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Order−Disorder Phase Transition in Poly(di-*n*-butylstannane) Observed by UV−Vis and Raman Spectroscopy

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ABSTRACT: Variable-temperature UV−vis and Raman spectra have enabled detection of a thermochromic phase transition for $[^{n}Bu_2Sn]_n$ with an onset temperature T_c at ca. 260 K. The exact T_c value depends on the sample prehistory and the rate of cooling. This transition proceeds over a temperature interval from ca. 260 to ca. 200 K, when it reaches completion, and it involves two modifications: one with a disordered polymer backbone, which corresponds to a UV band at ca. 390 nm and a broad Raman feature for the ν(Sn−Sn) mode at ca. 120 cm^{-1}, and a more ordered one (apparently, all-anti or transoid), to which a red-shifted UV band at ca. 420 nm and a very intense narrow Raman line for the ν(Sn−Sn) mode at ca. 145 cm^{-1} are assigned. No abrupt side chain ordering was observed at T_c, but a gradual ordering, involving rotational isomerism about the C−C bonds, occurs on further lowering of the temperature. Comparison is made with data obtained for other polystannanes $[^{n}R_2Sn]_n$ (R = *n*-hexyl, *n*-octyl).

Introduction

Poly(dialkylstannane)s, a novel class of $\sigma-\sigma$ conjugated polymers with a backbone consisting entirely of tin atoms, possess interesting electronic properties including relatively low band gaps.[1−7] Two of us previously reported the first high molecular weight polystannanes, of the type $[^{n}R_2Sn]_n$ (R = ^{n}Bu, ^{n}Hex, ^{n}Oct), prepared by the metal-catalyzed dehydropolymerization of secondary dialkylstannanes.[3] These polymers were shown to exhibit strong absorption bands in the near UV region (370−400 nm), attributed to $\sigma-\sigma^*$ transitions associated with the polymer backbone. The exact λ_{max} values for these bands were found to depend on the temperature and physical state of the polymer. Films of the polymers with R = ^{n}Hex and ^{n}Oct undergo a thermochromic phase transition upon warming to ca. 313 K, which manifests itself by an abrupt, reversible change in the λ_{max} value from ca. 400 nm to ca. 380 nm in electronic absorption spectra as well as by an endothermic event characterized by DSC.[3] However, no such phase transition was observed for $[^{n}Bu_2Sn]_n$ over the temperature range studied (263−363 K). Subsequently, it was shown that some of these polymers could be obtained by other synthetic methods.[5−7]

Interestingly, the onset temperatures of the phase transitions, T_c, for $[^{n}Hex_2Sn]_n$ and $[^{n}Oct_2Sn]_n$ (ca. 313 K) correspond closely to those observed for the analogous polysilanes $[^{n}Hex_2Si]_n$ and $[^{n}Oct_2Si]_n$.[8] For the latter polymers, the phase transitions have been characterized as involving transformation of a mesophase with a disordered main chain and disordered side groups to an ordered crystalline phase with a planar zigzag trans conformation of the backbone and ordered side groups. For both $[^{n}Hex_2Si]_n$ and $[^{n}Oct_2Si]_n$, the latter phase predominates at room temperature. However, for $[^{n}Bu_2Si]_n$ the predominant modification at room temperature was shown to be that with an orthohexagonal intermolecular packing of 7/3 helices.[9a] Transformation of this polymer to a crystalline phase with a planar zigzag trans backbone conformation could be achieved only at high pressure or by precipitation of the sample from a solution cooled to low temperature.[9] These observations for the Si congeners suggested, by analogy, that the phase transition for $[^{n}Bu_2Sn]_n$ should occur at temperatures lower than those observed for other poly(dialkylstannane)s.[3] Here we report a study of the UV−vis and Raman spectra of $[^{n}Bu_2Sn]_n$ over a wide temperature range (360−90 K), which has allowed us to detect this phase transition (possessing an onset temperature T_c in the region 260−250 K) and follow the behavior of spectral parameters on further cooling. Based on these observations and on XRD data, we are able to draw some conclusions regarding the nature of the phase transition.

Experimental Section

The polymer $[^{n}Bu_2Sn]_n$ was synthesized as described previously.[3] $^{n}Bu_2SnCl_2$ was purchased from Aldrich Chemical Co. and distilled before use. The UV−vis studies were performed on a M-40 Carl Zeiss spectrophotometer interfaced to a computer. Thin films of the polymer cast from hexane solution were found to be unstable upon irradiation in the spectrophotometer. Therefore samples employed in this study were obtained by the gentle pressing of a small amount of the polymer between two quartz windows under an inert atmosphere. After some rotation of one window with respect to the other, the sample was sealed with Parafilm. The details of this procedure for sample preparation were found to slightly influence the exact position (within 10 nm) and bandwidth (within 500 cm^{-1}) of the UV absorption bands observed.

The Raman spectra were determined using Jobin-Yvon U-1000 and T64000 and Dilor Labram laser Raman spectrometers, with excitation by the 514.5 nm line of an Ar^+ Spectra Physics 2025 laser, and also by the 632.8 nm line of a He−Ne SP 120 laser. A prism monochromator and interference filters were employed for exciting line filtering, as were photomultiplier and CCD detectors for recording spectra. Samples for Raman investigations were either small polymer chunks sealed

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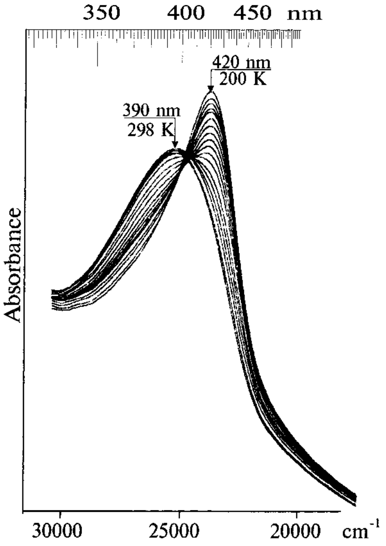


Figure 1. Order−disorder phase transition in [^{n}Bu$_2$Sn]$_n$ reflected by the variable-temperature UV−vis spectra.

in glass capillaries in vacuo or the same samples used for the UV−vis measurements. To avoid sample destruction in the laser beam, the latter was not focused and minimum light density was employed (exciting laser power was less than 10 mW). To judge sample purities, the slow degradation of [^{n}Bu$_2$Sn]$_n$ in air was studied by Raman spectroscopy. Variable-temperature studies involved various cryostats and heated cells. Temperatures were generally maintained to within ±1 K.

XRD data were collected with an automated DRON 3 powder diffractometer in Bragg−Brentano focusing geometry (Cu Kα radiation 20 kV/40 mA, graphite monochromator on the secondary beam, scan speed 1 deg/min, 0.1° steps, α-Al$_2$O$_3$ as an external standard).

Results and Discussion

UV−Vis and XRD Studies. In the temperature interval from ca. 360 to 260 K, only a broad asymmetric UV absorption band with λ_{max} in the region 380−390 nm (band I) is observed (Figure 1). Its position and half-width (fwhh $\Delta\nu_{1/2}$ 4500−5000 cm^{-1}) depend slightly on sample preparation and the sample's thermal history. This band is similar in appearance to the corresponding high-temperature bands observed for [^{n}Hex$_2$Sn]$_n$ and [^{n}Oct$_2$Sn]$_n$,[3,10] all being characteristic of a disordered polymer backbone. However, UV−vis data alone do not allow one to distinguish between an amorphous phase and a mesomorphic phase containing conformationally disordered macromolecules. The XRD patterns obtained at ambient temperature depend on the method of sample preparation, and two typical patterns are presented in Figure 2. Both contain a strong reflection at $2\theta \sim 8°$, which points to some interchain ordering and, hence, suggests a mesomorphic phase with lateral packing of the macromolecules into a two-dimensional lattice.[11a] The sharp reflections at 2θ values of 8.26 (strong), 14.35 (weak), and 16.57° (weak) correspond to d spacings in a $1{:}1/\sqrt{3}{:}1/\sqrt{4}$ relationship (pattern a of Figure 2), which is consistent with hexagonal packing. Pattern b in Figure 2, with its broadened main reflection, could result from the presence of some amorphous phase. Thus, modification I of [^{n}Bu$_2$Sn]$_n$, predominant at room temperature, seems to be analogous to the high-temperature hexagonal columnar mesophase (hcm) of [^{n}Bu$_2$Si]$_n$,[9] which exists above 353 K. However, the λ_{max} value of the UV band for the former polymer is red-shifted by about 60 nm compared to the latter, which seems to reflect a higher polarizability for the tin atoms.

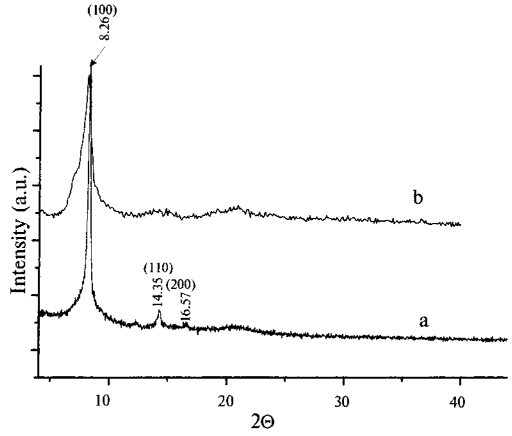


Figure 2. X-ray diffractograms of [^{n}Bu$_2$Sn]$_n$ obtained at room temperature.

We should also note that, for [^{n}Bu$_2$Sn]$_n$ samples at room temperature, an admixture of a modification with a helical backbone cannot be excluded, because for the polysilanes the λ_{max} values of the UV bands as well as XRD patterns observed for the mesomorphic phases with disordered or helical backbone conformations are very similar.[9,11b] The UV band corresponding to a helical conformation is more narrow and can be "hidden" in the broad asymmetric band of the hcm mesophase.

When the temperature of the [^{n}Bu$_2$Sn]$_n$ sample is lowered, a new band (II) appears in the region above 400 nm of the UV−vis spectrum (Figure 1), evidently corresponding to the nucleation of a new modification. The onset of this phase transformation occurs between 260 and 250 K, the exact value for T_c being dependent on the sample prehistory and the rate of cooling. Band II grows on further cooling at the expense of band I.

Obviously, the new phase is more ordered, since band II is red-shifted by about 30 nm with respect to band I, and it is more narrow ($\Delta\nu_{1/2}$ 2500−3200 cm^{-1}). The corresponding red shift of the UV band in the spectrum of the silicon analogue [^{n}Bu$_2$Si]$_n$, attributed to a transformation from an hcm modification to an all-trans conformation of the backbone, was about 30 nm.[9] Assuming an analogy in the phase behaviors of corresponding polysilanes and polystannanes, it could be concluded that band II of [^{n}Bu$_2$Sn]$_n$ also corresponds to an all-trans (or all-anti, according to a new nomenclature proposed by Michl and West[12]) conformation. However, the $\Delta\nu_{1/2}$ value of this band II is much greater than those observed for bands corresponding to the trans conformations of polysilanes (800−1500 cm^{-1}).[11] From this observation, it is evident that a complete analogy between the polysilanes and polystannanes, with respect to phase behavior as reflected in the UV−vis data, may not exist. In addition, our experience in studies of phase transitions for various polysilanes has shown that the magnitude of a red shift in the UV−vis spectrum alone cannot be correlated unambiguously with the backbone conformation.[11]

It is pertinent to mention here that a Sn−Sn bond is much longer (2.85 Å) than Si−Si (2.35 Å) or Ge−Ge (2.50 Å) bonds,[13] and the barrier to rotation for the Sn−Sn bond is calculated to be smaller than those for the Si−Si and Ge−Ge bonded analogues (for isolated H$_3$M−MH$_3$ molecules).[13,14] The latter difference is significant, in that only for the Sn−Sn bond is this barrier lower

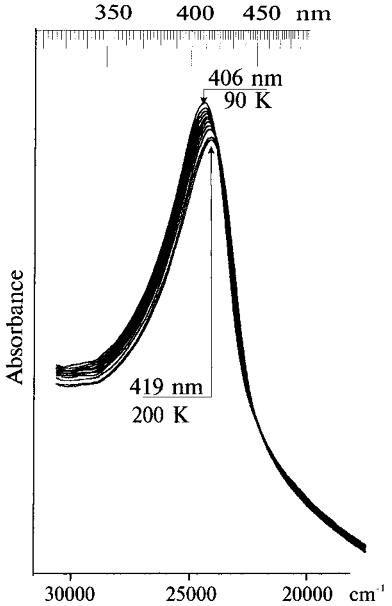


Figure 3. Low-temperature behavior of the UV band corresponding to a more ordered modification of $[^n\mathrm{Bu_2Sn}]_n$.

than the room-temperature *RT* value. Thus, it is not reasonable to expect similar conformational behaviors for corresponding polysilanes and polygermanes, on one hand, and of polystannanes, on the other. Due to this low barrier, rotational motion about the Sn−Sn bonds is expected to be essentially free. Therefore, the backbone conformation of a polystannane should be dictated primarily by external factors such as intra- and intermolecular nonbonded interactions of alkyl groups, and close packing forces. The longer Sn−Sn bond distances also leave more room for internal rotations of the alkyl side groups. Thus, for various reasons it is difficult to make an ultimate conclusion on the basis of the UV−vis data regarding the backbone conformation in the ordered modification II of $[^n\mathrm{Bu_2Sn}]_n$.

A temperature-reversible UV−vis pattern with two overlapping bands and a clear-cut isobestic point is observed in the temperature interval from ca. 260 to ca. 200 K, reflecting an equilibrium between the two modifications (Figure 1). This phase transition seems to be virtually complete by 200 K, since only band II is seen in the spectrum at this temperature. However, the presence of a small amount of the disordered modification cannot be excluded, since band II is asymmetric with a wing on the low-wavelength side. The $\lambda_{\max}$ value of band II is temperature dependent, exhibiting a 10 nm blue shift and narrowing upon further cooling to 90 K (Figure 3). Similar behavior has been displayed by all the UV−vis bands corresponding to ordered modifications of poly(dialkylsilane)s.[11]

It is notable that the $\lambda_{\max}$ values for both the UV−vis bands of solid $[^n\mathrm{Bu_2Sn}]_n$ polymer and for the only band exhibited by its solutions[7] are significantly higher than 362 nm, reported as the limiting value for the series of oligomers $\mathrm{H}[^n\mathrm{Bu_2Sn}]_n\mathrm{R}$ with $n = 3-15$.[15] In addition, no phase transition was observed[7] for pentane solutions of $[^n\mathrm{Bu_2Sn}]_n$ by UV−vis spectroscopy down to 153 K. This is perhaps to be expected as the T_c value for solid $[^n\mathrm{Hex_2Si}]_n$ is ca. 313 K, and a phase transition for the dissolved polymer does not occur until cooling to ca. 238 K.[8]

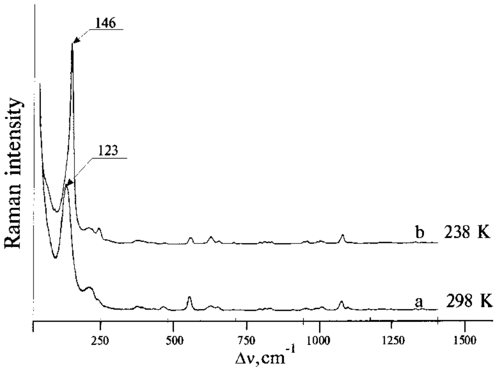


Figure 4. Raman spectra of $[^n\mathrm{Bu_2Sn}]_n$ above (a) and below (b) the phase transition.

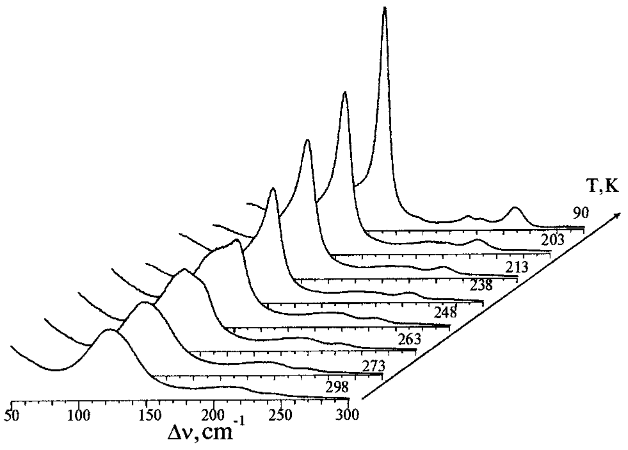


Figure 5. Temperature evolution of the ν(Sn−Sn) region of the Raman spectrum of $[^n\mathrm{Bu_2Sn}]_n$ during the phase transition.

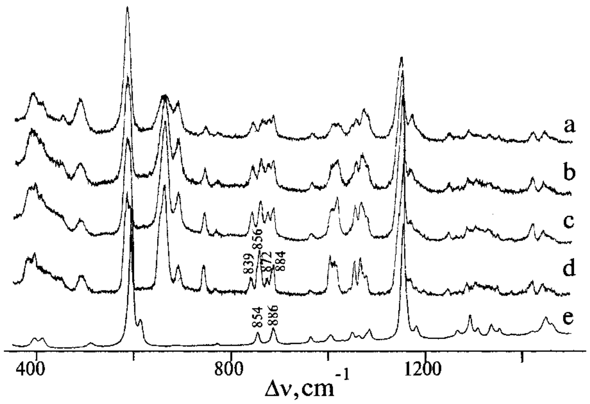


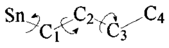
Figure 6. Region of the ν(Sn−C) mode and of internal vibrations of the ^{n}Bu groups in the Raman spectra of the polymer $[^n\mathrm{Bu_2Sn}]_n$ at various temperatures (a−d) and of the solid monomer $^n\mathrm{Bu_2SnCl_2}$ at room temperature (e). Key: (a) 298 K; (b) 248 K; (c) 213 K; (d) 90 K.

Raman Studies. Raman spectra for the $[^n\mathrm{Bu_2Sn}]_n$ polymer are presented in Figures 4−6. Band assignments were made on the basis of previously reported vibrational studies of monomeric stannanes of the types $\mathrm{R}_n\mathrm{SnX}_{4-n}$ and $\mathrm{R_3SnXSnR_3}$,[16−18] distannanes,[19,20] and linear[21] and cyclic[22] oligomeric polystannanes. Also, assignment of the Raman lines was facilitated by a much higher polarizability of the Sn atom compared to that of the C and H atoms, which leads to enhanced intensities for the normal modes involving vibrations of the Sn atoms.[20]

To our knowledge, the only vibrational spectroscopic study of a polystannane, including a normal coordinate analysis, focuses on $\mathrm{Me_3SnSnMe_3}$.[19] In its Raman spectrum, a very intense, strongly polarized line at 192 cm^{-1} was assigned as the stretching vibration of the Sn−Sn bond, ν(Sn−Sn). However, this normal mode is not well localized, being heavily mixed with the CSnC bending coordinate, δ(CSnC), but not with the ν(Sn−C) stretch. Presumably, the same mixing of ν(Sn−Sn) and δ(CSnC) coordinates exists for longer polystannanes with alkyl substituents. For linear oligomeric polystannanes, the totally symmetric ν^s(Sn−Sn) mode was reported[21] as an intense Raman line in the region 110−140 cm^{-1}. Based on these data, we unambiguously attribute the most intense feature observed in the 120−150 cm^{-1} region of the Raman spectrum of [^{n}Bu$_2$Sn]$_n$ to the ν^s(Sn−Sn) mode.

From literature data,[16−19] the ν(Sn−C) stretching vibrations should occur in the region 490−600 cm^{-1}. The frequency of the ν^s(Sn−C) mode has been shown to depend on the sum of the electronegativities of the substituents at the Sn atom.[17] The highest value known for a Raman ν(Sn−C) mode, 599 cm^{-1}, is reported for ^{n}BuSnCl$_3$.[17a]

For all compounds containing the ^{n}BuSn moiety[17] as well as for other mono- or poly(*n*-propyl) and -(*n*-butyl) derivatives of main group metals (M = Ga, In, Ge, Hg),[23] rotational isomerism is observed due to hindered rotation about the C^1−C^2 bond in the MC^{1}H$_2$−C^{2}H$_2$R fragment. This is a very interesting phenomenon, in that all these compounds exhibit two intense Raman bands in the liquid state corresponding to the ν^s(M−C) modes of two conformers, with a surprisingly great difference in frequency of about 100 cm^{-1} (520 and 600 cm^{-1} for M = Ga; 495 and 593 cm^{-1} for M = In; 505 and 602 cm^{-1} for M = Hg;[23] ca. 500 and 590 cm^{-1} for M = Sn[17]). For *n*-butyl derivatives of the type:



hindered rotation about the second, C^2−C^3 bond can also occur, and this has been shown to broaden these bands. Only the higher energy band (at ca. 600 cm^{-1}, assigned to a trans conformer by analogy with previous work on 1,2-dihaloethanes[24]) persists or predominates in the solid state. Based on analyses of these data, for [^{n}Bu$_2$Sn]$_n$ two Raman lines can be reliably attributed to the ν^s(Sn−C) modes: a weak one at 483 cm^{-1} and a strong one at 578 cm^{-1}. Thus, two rotational isomers about the C^1−C^2 bond in the side groups are observed for solid polymer at room temperature, with the trans one being predominant.

All of the modes with frequencies higher than 650 cm^{-1} belong to internal vibrations of the ^{n}Bu groups. Their assignments are based on variable-temperature vibrational studies of the related compounds ^{n}Bu$_{4-n}$SnCl$_n$[17] and ^{n}Bu$_2$SiCl$_2$.[25]

The variable-temperature Raman data for [^{n}Bu$_2$Sn]$_n$ confirm the phase transition, manifested as dramatic changes in the ν(Sn−Sn) region in the temperature interval given above. More specifically, a broad intense band at ca. 123 cm^{-1} is observed above T_c and this feature is gradually replaced on cooling by a very intense narrow line at ca. 146 cm^{-1} (Figures 4,5). Further cooling gradually shifts this line to higher frequencies (to 151 cm^{-1} at 90 K). The intensity of the latter line exceeds the intensity of all the other Raman lines by a factor of >10. The temperature evolution of the ν(Sn−Sn) region, presented in detail in Figure 5, corresponds to an ordering of the polymer backbone, as reflected by the UV−vis spectra in Figure 1. A great enhancement of the ν(Sn−Sn) line observed for the ordered phase suggests preresonance character of the Raman spectrum and this is an argument in favor of an all-anti (trans) or transoid conformation of the tin backbone in this phase. However, this assumption requires further supporting evidence.

Temperature-dependent changes are also observed in the ν(Sn−C) region of the Raman spectrum of [^{n}Bu$_2$Sn]$_n$ (Figures 4 and 6), but they are not analogous to those found for some polydialkylsilanes and for [^{n}Hex$_2$Ge]$_n$.[9b,11,26,27] During the phase transitions of the latter polymers, appearance of the more ordered crystalline modification was accompanied by an abrupt and dramatic enhancement of the line attributed to the ν^s(M−C) mode. This has been associated with formation of an all-trans (all-anti) conformation of the main chain, which maximizes $\sigma-\sigma$ conjugation[26,27] and thus leads to a preresonance increase in intensity of the corresponding Raman lines. This effect is not observed in the Raman spectrum of [^{n}Bu$_2$Sn]$_n$. That is, the line at 578 cm^{-1} does not exhibit substantial changes (Figure 6). At the same time, the neighboring line at 658 cm^{-1} undergoes a surprising increase in intensity below T_c. It is tempting to assign this band to the ν(Sn−C) mode of the more ordered polymer modification, as this assignment would have been consistent with the overall changes in the spectra of the Si and Ge congeners mentioned above. However, the frequency value of 658 cm^{-1} is too high to be assigned to the ν^s(Sn−C) mode of the [^{n}Bu$_2$Sn]$_n$ polymer. The latter frequency must be lower than that for ^{n}Bu$_4$Sn (594 cm^{-1}),[17a] because the electronegativity of Sn atoms is lower than that of C atoms, and thus the sum of electronegativities of all four atoms bonded to the Sn atom in the polystannane macromolecule is less than that in the ^{n}Bu$_4$Sn molecule. The real ν^s(Sn−C) value for [^{n}Bu$_2$Sn]$_n$, 578 cm^{-1}, is in good accord with this consideration.

For ^{n}Bu$_4$Sn, Geissler and Kriegsmann[17a] have assigned very weak Raman bands at 650 and 694 cm^{-1} to the r(CH$_2$) modes of the two different conformers of the ^{n}Bu groups. By analogy, the lines at 658 and 684 cm^{-1} in the Raman spectrum of [^{n}Bu$_2$Sn]$_n$ could be assigned to the r(CH$_2$) mode of the more stable and less stable conformers, respectively. This assignment is confirmed by their temperature behavior. However, the enhanced Raman intensity for these lines, especially of the line at 658 cm^{-1} at low temperature, seems strange and unusual for a deformational mode. All the members of the series ^{n}Bu$_{4-n}$SnCl$_n$ $n = 1,2,3$ and ^{n}Bu$_3$SnXSn^{n}Bu$_3$ do not exhibit Raman features in this region.[17] A possible explanation is that the normal mode of [^{n}Bu$_2$Sn]$_n$ at 658 cm^{-1} is not well-localized but is of a complex eigenvector, with strong coupling of the r(CH$_2$) coordinate with some coordinates involving displacements of the Sn atoms. Participation of the latter in this normal mode will increase its Raman intensity. For confirmation of this assumption, normal coordinate calculations are planned.

The results presented in Figure 6 are consistent with temperature-dependent rotational isomerism in the ^{n}Bu side groups, which is not correlated with the ordering of the main chain starting at T_c. This interpretation follows from a detailed examination of the spectral region above 450 cm^{-1}.

On lowering the temperature of [^{n}Bu$_2$Sn]$_n$, the relative intensities of the two ν^s(Sn−C) lines change such that the weak line at 483 cm^{-1} becomes weaker.

However, it does not completely disappear even at 90 K, indicating that a small amount of the less stable gauche conformer of the ^{n}Bu group is still present at this temperature.

For interpretation of the Raman region above 700 cm^{-1}, the model compound $^{n}Bu_2SnCl_2$, which is a polycrystalline solid at room temperature, proved highly useful. According to its Raman spectrum (Figure 6e), the ^{n}Bu groups in this solid adopt predominantly one, trans conformation because the ν(Si−C) line at 512 cm^{-1} is very weak compared to that at 592 cm^{-1}. Figure 6 also presents the corresponding variable-temperature spectra of the $[^{n}Bu_2Sn]_n$ polymer. This comparison demonstrates that the spectral pattern characteristic of internal vibrations of the ^{n}Bu groups is substantially more complex for $[^{n}Bu_2Sn]_n$ vs solid $^{n}Bu_2SnCl_2$. The greatest differences are observed not only in the region 600−700 cm^{-1} discussed above but also in the vicinity of 850 cm^{-1}, where the conformationally sensitive[28] external deformational modes of the CH_2 and CH_3 groups occur. Both modes of the ordered *n*-butyl groups in $^{n}Bu_2SnCl_2$ (850 and 886 cm^{-1}) are doubled in the spectrum of the polymer, the relative intensity in each pair being temperature-dependent. This points to a disordered state of the side groups in the polymer down to very low temperature, with the relative amount of the less stable conformers regularly decreasing with temperature. Thus, conformational disorder in the ^{n}Bu groups due to hindered rotation about the C−C bonds persists in the polymer even at low temperature in the more ordered modification. It is evident that the molecular mobility necessary for conformational transitions in the alkyl groups still exists in the solid state. An analogous phenomenon was observed by two of us for the low-temperature glassy state of $^{n}Bu_2SiCl_2$.[25]

Thus, the Raman results show that an order−disorder phase transition for $[^{n}Bu_2Sn]_n$ does not involve abrupt ordering of the side chains, but only changes in conformation of the Sn−Sn bonded main chain, presumably to an all-anti or transoid conformation. Very similar results have been observed for $[^{n}Hex_2Sn]_n$ and $[^{n}Oct_2Sn]_n$, which display analogous temperature-dependent Raman spectra but a higher temperature (ca. 313 K) phase transition.[10]

Conclusion

The phase transition of $[^{n}Bu_2Sn]_n$ has been observed by Raman spectroscopy, and reflects a 390 → 420 nm abrupt shift of the electronic absorption band corresponding to the σ−σ* transition. This phase transition proceeds on cooling over the temperature interval 260−200 K and involves transformation of the tin backbone from a disordered into a more ordered conformation (presumably, all-anti or transoid) without an abrupt ordering of the side groups. The Raman data point to the presence of conformational isomerism in the ^{n}Bu groups that results from hindered rotation about the C−C bonds. The amount of the less stable conformers gradually diminishes with temperature but does not vanish even at 90 K.

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