internal freedom

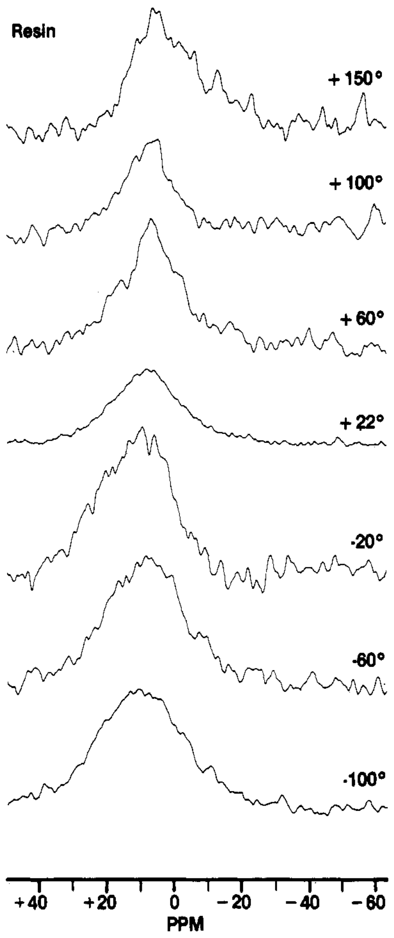
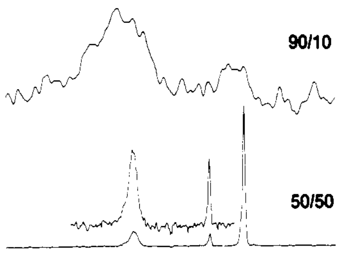


Figure 3. ^{29}Si variable-temperature spectra of silicone resin.

a. Resin/Silanol



b. Resin/DC 200

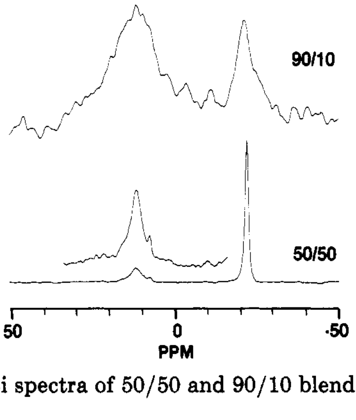


Figure 4. ^{29}Si spectra of 50/50 and 90/10 blends of resin and fluids.

Table IV
Transition Temperatures (°C)

	NMR		DSC			
	gum T_c	resin T_c	onset	midpoint[b]	end	DMA T_{max}
0/100 resin/PDMS	-93		-115.0	-112.9	-110.9	
33/67 resin/PDMS	-89	-56	-114.1	-111.5	-108.9	*a*
50/50 resin/PDMS	-86	-42	-114.6	-110.8	-107.0	7
60/40 resin/PDMS	-83	-28	-116.4	-108.9	-101.3	78
0/100 resin/PDMDPS	-76		-89.2	-82.1	-75.0	
33/67 resin/PDMDPS	-68	-46	-87.3	-77.9	-67.5	-54
50/50 resin/PDMDPS	-61	-26	-82.6	-71.8	-60.3	-6
60/40 resin/PDMDPS	-53	-6	-82.6	-69.0	-55.3	+23

[a] Not obtained because of crystallinity developing in the sample during low-temperature dynamic mechanical testing. [b] T_g.

of the methyl group, which reduces the effectiveness of the dipolar coupling to the directly bonded protons.[25]

Silicon Relaxation Times. The silicon relaxation times at +22 °C of the solid elastomer are much longer than the carbon values but about 2-fold shorter than the 46 s found for a typical poly(dimethylsilicone) in solution.[26] The silicon NOEF is also appreciably less than the maximum possible −2.5. This suggests contributions to the relaxation time from other than dipolar relaxation mechanisms, since the full NOEF observed in the ^{13}C spectra indicates segmental motion is fast enough for the extreme narrowing condition to apply.[24] For dipolar relaxation, T_1 is proportional to the 6th power of the distance between ^{29}Si (or ^{13}C) and the protons. Since the two-bond Si–H distance is at least twice the one-bond C–H distance, the dipolar contribution to $T_1(^{29}Si)$ should be 60-fold less than that for $T_1(^{13}C)$. Because dipolar relaxation is much less effective, other relaxation mechanisms are relatively more important in ^{29}Si spectra.[26]

^{29}Si Variable-Temperature Spectra. Spectra of the resin vs. temperature show a gradual decrease in line width as the temperature is increased from −100 to +150 °C (Figure 3). The line width, 1200 Hz at −100 °C, decreases to 850 Hz at +22 °C and to 450 Hz at +150 °C. The variation with temperature is approximately linear and there is no evidence for an abrupt change in the slope. In contrast to the pure resin, solid blends of resin and silicone gums give a rubbery elastomer at ambient temperature. Unlike the pure resin spectra, the resin peak in these blends at ambient temperature (top row of spectra in Figures 1 and 2) is much sharper.

Variable-temperature spectra were obtained on the solid resin/gum blends to determine T_c for the resin and gum,[1] i.e., the temperatures at which these absorptions broaden and become unobservable (Figures 1 and 2). The ^{29}Si line widths of the resin trimethylsilyl absorption are plotted as a function of temperature for the six resin/gum blends in Figure 5. The lines in the figure are smooth curves through the points, subject to the constraint that line widths were too broad to measure at low temperatures. The spectra of the resin/gum blends at low temperatures resemble the spectrum of pure resin, showing a broad absorption with a line width approximating 1200 Hz. An approximate value of T_c was determined from the curves in Figure 5. In order to quantitatively compare samples, T_c was taken as the point where the resin absorption exceeds a line width of 400 Hz since the signal/noise is insufficient to measure line widths appreciably above 400 Hz. Values of the resin T_c for the resin/gum blends are given in Table IV. Because of the poor signal/noise on the broad resin absorption, these temperatures are clearly approximate.

The dimethylsilyl absorption of the gum is a sharper absorption which was more readily followed vs. temperature (Figures 1 and 2). For the pure gums, peak broadening occurs slowly as the temperature is lowered until the width reaches about 200 Hz. Then a more rapid increase in line width occurs until the silicon line width becomes too broad to measure on a high-resolution instrument, exceeding 2000 Hz at −120 °C. The dimethylsiloxane gum peak becomes too broad to observe in the gum/resin blends at low temperature because, with a width estimated as 2000 Hz, it is broader than the resin absorption, which has an estimated width of 1200 Hz.

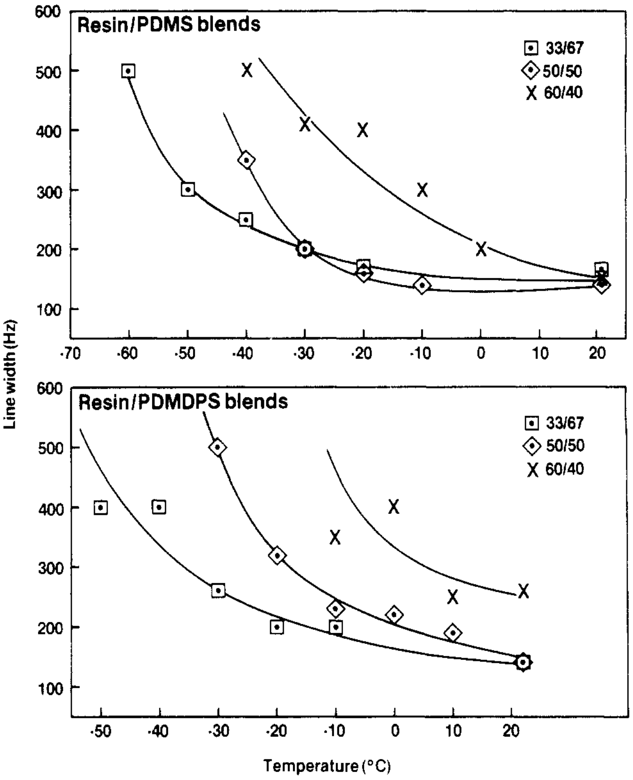


Figure 5. Line widths of resin peak, $^{29}SiMe_3$.

Both the $SiMe_2$ and $SiPh_2$ absorptions show similar thermal behavior. Although the $^{29}SiPh_2$ appears to broaden so much that it is unobservable before the $^{29}SiMe_2$ broadens, this effect should be attributed to the lower intensity of the former peak. This lower intensity makes observation of the weak $SiPh_2$ absorption impossible when the $SiMe_2$ line width approximates the difference in chemical shifts of the two absorptions. Differences in line widths vs. temperature within the same polymer have been observed in poly(butylene terephthalate); in that case the OCH_2 width remains much greater than the CCH_2 width at high temperatures when the absorptions are sharp.[21]

The line widths of the gum absorption in the resin/gum blends do not show as rapid a change with temperature as that observed in the pure gums. The line widths of the dimethylsilyl absorption vs. temperature are plotted in

Figure 5. The temperature at which the ^{29}Si line width exceeded 400 Hz was again taken as T_c in order to quantitatively compare the samples. Values of T_c were determined from the plots in Figure 5 and are tabulated in Table IV.

^{13}C Variable-Temperature Spectra. The ^{13}C resonance line widths for the pure gum and 50/50 blends as a function of temperature were also obtained. The pure gum spectra showed line widths comparable to the ^{29}Si spectra and a similar T_c. The line widths of the resin carbon were independent of temperature. Spectra of the blends were not meaningful because the methyls of the gum and resin have similar chemical shifts.

Discussion

The relatively sharp resin peak (width ~100 Hz) for 50/50 blends of resin and silicone fluids suggests they are solutions of resin in the silicone fluid. The narrow line widths for these 50/50 blends indicate rapid internal motion of the silicone fluid similar to that observed in ^{13}C NMR spectra of elastomers. The 90/10 blends, on the other hand, are glassy powders. The large line widths observed in these samples indicate very limited internal motion.

The line widths in the spectra of the resin/gum blends are very similar to those of the 50/50 resin/silicone fluid blends despite the rubbery nature of the gums. The resin absorption is considerably sharper in the blend than in pure resin. This observation is significant because it indicates that the resin in the resin/gum blends is miscible with at least a fraction of the gum. Further, it will be shown that these blends are two-phase blends, thus leading to the conclusion that the resin phase contains some fraction of the gum. The pure gums and the resin/gum blends show broadening of both the gum and resin absorptions as the temperature is lowered. The plots of line width vs. temperature indicate an abrupt change from a high-resolution peak with a line width under 200 Hz to a broad absorption with a line width exceeding 500 Hz (Figures 5 and 6). Because of experimental error in measuring line widths of broad absorptions, accurate determination of the exact temperature at which the NMR spectrum collapses, T_c, is difficult. For purposes of quantitatively comparing spectra in different samples, line widths of 400 Hz were selected as "broad" and the T_c determined from Figures 5 and 6. Spectra of pure gum resonances are still observable at the lowest temperature accessible, −120 °C, but the line width is over 2000 Hz (Figures 1 and 2). The spectra show no evidence for a second abrupt increase in line width at low temperature.

An absolute T_c is not well-defined because it depends on the spectrometer conditions (signal filtering and signal/noise) and probably also on the spectrometer frequency. A comparison of the T_c obtained in this work and those reported by Axelson and Mandelkern[1] is not possible because the precise conditions under which most of the T_c values were obtained have not been reported. However, comparisons between the siloxane/resin blends studied here are meaningful because all spectra were obtained under identical conditions.

The spectra of the resin/gum blends in Figures 1 and 2 show that the degree to which the resin motion is maintained as the temperature is lowered is a function of the resin/gum ratio. The temperature at which the trimethylsilyl resin absorption becomes broad increases 15–20 °C as the resin level is increased from 33% to 50% or from 50% to 60%. The temperature shifts with resin concentration are similar in both the resin/PDMS and resin/PDMDPS blends, but line broadening occurs at 10–20 °C higher temperature in the latter. In contrast to the resin trimethylsilyl absorption, much smaller increases in T_c of the dimethylsilyl resonance of the siloxane gum are observed as the resin/gum ratio increases. However, this line width is also a function of resin concentration in the resin/PDMS blends and the apparent T_c increases 10 °C in going from pure gum to 60% resin/gum blend. The dependence of T_c of the dimethylsilyl group on resin is a factor of 2 higher in the resin/PDMDPS blends.

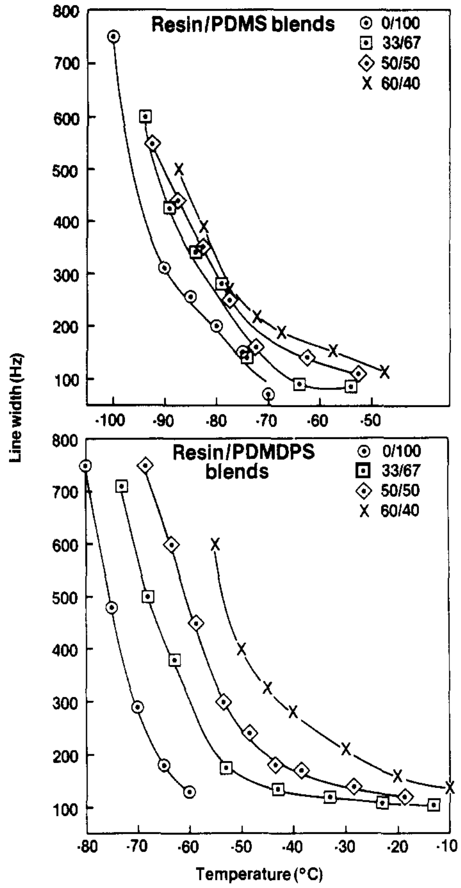


Figure 6. Line widths of gum $^{29}\mathit{Si}Me_2$ peak; plots have been corrected for temperature and homogeneity variations (see text).

The NMR spectra of the blends prove that they are two-phase systems since the two components show line broadening at different temperatures. At +22 °C the resin trimethylsilyl absorption is a readily detected 150-Hz broad resonance. As the temperature is lowered, this resonance broadens very quickly to a width in excess of 400 Hz, whereas the gum dimethylsilyl absorptions show minor broadening. If the sample were a compatible single-phase system, then both the resin and gum peaks would broaden at the same temperature. On the other hand, the variation in spectra vs. blend ratio indicates neither phase is pure. The gum phase must contain small amounts of resin and the resin phase small amounts of gum in order to explain the variation of T_c with blend ratio. An identical model is independently derived from the DSC and DMA results.[14,15]

There is an excellent correlation between the T_c measured in the NMR spectra and the glass transition temperatures measured by DSC. The continuous siloxane gum phase exhibits a glass transition temperature (T_g) by DSC which shifts to slightly higher temperatures and broadens considerably as the resin/gum ratio increases.[14] These T_g values are included in Table IV. The temperature shift is much smaller for the resin/PDMS blends compared to the resin/PDMDPS blends. Comparison of the gum T_c, from the NMR data, and the midpoint of the glass transition indicates that T_g of the gum phase is being detected by the NMR experiment. The ratio of T_c to T_g (calculated for K) varies from 1.12 to 1.16 in the resin/PDMS blends and from 1.03 to 1.08 in the resin/PDMDPS blends. These ratios are somewhat lower than the reported values of 1.20 ± 0.05 found for ^{13}C spectra of elastomers[1,11] and would be even lower if T_c were determined at a line width greater than 400 Hz. Thus, it appears the ^{29}Si T_c/T_g ratios are significantly lower than the ratios determined from ^{13}C NMR of elastomers.

The NMR line widths show a slower change with temperature as the resin level increases. This is observable as a decrease in the slopes of the line width vs. temperature curves in Figure 6. This correlates with the wider transition observed in the DSC for the samples as the resin/gum ratio increases. Although the variation in T_c between 0/100 and 60/40 resin/gum is twice the variation observed in T_g in both systems, the end point of the DSC transition shows the same total spread in temperature as T_c. This is probably because the end point of the DSC transition is a measure of the temperature at which the blend is starting to increase in modulus and viscosity due to stiffening of the polymer backbone.

Since the resin does not exhibit a glass transition from -140 to +125 °C by DSC, the resin-rich phase is not detected by DSC. Both the resin-rich phase and the gum phase are detected by dynamic mechnical analysis (DMA). The transition temperatures of the resin phases have been determined by dynamic mechanical testing and are given in Table IV. The transition is reported as T_{max}, the temperature at which tan δ reached a maximum value under an oscillating strain of 10 rad/s.[14,15]

Correlation of T_{max} for the resin with T_c is not nearly as good as the correlation of T_g with T_c. Still, the general trend of increasing transition temperature with increasing resin/gum ratio is noticed for both T_c and T_{max}. Several reasons for the poorer correlation are plausible. Since the dynamic mechanical transition is very broad (spanning more than 50 °C), the T_{max} cannot be assigned as the actual glass transition temperature of the resin phase. In fact, T_{max} will be affected by the composition and volume fraction of the two coexisting phases. During a NMR temperature scan, the NMR signal due to the portion of the resin in the resin-rich phase would undergo line broadening at a different rate from the signal of the resin in the gum phase. The presence of both phenomena taken together may cause a systematic shift of T_c relative to the dynamic mechanical method[27] of assigning T_{max} to the resin phase. In particular, the line width of the resin should be anomalously narrow and the line width of the gum should be anomalously broad, as the temperature decreases, due to the presence of the resin in the gum phase and gum in the resin phase.

This interpretation is supported by the ^{29}Si NMR spectra of the resin with low molecular weight fluids (Figure 4). The 90/10 blends are glassy at room temperature and the line widths are broad. The 50/50 blends are viscous fluids with resin dissolved in the fluid phase at room temperature and the line width is narrow.

It is possible to speculate on the level of resin in the gum phase from a comparison of the T_g of the pure gum and resin phases and to compare this calculation with the observed NMR spectra. If a significant portion (over 10%) of the resin were in the gum phase, then the resin peak would be a superposition of a broad and sharp absorption. The signal/noise on the broad peak in Figures 1 and 2 is insufficient to observe a second resin component. On the basis of the observed T_c, the most likely temperature at which two resin peaks should be observed is -50 °C for the 60/40 resin/PDMS gum and -30 °C for the 60/40 resin/PDMDPS gum. Spectra of these two samples were obtained with much better sensitivity (Figure 7) but still showed no evidence of a second resin component with a narrower line width.

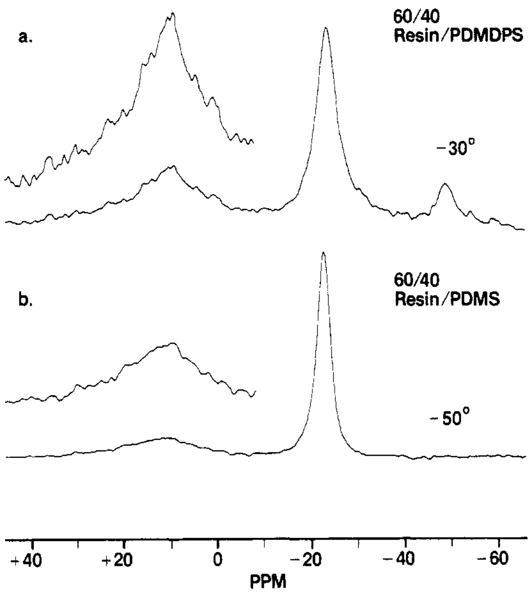


Figure 7. ^{29}Si spectra of 60/40 resin/siloxanes. Each spectrum was obtained by time-averaging 200 transients in 2 h.

In order to calculate the composition, it is necessary to estimate T_g of the resin. However, T_g has not been observed for pure resin by DSC. A broad ^{29}Si absorption is observed for the trimethylsilyl absorption in the silicone resin with an approximately linear dependence on temperature between -100 and +150 °C (figure 3). There is no evidence for an abrupt change in line width vs. temperature as observed in the gum or resin/gum blends. This resin appears to be a solid glassy material up to +150 °C. The NMR spectra indicate rapid motion of the trimethylsilyl groups throughout this temperature range. The observed line widths probably correspond to motional freedom of the trimethylsilyl group since rotation of the methyl groups persists to very low temperatures based on ^{13}C relaxation measurements.[28] The plot of line width vs. temperature for pure resin indicates that a line width of 400 Hz, corresponding to the T_c values determined in the blends, would be observed at +170 °C. The good correlation between NMR collapse temperatures, T_c, and glass transition temperatures observed for the resin/gum blends and for many elastomers[1] suggests T_g of the resin is between 175 and +250 °C. It is not possible to perform NMR or DSC measurements above +150 °C because the resin foams and degrades.

The Fox equation[29] can be used to estimate the glass transition temperature (T_g) of a miscible blend of two polymers A and B from their weight fractions (w_A and $w_B = 1 - w_A$) and homopolymer T_g (T_{gA} and T_{gB}):

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} = \frac{w_A}{T_{gA}} + \frac{1 - w_A}{T_{gB}}$$

Alternatively, if T_g of the blend and T_g of the homopolymers are known, then w_A can be calculated from the Fox equation. The T_g's of the homopolymer gums and the 60/40 resin/gum blends are given in Table IV. A lower limit for T_g of the resin is 175 °C. From the Fox equation and these T_g's, the weight fraction of resin in the gum phases is calculated as 3.8% for 60/40 resin/PDMS and 11.2% for 60/40 resin/PDMDPS. However, since the gum phase comprises 40 wt % of the total sample, only 7 wt % of the resin in the total sample is needed to make the gum phase an 11:89 resin/PDMDPS mixture. Thus, the ratio of resin in the resin-rich phase to resin in the gum phase is 93:7. Even after the additional time averaging in Figure 7, the signal/noise is inadequate to observe a minor sharp resonance at the 7% level with a chemical shift identical with that of the major component.

In conclusion, this work proves that the temperature, T_c, at which the NMR spectrum of the solid becomes too broad to measure is a function of the actual ratio of resin/gum within each phase. The model thus proposed for these blends is a resin phase containing a small amount of low molecular weight gum and a gum phase containing some resin. The rapid broadening of the gum signal in the ^{29}Si NMR analysis is quite easily detected because both phases have become glassy at this temperature. The rather slow broadening of the resin signal at higher temperature is probably due to the presence of resin becoming glassy in one phase and fluid in the second phase. However, less than 10% of the resin is dissolved in the gum phase since no sharp resin peak is observable at intermediate temperatures superimposed on the broad resin peak from the resin-rich phase.

Experimental Section

All NMR spectra were obtained on a Varian XL-200 NMR spectrometer operating at 50.32 MHz (^{13}C) or 39.75 MHz (^{29}Si). The pure gums flowed slowly (about 24 h) to form a clear dense solid at the bottom of the 10-mm-o.d. tube. The resin/gum blends were cut into small pieces and packed tightly in the NMR tube. Spectra were first obtained on these solid samples. However, since thermal equilibrium is approached more slowly on solid samples containing entrapped air spaces, an inert fluorochemical, FC 72 (pour point −90 °C, available from Commercial Chemicals Division, 3M) was subsequently added to all the samples. Swelling measurements showed no observable (under 0.5%) uptake of the inert liquid. The spectra of the 50/50 blends were obtained both with and without the inert fluid. No difference beyond experimental error was observed in the spectra of samples run with or without the inert fluid, and subsequent spectra were all run with it. The magnetic field was adjusted on a reference dioxane/benzene-d_6 sample; spectra of the solid samples were then obtained unlocked. Chemical shifts were measured relative to the external dioxane (+67.4 ppm) sample (^{13}C) or to a $SiMe_4$ solution in chloroform-d (^{29}Si). Positive values are downfield from $SiMe_4$. Field drift of the solenoid was insignificant compared to the line widths of the spectra. However, the proton homogeneity, measured on a 90:10 CH_3OH–CD_3OH solution at −70 °C, varied between 20 and 120 Hz in different experiments run on different days. These correspond to ^{29}Si line widths of 2–24 Hz, respectively. Temperatures are accurate to +2 °C and were measured using neat CH_3OH, the decoupler coil to observe resonance, and the calibration curve of van Geet.[30] Quantitative comparison of the gum dimethylsilyl ^{29}Si line widths required correction for errors in the temperature calibration and spectrometer homogeneity. Consequently, spectra were obtained on the three blends and the pure gum consecutively at a given temperature. These values were then used to shift the curves in Figures 4 and 5 to give the exact widths recorded at −65 °C for the resin/gum blends of PDMDPS and at −80 °C for the blends of PDMS. (These shifts were under 2 °C, which approximates the accuracy of the temperature calibration method used to obtain the spectra.)

The gated decoupling technique was used to obtain NOE-suppressed spectra with the decoupler on for a time interval of 0.4 s during the free induction decay (fid) acquisition and off for a period exceeding $3T_1$.[31] Spin–lattice relaxation times were determined by using the standard inversion–recovery method with a three-parameter fit to the data.[19] The delay between repetitions of the experiment was at least $3T_1$. Longer delays were not always possible because of the long relaxation times. Reasonable signal/noise could be achieved with as few as 10 transients on solid silicones; comparable sensitivity on resins required at least 4 times longer. Long-range silicon–proton coupling is under 10 Hz in these samples.[18] Thus proton decoupling was not necessary to narrow the lines and the ^{29}Si variable-temperature spectra were run in the absence of proton decoupling to eliminate radio-frequency heating of the sample. Proton decoupling was necessary to observe narrow carbon resonances since J(CH) = 130 Hz in a trimethylsilyl group. To minimize sample heating, the spectra were obtained with the spin decoupler on only during the fid acquisition, and the delay between transients was alwyas at least 10 times the acquisition time. Typically, variable-temperature carbon spectra were obtained by averaging 16 transients with an acquisition time of 0.1 s, 10-kHz sweep width, delay between pulses of 2.1 s, and 17-μs (90°) pulse widths. For silicon variable-temperature spectra in Figures 1 and 2, 40 transients were obtained with an acquisition time of 0.1 s, 10-kHz sweep width, 10-s delay, and 16-μs (40°) pulses. The spectra in Figure 7 were obtained with 35-μs (90°) pulses and a 30-s delay. Exponential filtering of 30 Hz is present in the variable-temperature spectra for sensitivity enhancement. Filtering in the +22 °C spectra is 30 Hz for 60/40 blends but 5 Hz for the other blends and pure gums. Eight minutes was allowed for thermal equilibrium to be attained for a 10 °C temperature change.

The resins, gums, and low molecular weight fluids have been fully characterized by Copley.[14,15] Values of $\bar{M}_n$ and $\bar{M}_w$ from GPC analyses for the five materials are as follows: PDMS, 357 000 and 697 000; PDMDPS, 250 000 and 830 000; Silanol, 1046 and 5985; DC-200 silicone fluid, 5265 and 12 885; resin, $\bar{M}_w$ = 5850. The blends were prepared by dissolving the gums in toluene and then blending the solution with a 70 wt % solution of MQ resin in xylene. The resin/gum solution was then dried in thin films under vacuum.

References and Notes

(1) Axelson, D. E.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1135.

(2) Komoroski, R. A.; Maxfield, J.; Mandelkern, L. *Macromolecules* **1977**, *10*, 545.

(3) Komoroski, R. A.; Mandelkern, L. *J. Polym. Sci., Symp.* **1976**, *No. 54* 201.

(4) Duch, M. W.; Grant, D. M. *Macromolecules* **1970**, *3*, 165.

(5) Schaefer, J. *Macromolecules* **1972**, *5*, 427.

(6) Engelhardt, G.; Jancke, H.; Lippmaa, E.; Sampson, A. *J. Organomet. Chem.* **1981**, *210*, 295.

(7) Jelinski, L. W.; Dumais, J. J.; Watnick, P. I.; Bass, S. V.; Shepherd, L. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3285.

(8) Fyfe, C. private communication.

(9) Lee, C. L.; Haberland, G. G. *Polym. Lett.* **1965**, 883.

(10) Haberland, G. G.; Carmichael, J. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1965**, *6*, 637.

(11) Boyer, R. F.; Heeschen, J. P.; Gillham, J. K. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 13.

(12) Mandelkern, L. M. *Pure Appl. Chem.* **1982**, *54*, 611.

(13) Williams, M.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.

(14) Copley, B. C. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, *48*, 121.

(15) Copley, B. C. MS Thesis, submitted to the Department of Chemical Engineering, University of Minnesota, Minneapolis, MN.

(16) Harris, R. K.; Robins, M. L. *Polymer* **1978**, *19*, 1123.

(17) Jancke, H.; Engelhardt, G.; Magi, M.; Lippmaa, E. *Z. Chem.* **1973**, *13*, 392.

(18) Williams, E. A.; Cargioli, J. D. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 221.

(19) Kowalewski, J.; Levy, G. C.; Johnson, L. F.; Palmer, L. *J. Magn. Reson.* **1977**, *26*, 533.

(20) Harris, R. K.; Kimber, G. J. *Appl. Spectrosc. Rev.* **1975**, *10*, 117.

(21) Horii, F.; Hirai, A.; Murayama, K.; Kitamaru, R.; Suzuki, T. *Macromolecules* **1983**, *16*, 273.

(22) Komoroski, R. A.; Maxfield, J. F.; Sakaguchi, F.; Mandelkern, L. *Macromolecules* **1977**, *10*, 550.

(23) Jelinski, L. W.; Schilling, F. C.; Bovey, F. A. *Macromolecules* **1981**, *14*, 581.

(24) Schaefer, J.; Natusch, D. F. S. *Macromolecules* **1972**, *5*, 416.

(25) Schaefer, J. *Top. Carbon-13 NMR Spectrosc.* **1974**, *1*, 149.

(26) Levy, G. C.; Cargioli, J. D.; Juliano, P. C.; Mitchell, T. D. *J. Am. Chem. Soc.* **1973**, *95*, 3445.

(27) Rudin, A. "Elements of Polymer Science and Engineering"; Academic Press: New York, 1982; Chapter 11.
(28) Grapengeter, H. H.; Kosfeld, R.; Offergeld, H. W. *Polymer* **1980**, *21*, 829.
(29) Zeman, A.; Patterson, D. *Macromolecules* **1972**, *5*, 513.
(30) van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.
(31) Opella, S. J.; Nelson, D. J.; Jardetzky, O. J. *J. Chem. Phys.* **1976**, *64*, 2533.

Poly(1,4-*trans*-cyclohexanediyldimethylene succinate): A Structural Determination Using X-ray and Electron Diffraction

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ABSTRACT: Poly(1,4-*trans*-cyclohexanediyldimethylene succinate) or poly(*t*-CDS) has a monoclinic unit cell of dimensions $a = 6.486$ Å, $b = 9.482$ Å, $c = 13.51$ Å, and $\beta = 45.9°$ and belongs to the space group $P2_1/n$. The calculated crystalline density of 1.259 g cm^{-3} indicates that there is one chemical unit per fiber repeat and two chains per unit cell. Micro single crystals of poly(*t*-CDS) were obtained by recrystallization from toluene. The crystals are lamellar, 100 Å thick, and diamond-shaped with typical spiral growths. Electron diffraction intensities were recorded for three distinct orientations of the micro single crystals of poly(*t*-CDS) using an electron microscope equipped with a tilting stage. The geometry of the chemical repeat unit was derived from the crystal structure of 1,4-*trans*-cyclohexanedimethylene 3,3'-bis(methoxycarbonyl)dipropionate, a model compound for this polymer. The structure was established by conformational and packing analyses and confirmed by X-ray and electron intensity calculations. The value of the conventional R_w factor is 0.206 for 29 observed diffraction spots. With the electron diffraction data, $R_w = 0.199$ for 87 observed reflections. The chain conformation and the packing of the chains in the unit cell are discussed and compared with the crystal structures of other aliphatic polyesters. The $—O—CH_2—(C_6H_{10})—CH_2—O—$ "flexible" segment of the polyester has the conformation $t_{g}^{t}(t\pm gt)_{t}^{\bar{g}}t$ (g, gauche; t, trans) while the succinate group is in the trans conformation.

Introduction

The first studies on aliphatic polyesters were reported in the late 1930s by Fuller and Erickson[1] or a series of ethylene glycol polyesters and by Fuller, Frosch, and Pape[2] for a series of trimethylene glycol polyesters. Only qualitative conclusions concerning the crystalline conformations of the polymers were drawn. The first crystalline structures were established in the ethylene glycol polyesters series, $\{O(CH_2)_2OCO(CH_2)_xCO\}_n$, where x = 0, 2, 4, and 6. Ueda, Chatani, and Tadokoro[3] studied the crystalline structure of poly(ethylene oxalate) (PE0) and poly(ethylene succinate) (PE2) (x = 0 and 2, respectively) and Turner-Jones and Bunn[4] determined the crystal structure of poly(ethylene adipate) (PE4) and poly(ethylene suberate) (PE6) (x = 4 and 6, respectively). In each case, the glycol portion shows a considerable deviation from the fully planar conformation, while the acid portion is in the fully extended conformation, except for PE2.

The crystal structure of poly(1,4-*trans*-cyclohexanediyldimethylene terephthalate) or poly(*t*-CDT) has recently been reported.[5] Since it has been observed that a succinate and a terephthalate group are often interchangeable, we have undertaken to determine the crystal structure of poly(1,4-*trans*-cyclohexanediyldimethylene succinate) or poly(*t*-CDS), $\{OCH_2(C_6H_{10})CH_2OCO(CH_2)_xCO\}_n$, where $x = 2$.

Electron diffraction patterns of polymer single crystals have often been obtained but were rarely used for the elucidation or the confirmation of the polymer structure. In this case, good-quality micro single crystals of poly(*t*-CDS) were grown and their electron diffractograms were recorded in an electron microscope fitted with a tilting stage. The three-dimensional intensity data have been used to confirm the proposed structure of poly(*t*-CDS).

Experimental Section

Sample Preparation. Poly(*t*-CDS) powder was obtained from Aldrich Chemical Co., Inc. The molecular weight of the polyester, calculated from tonometric analysis,[6] is equal to 4200. At this low molecular weight, the polyester is highly crystalline but could not be drawn. Therefore, the polymer was treated with tolylene 2,4-diisocyanate to produce a higher molecular weight compound, using the method described by Iwakura, Taneda, and Uchida.[7] After treatment, the molecular weight was increased to 6900. A similar approach has been used by Ueda et al.[3] and Turner-Jones and Bunn[4] and for PE2 and PE4, respectively. This treatment does not affect the structural determination since it is believed that only the pure ester sections of the chains crystallize while the amide portions remain in the amorphous region of the polymer. Fibers of poly(*t*-CDS) were then obtained by quick quenching of the molten polymer in a mixture of dry ice/methanol followed by cold drawing. The fibers were annealed under tension at 90 °C for about 30 min. Micro single crystals of poly(*t*-CDS) suitable for electron diffraction could be grown in the following manner: a solution of 0.5% of commercial poly(*t*-CDS) in toluene was prepared at 80 °C. The solution was cooled slowly to 48 °C, where a slight precipitation was observed. The solution was kept 12 h at this temperature. The polymer was redissolved and the solution was brought down to 55 °C. Cooling the 55 °C solution at a rate of 1 °C/12 h brought about reprecipitation at 51 °C. This temperature was maintained for 48 h. Room temperature was reached

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