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Structural Studies of Phase Transitions in Poly(di-*n*-alkylsiloxanes). 1. Poly(dimethylsiloxane) and Poly(diethylsiloxane)

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ABSTRACT: Raman studies of poly(dimethylsiloxane) [PDMS] and poly(diethylsiloxane) [PDES] have been carried out from room temperature to −263 °C (10 K). Several bands characteristic of either the backbone or the allyl side chains have been identified and their bandwidth and frequency position followed as a function of temperature. A number of phase transitions, initially observed by DSC measurements, have been evaluated in terms of the molecular mobility introduced into the backbone and side chain at the transition temperature. In the case of PDES, the low-temperature transition (−60 °C) can be classified as an order–disorder transition leading to the formation of a "condis" crystal.

Introduction

The chemical incorporation of mesogenic groups into the backbone and side chain of long-chain polymers has led to the generation of a large number of liquid crystalline polymers,[1,2] which exhibit both novel molecular structures and unique functional properties. Whereas much of the focus of recent scientific activities has been on the latter, few comprehensive structural studies of liquid crystalline polymers have appeared. The motivation for such investigations lies in the fact that the characterization of the conformational, crystal, and morphological structure responsible for liquid crystalline behavior will provide a general understanding of the role of these parameters on mesogenic activity.

From a structural point of view the poly(di-*n*-alkylsiloxanes) have received a considerable amount of attention over the past 10 years. Although one of the simplest of these structures, poly(dimethylsiloxane) (PDMS) shows no liquid crystalline properties,[3,4] it has been the subject of a considerable amount of theoretical and experimental interest.[3-7]

Poly(di-*n*-ethylsiloxane), on the other hand, has been shown to exhibit a crystal–crystal transition and at least one liquid crystalline phase.[8-12] Pochan et al.[8] have investigated all three transitions by DSC, NMR, WAXD, optical microscopy, and light scattering methods and have concluded that the high-temperature phase exists as a "viscous crystalline" phase and is a composite of a partially ordered and a totally amorphous phase. More recent work by Papkov et al.[4] and Tsvankin et al.[3] has used WAXD and SAXS to determine that PDES is polymorphic, existing in either a monoclinic and/or a tetragonal form depending on the thermal history. Each of these forms independently showed a low-temperature transition in the −83 to −63 °C (190–210 K) range that did not involve a dramatic change in crystal structure, i.e., the monoclinic form remained monoclinic while the tetragonal polymorph also retained its structure above the low-temperature phase transition. The primary changes that occur at −83 to −63 °C (190–210 K) are in the *a* and *b* dimensions of the unit cell which is accompanied by a drop in the crystalline density. A further lowering[3] of the density was observed to occur in the 7–27 °C (280–290 K) range but in this case was attributed to a transition from the monoclinic and tetragonal polymorphs to a mesomorphic phase.

Vibrational spectroscopy has shown considerable promise in studying molecular motion in polymers due to the extent of information available through studies of peak position, bandwidth, and band intensity as a function of temperature. In the low-frequency (100–600-cm^{-1}) region[13,14] of nonlocalized vibrations, information about conformational disorder can be obtained while in the higher frequency regions an assessment of localized molecular motion should be possible. It was this capability to use bandwidths and peak intensities to describe the overall picture of the temperature-induced phase transitions in PDMS and PDES that motivated this study.

Experimental Section

All Raman spectra were obtained with a Spectra Physics 165-08 argon ion laser operating at wavelengths of either 488.0 or 514.5 nm with a power level of 0.1–0.2 W. Light scattered at 90° to the incident laser direction was collected and focused into a Jobin-Yvon Ramanor HG2S double monochromator equipped with an RCA 31034A-02 cooled photomultiplier and standard photon-counting electronics. Data from multiple scans were

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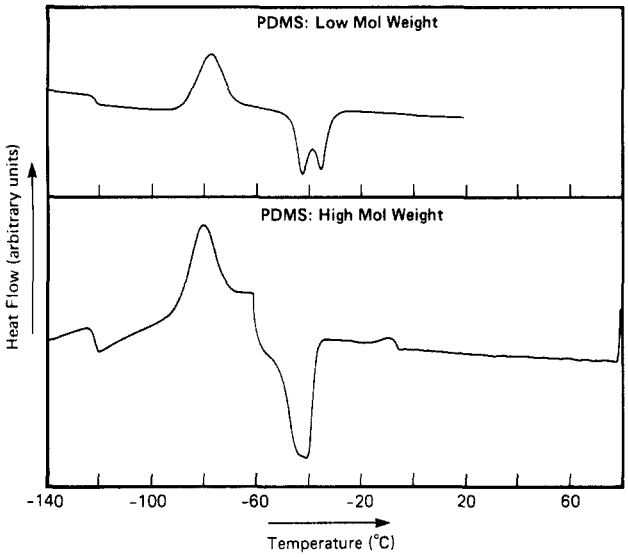

Figure 1. DSC traces of PDMS obtained at a heating rate of 10 °C/min: upper trace, low molecular weight; lower trace, high molecular weight.

collected and averaged with a Nicolet 1180 data system.

Low-temperature data were obtained with a Harney-Miller cell through which was passed helium gas that had been cooled in a liquid nitrogen heat exchanger. The cooled gas was used in conjunction with a cartridge heater and a platinum resistor to adjust the temperature to within ±1 °C using an electronic feedback system designed in this laboratory.

For Raman measurements down to -269 °C (4 K) an Oxford CF104 continuous flow cryostat was used. In this case the sample was melted onto a copper block which was attached to the cryostat head. When viscous fluid specimens were used, a small quantity was poured on the block followed by quenching into liquid nitrogen. The frozen cryotip was then quickly placed in the vacuum shroud and evacuated while simultaneously beginning liquid helium flow. The temperature precision in these experiments is estimated to be ±3 °C.

The samples of PDMS used in this study were obtained from Celomer Associates, Webster, NY. For comparison purposes, a viscous ultrahigh molecular weight sample and a low molecular weight sample were investigated. The PDES was provided by Dr. Chi-Long Lee (Dow Corning) and had an approximate $\bar{M}_n$ = 100 000.

Integrated intensities and bandwidths were determined with a Nicolet 1180 curve analysis program (CAP) which allowed each band or group of bands to be fit to a superposition of Lorentzian and Gaussian band shapes. The percentage of the Gaussian part varied between 20 and 50% depending on the temperature of the sample. Position, width and height were adjusted interactively with a fitting routine such that the root-mean-square deviation was minimized. The accuracy of these data is estimated to be within 10–15%.

It should also be pointed out that changes in Raman band intensities due to lowering of the temperature alone (over the range studied) were calculated to be ~3% at ν = 480 cm^{-1} and to be negligible at 1456 cm^{-1}.

Results and Discussion

A. Thermal Analysis. Shown in Figure 1 are the DSC traces of low and a high molecular weight PDMS samples. The glass transition is observed to occur at -120 °C (153 K) followed by an exotherm in the vicinity of -80 °C (193 K). This latter feature is believed to occur due to crystallization of the PDMS which had been quenched from the melt into an amorphous phase prior to beginning these measurements. Subsequently these crystallites melt, giving rise to the melting endotherm found in the vicinity of -40 °C (233 K). The area under the melting curve is approximately the same as that under the crystallization peak, thus lending credence to the interpretation of the -80 °C (193 K) exotherm described previously.

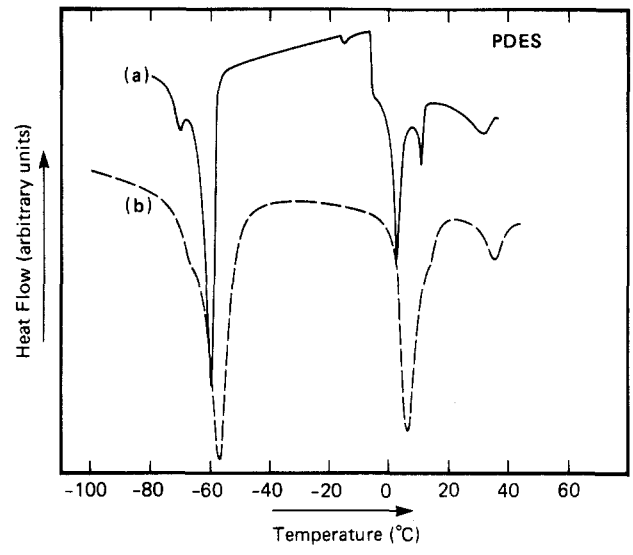

Figure 2. DSC traces of PDES obtained at identical heating rates after two different thermal histories.

An obvious difference observed between the low and high molecular weight samples occurs in the shape of their respective melting curves. As is apparent from Figure 1, the lower molecular weight material exhibits a resolvable two-component melting endotherm, whereas the high molecular weight sample shows a clearly asymmetric melting endotherm. The most probable explanation would attribute the two peaks to the melting of different crystal populations: either from different crystal structures or by reorganization to a more perfect crystal during heating.

A second, remote possibility is that the higher temperature peak is actually a transition from a mesomorphic state to one that is isotropic. However there have been no reports[3,4] of a liquid crystalline phase in PDMS.

PDES, on the other hand, has been shown[8,10,12] to exhibit a number of thermal transitions as can be seen in Figure 2. As pointed out earlier, PDES is polymorphic[3,4] existing in both a monoclinic and tetragonal form. These undergo a crystal–crystal transition in the -70 to -60 °C (203–213 K) range followed by a second transition to a liquid crystalline[8,9] state in the vicinity of 5–15 °C (278–288 K). At approximately 40 °C (313 K), studies indicate that there is a transition to the isotropic state. As shown in Figure 2 both the relative concentration of the two low-temperature crystalline forms (as indicated by the presence of two endotherms near -60 °C (213 K) and another two at 5 °C (278 K)) and their transition temperatures can be influenced by the thermal history. In both cases the weak endotherm at ~40 °C (313 K) has been attributed to the transition from a liquid crystalline to an isotropic state.

B. Assignment of Raman Bands. In general, the bands of poly(di-*n*-alkylsiloxanes) can be divided into two groups: (1) vibrations of the alkyl side chains and (2) those bands attributable to the Si–O backbone motions. In addition, in the region below 150 cm^{-1}, bands often assignable to the intermolecular vibrations of the crystal lattice[13,14] can usually be found. A useful way to identify such vibrations is through temperature studies[13] since, at low temperatures, a contraction of the lattice can give rise to a large change in frequency and intensity of lattice vibrations. In the other extreme,[14] these same intermolecular vibrations will disappear when the temperature exceeds the crystalline melting point.

Raman spectra of high molecular weight PDMS at room temperature, 23 °C (296 K), and at -267 °C (6 K) are shown in Figure 3. In the former, bands are broad and

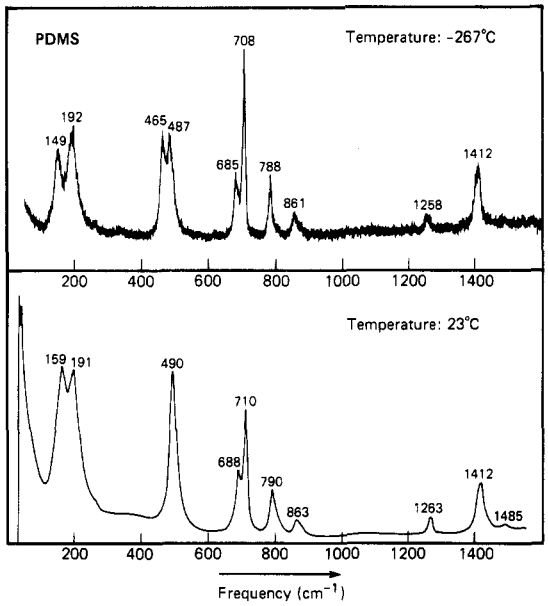

Figure 3. Raman spectra of high molecular weight PDMS obtained at +23 and -237 °C. (Excitation wavelength, 488.0 nm; resolution, 2.0 cm^{-1}.)

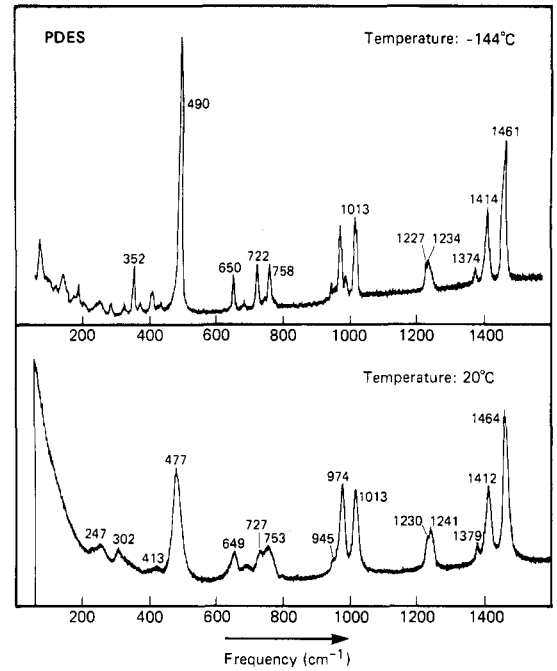

Figure 4. Raman spectra of PDES obtained at +23 and -144 °C. (Excitation wavelength, 488.0 nm; resolution, 2.0 cm^{-1}.)

indicative of the molecular motion characteristic of the melt since this spectrum was recorded above the melting point (-40 °C). On the other hand the spectrum at -267 °C (6 K) contains bands that are generally sharper and characteristic of the crystalline state.

From a comparison of the two spectra in Figure 3, it becomes apparent that they are quite similar in all regions except for those bands located near 490 cm^{-1}. This band is assigned[6,7] to the symmetric Si–O stretching vibration, ν_s(Si–O), and the doubling observed in the spectrum at -267 °C (6 K) reflects the semicrystalline nature of this sample at low temperatures. The peak at 486 cm^{-1} is attributable to ν_s(Si–O) in the amorphous region while that at 466 cm^{-1} is the corresponding crystalline component. This particular set of bands will be discussed in detail in a later section when considering the kinetics of the various phase transitions.

Although a complete band assignment is beyond the scope of the present work, the CH_3 bending vibrations in the 1400-cm^{-1} region and the rocking and wagging vibrations of the $Si(CH_3)_2$ group at 1253 cm^{-1} have been monitored as a function of temperature in order to assess the extent of molecular motion of the methyl groups introduced at various phase boundaries.

There is a noticeable increase in complexity when comparing the spectra of PDMS in Figure 3 with that of PDES in Figure 4. This is due to the addition of a CH_2 group to each side chain resulting in the obvious addition of a CH_2 bending vibration at 1464 cm^{-1} and several bands in the vicinity of 950–1050 cm^{-1} resulting from the stretching of $C(H_3)$–$C(H_2)$ bonds. As in the previous discussion of PDMS, the ν_s(Si–O) vibration at 477 cm^{-1} in the spectrum of PDES at room temperature shows the most change upon lowering the temperature to -144 °C. Interestingly enough there is only a single narrow component (attributable to the crystalline phase) at 490 cm^{-1} in the low-temperature spectrum, suggesting that the PDES is highly crystalline in its low-temperature phase. Similar conclusions about the crystallinity of PDES were reported by Papkov et al.[4] when a specimen was slow cooled from the mesomorphic phase. Although the PDES sample used to obtain the spectrum in Figure 4 was cooled slowly in a cryostat, the cooling process began at 23 °C (296 K), somewhat below the mesophase-to-isotropic transition. It

Table I
Assignment of Bands

PDMS	PDES	assignment[a]
	1464	$\delta(CH_2)$[b]
1412	1412	$\delta(CH_3)$
1263		r($Si(CH_3)$) + w($Si(CH_3)$)
	1235	r($C(CH_3)$) + w($C(CH_3)$)
490	477	ν_s(SiO)

[a] References 6, 7, and 15. [b] δ, bend; r, rock; w, wag; ν_s, symmetric stretch.

should be pointed out that the fact that the location of the crystalline component of ν_s(Si–O) in PDMS (466 cm^{-1}) is lower than that of its amorphous counterpart (486 cm^{-1}) while the opposite is true for PDES merely reflects the different conformations (helical vs. cis-trans type[3]) assumed by the homopolymers in the solid state.

A final observation regarding the effect of cooling on the Raman spectrum of PDES can be made by consulting the low-frequency region (100–300 cm^{-1}) of Figure 4. It is immediately apparent that going from the mesomorphic phase at 20 °C (293 K) to below the crystal–crystal transition results in the appearance of a number of sharp bands of medium-weak intensity below 400 cm^{-1}. Due to the nature of nonlocalized vibrations which occur in this region, those bands between 400–150 cm^{-1} can be assigned to the bending and torsional vibrations of the Si–O–Si backbone while those below 150 cm^{-1} most likely have at least some contribution from interchain interactions in the lattice.[14] It is these latter vibrations that obviously disappear in the spectrum of the high-temperature phase due to the introduction of positional disorder into the lattice.

A summary of the bands used to monitor the transition kinetics in this study and their assignment is shown in Table I.

C. Nature of the Phase Transition in PDMS. As discussed previously, the ν_s(Si–O) vibration appears to be the most sensitive to temperature variations, becoming a doublet (486 and 466 cm^{-1}) at low temperatures. This doublet can be resolved into a broad ($\Delta\nu$ = 26 cm^{-1}) component at 486 cm^{-1} belonging to the amorphous phase and a narrow ($\Delta\nu$ = 15 cm^{-1}) component at 466 cm^{-1} thought

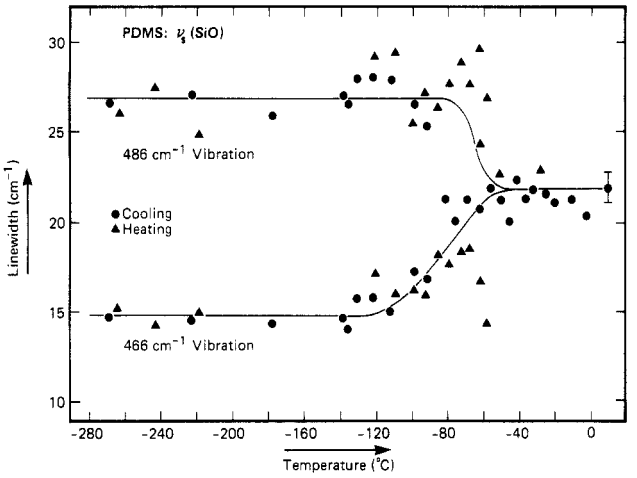

Figure 5. Plot of bandwidth of the amorphous and crystalline ν_s(Si–O) peaks of high molecular weight PDMS. Data obtained upon heating and cooling is included. Lines are drawn merely to guide the eye.

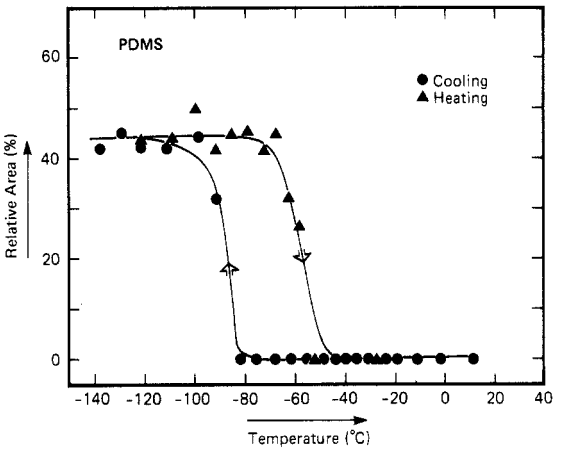

Figure 6. Plot of the relative area of the 466-cm^{-1} crystalline band (as compared to the total integrated area of 466- and 486-cm^{-1} bands) of PDMS as a function of temperature. Lines are drawn merely to guide the eye.

to originate in the crystalline phase. As shown in Figure 5, there is little change in bandwidth of either the 486- or the 466-cm^{-1} peaks until considerably above T_g (–120 °C). This is not unexpected since the bandwidth merely reflects the extent of backbone segmental motion which, below T_g, will be minimal. In the vicinity of –90 to –80 °C (183–193 K) an interesting observation was made as shown in Figure 5. The bandwidth of the two components of ν_s(Si–O), attributed earlier to a crystalline (466 cm^{-1}) and an amorphous (486 cm^{-1}) component, began to change, eventually collapsing into a single line at 490 cm^{-1} having an intermediate bandwidth. The collapse into one Raman band occurs in the –60 to –40 °C (213–233 K) temperature range. Not surprisingly, this corresponds to the crystalline melting range of PDMS as shown in Figure 1. Correspondingly the integrated intensity of the 466-cm^{-1} crystalline band is shown to decrease dramatically in this temperature range as indicated in Figure 6 where the integrated area of the 466-cm^{-1} band relative to that of the 466/486-cm^{-1} doublet is plotted as a function of temperature. The hysteresis observed upon cooling PDMS reflects the effect of supercooling which is commonly observed in polymeric materials. The constancy of this ratio up to –70 °C (203 K) is somewhat surprising since the exothermic transition observed at –80 °C (193 K) in the DSC of PDMS (Figure 1) was attributed to crystallization. The natural expectation was that there would be an increase in peak intensity ratio at this temperature, but no dramatic change was observed. Instead this ratio begins to fall dramatically in the –70 °C (203 K) range, most assuredly reflecting the onset of melting which is complete at –40 °C (233 K). This then also explains the replacement of the 466/486-cm^{-1} doublet by a single band at 490 cm^{-1} in this same temperature range. By –40 °C (233 K) there is no longer any evidence of a doublet. Interestingly, the bandwidth of the 486-cm^{-1} band, attributed to the existence of a polymer glass, actually becomes narrower after the transition to the melt above –40 °C (233 K). This would then suggest that the process of cooling PDMS to temperatures below the phase transition actually freezes in a nonequilibrium distribution of conformers which gives rise to a broad amorphous band. As the sample is heated above the melting point, an equilibrium distribution of conformers is obtained and the amorphous band becomes sharper due to the freedom of motion in the liquid state. The data of Figure 5 would then also imply that between T_g and T_m there would also be a nonequilibrium distribution of conformers even though the backbone does exhibit Brownian segmental motion. A plausible explanation of this observation must invoke the role of entanglements which are certainly prevalent in high molecular weight polymers.

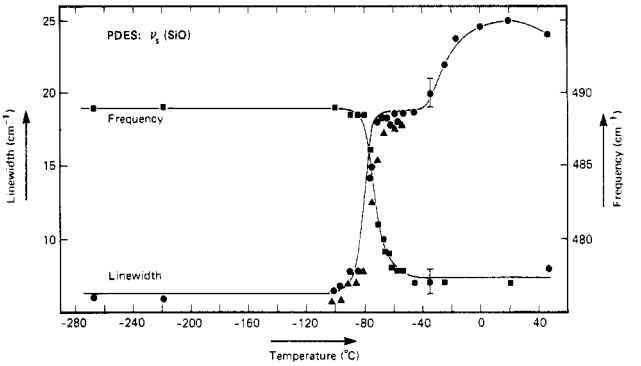

Figure 7. Bandwidth and frequency of ν_s(Si–O) band of PDES as a function of temperature.

D. Nature of the Phase Transition in PDES. The behavior of both the frequency and bandwidth of the 490 cm^{-1} ν_s(Si–O) band of PDES as a function of temperature is shown in Figure 7. Very little changes are observed in the –265 to –100 °C (8–173 K) range even in the vicinity of T_g (–120 °C). As discussed previously this can be attributed to the lack of a significant amount of amorphous material present in PDES. Thus the presence of a single component of the ν_s(Si–O) attributable to crystalline material would suggest that the amorphous component is negligible and therefore the lack of any variation of either the position or bandwidth of the 490-cm^{-1} band in the vicinity of T_g is understood. However between –100 and –65 °C (173–208 K) a dramatic change occurs as shown in Figure 7. This region corresponds to the phase transitions observed in the DSC in the –60 °C (213 K) range which have been attributed to a transformation of the two low-temperature polymorphs (monoclinic α_1 and tetragonal β_1) to the two high-temperature modifications (monoclinic α_2 and tetragonal β_2 form) by Tsvankin et al.[3] Surprisingly they[3] assumed no changes in conformation accompanied this crystal–crystal transition. This is not supported by the data shown in Figure 7. The shift in ν_s(Si–O) from 490 to 477 cm^{-1} at this transition temperature definitely indicates a change in conformation. The concommittant change in bandwidth reflects a sizeable increase in molecular motion of the backbone, most likely attributable to the introduction of disorder. By comparison, the in-

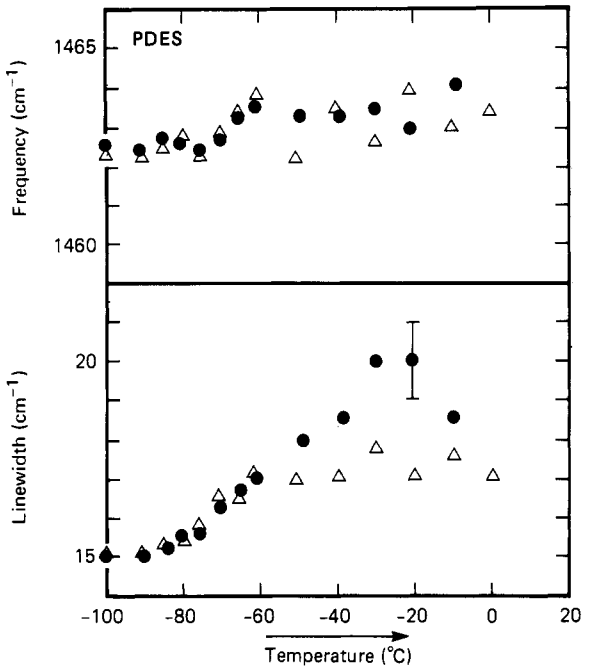

Figure 8. Bandwidth and frequency of $\delta(CH_2)$ bending mode of ethyl side chain of PDES as a function of temperature: (●) cooling; (△) heating.

crease in molecular motion of the side chain is small as indicated by Figure 8 in which the frequency and bandwidth of the 1462-cm^{-1} CH_2 bending vibration is plotted as a function of temperature. Although the bandwidth appears to change continuously over the −100 to 0 °C (173–273 K) range, the frequency change is negligible, indicating that the ethyl side chain is relatively unaffected by the low-temperature phase transitions. This would then suggest that the −80 °C (193 K) transitions involve primarily a change in backbone conformation and thus can be classified as a transformation from an ordered structure to a partially disordered one. The structure above this low-temperature transition could most accurately be classified as a "condis" crystal.[1]

The second set of transitions which occur in the vicinity of 0 °C (273 K) has been attributed to transformations from the monoclinic α_2 and tetragonal β_2 forms to the mesomorphic phase characterized by a monoclinic structure slightly different from hexagonal packing. Spectroscopically there appears to be a further introduction of backbone motion as manifested by a change in bandwidth of ν_s(Si–O) as shown in Figure 7 but no apparent change in conformation as would be indicated by a shift in ν_s(Si–O). It is intersting to note that no further change occurs in either the bandwidth or frequency of the 477-cm^{-1} band even upon transformation to the isotropic state at 40 °C (313 K). Thus it would appear that the introduction of conformational disorder at the low-temperature transitions is by far the most dramatic effect while the higher temperature transitions merely alters the molecular mobility of the PDES backbone. Likewise the role of the ethyl side chain is minimal in any of these transitions with its molecular motion increasing continuously over the entire temperature region studied.

Conclusion

The structural behavior of PDMS and PDES has been monitored as a function of temperature in the range from −267 to 40 °C (6–313 K). By following changes in the Raman bandwidth of the ν_s(Si–O) backbone vibration and $\delta(CH_2)$ of the side chain (in PDES) it was concluded that backbone conformational changes were primarily involved in both sets of transitions studied.

In particular it was found that cooling high molecular weight PDMS from the melt gave rise to a nonequilibrium distribution of conformers in the glassy and rubbery state due to the presence of entanglements. Molecular relaxation resulting in a distribution more characteristic of equilibrium was observed upon heating.

In contrast, studies of PDES indicated that a sample cooled to liquid helium temperatures contained very little, if any, amorphous material. As the sample was heated, the ordered PDES backbone was observed to undergo a transition to a conformationally disordered (or "condis") crystal in the −60 °C (213 K) range. Further heating to either the mesomorphic or isotropic state caused a small change in the molecular mobility but no change in the average conformation of the PDES backbone.

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