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Structure, Crystallization, and Infrared Spectra of Amorphous Perfluoro-*n*-alkane Films Prepared by Vapor Condensation

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ABSTRACT: Amorphous films of n-C_8F_{18}, n-$C_{14}F_{30}$, n-$C_{16}F_{34}$, and n-$C_{20}F_{42}$ were prepared by vapor deposition under vacuum onto the surface of a CsI crystal at 8 K and studied by infrared spectroscopy. The amorphous films thus prepared consist of conformationally disordered perfluoro-*n*-alkane chains that contain both trans and gauche bonds. Annealing the as-deposited films at successively higher temperatures resulted in increased conformational ordering. The highest annealing temperatures attained for C_8, C_{14}, C_{16}, and C_{20} were 180, 150, 210, and 250 K, respectively. Relative to the other chains, however, C_8 was transformed very little. At the highest annealing temperature, the C_{16} and C_{20} films were highly ordered but retained a small but significant fraction of conformational disorder that appeared to be similar to the disorder observed for these compounds at room temperature. The C_{14} film underwent a well-defined crystallization at a temperature between 135 and 150 K, producing essentially complete conformational ordering. The gauche–trans energy difference E_g was estimated from infrared band intensities for C_{14} and C_{16}, resulting in a value of 1.1 ± 0.1 kcal/mol. The concentration of conformationally ordered chains in a film of C_{20} was determined as a function of annealing temperature. The onset of ordering was found to occur near 65 K and to be one-half completed near 130 K. These temperatures are somewhat higher than those found for n-$C_{20}H_{42}$ in our earlier study. An activation energy for conformational ordering in amorphous C_{20} was also estimated and found to be significantly larger than that for the corresponding *n*-alkane. These results were obtained from an analysis of the infrared bands observed in the 1150–700-cm^{-1} region, which is associated with the ν_3 dispersion curve. The ν_3 infrared bands identified with ordered chains have been used to extend the earlier analyses of the ν_3 dispersion curve. For amorphous films of the perfluoro-*n*-alkanes, the 1150–700-cm^{-1} region is extremely complex, but it displays a band pattern that resembles the pattern predicted for a model system of conformationally disordered chains.

I. Introduction

The perfluoro-*n*-alkanes are simple prototype chains of longstanding theoretical and practical interest. The conformational properties of these chains are complex and in spite of many studies are still not well understood. One manifestation of this complexity is the well-known tendency of perfluoro-*n*-alkane chains in the solid state to assume helical rather than planar structures. The conformational structures of these chains, in both their ordered and disordered states, are significantly more complex than those of the *n*-alkanes that in many other ways they resemble.[1]

Both the perfluoro-*n*-alkanes and the *n*-alkanes contain C–C bonds whose potential energy curve for internal rotation is approximately 3-fold. For both kinds of chains, the gauche conformation of the C–C bond has a higher energy than that of the trans conformation. The energy separation between the gauche and trans states is, however, significantly different in the two cases. For the *n*-alkanes, the difference, E_g, is between 500 and 600 cal/mol,[1,2] while for the perfluoro-*n*-alkanes it is at least twice that.[3] Another difference between the chains is in the value of the dihedral angle at the energy minimum of a "trans" C–C bond. For the *n*-alkane the local equilibrium value of this angle is exactly 180°, so that the chain in its all-trans form is planar. For the perfluorocarbons the dihedral angle at minimum energy is not exactly 180°. This leads to the aforementioned helical structures that are characteristic of these chains in their so-called "trans" conformation.

In the present work, we report on a study of completely amorphous films of a series of perfluoro-*n*-alkanes (n-C_nF_{2n+2}, $n = 8, 14, 16, 20$) prepared by vacuum deposition from the vapor state onto an infrared-transparent window maintained near 8 K. The films prepared in this way are conformationally highly disordered but become ordered if annealed. We have used infrared spectroscopy to characterize the disorder and to monitor changes in the conformation upon annealing.

The present study is similar to an earlier study in which we characterized amorphous *n*-alkanes prepared in the same manner and followed their crystallization upon warming.[4] We have found that infrared spectra obtained at a low temperature show important details that are lost at higher sample temperatures, especially for the liquid state due to the thermal broadening of bands. Another advantage, as we have already noted, is that the structural changes that result from annealing the amorphous films can be readily followed. The deposition technique permits us to obtain samples having a high degree of conformational disorder. As we have found in the case of the *n*-alkanes, the distribution of conformational disorder in the chains that constitute the deposited film is very near that of the chains in a liquid whose temperature is near that at which the sample in the deposition experiment is sublimed. For the samples studied here, this temperature is at or slightly above room temperature.

Our understanding of the vibrational modes of the perfluoro-*n*-alkanes is significantly less than that for the *n*-alkanes, and consequently our analysis of conformational

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Table I
Melting Points (T_m) and Solid–Solid Transition Temperatures (T_t) for Perfluoro-n-alkanes

n	T_m,[a] K	T_t,[a] K
8	254.2	175.6, (190, 200)[b]
14	375[c]	
16	402.2	176.5, 177.7, 186.7
20	437.9	149.5, 202.9

[a] From ref 16 unless otherwise noted. [b] From ref 10. [c] From ref 23.

structure falls short of what is possible for the *n*-alkanes. This limitation is particularly frustrating because, relative to the *n*-alkane case, there is more conformational information potentially available from the infrared spectra of the perfluoro-*n*-alkanes. Thus, in the frequency region 1150–700 cm^{-1} the spectra of the as-deposited films show many more individual bands than in the spectra of the *n*-alkanes. This happens in part because the value of E_g for the perfluoro chains is larger than that for the *n*-alkanes. Consequently, the vapor, and hence the amorphous condensate, consists of relatively few conformers. Moreover, the spectra of these conformers, which are largely trans, are relatively simple, so that the spectrum of the sample tends to display single bands, many of which can be associated with individual conformers. The separation of the bands is also promoted by the high-frequency dispersion that characterizes the vibrational modes in the 1150–700-cm^{-1} region. In contrast, the spectral features associated with amorphous *n*-alkanes tend to be broad, consisting of unresolvable contours that result from overlapping bands.

In what follows, we first describe the preparation of the films of amorphous perfluoro-*n*-alkanes and the measurement of the infrared spectra. Then we discuss some general aspects of the vibrational modes of these chains and describe the spectra of the as-deposited and annealed films of the various individual perfluoro-*n*-alkanes. Next, we consider the ν_3 vibrational progression for both ordered and disordered samples and then the conformational-ordering behavior upon annealing. Finally, we examine the energy difference between gauche and trans C–C bonds.

II. Experimental Procedures

The perfluoro-*n*-alkanes *n*-C_8F_{18}, *n*-$C_{14}F_{30}$, and *n*-$C_{20}F_{42}$ were obtained from Specialty Chemicals and were used as received. *n*-$C_{16}F_{34}$ was kindly supplied by Dr. John Rabolt of the IBM Almaden Laboratory. The latter sample was originally obtained from the Du Pont Co. The melting points and solid–solid transition temperatures reported for these fluoroalkanes are summarized in Table I.

The infrared spectra of the films were measured with a Nicolet Model 8000 FTIR spectrometer. The spectra of the perfluoro-*n*-alkanes in the liquid state were measured with an IBM Model 98 FTIR spectrometer. Both spectrometers were evacuated and were used under conditions that gave a resolution of 2 cm^{-1}.

Amorphous films were prepared by vacuum deposition of the vapor onto a CsI window maintained near 8 K. The deposition was carried out in a CTI Model 21 closed-cycle helium cryocooler equipped with a heater and a temperature controller that allowed the temperature of the film to be varied from 8 to 300 K. Just prior to cooling the CsI window for the deposition, we raised the temperature of this window to ca. 350 K in order to remove, in some measure, the surface-adsorbed molecules.

To prepare amorphous films of C_{14}, C_{16}, and C_{20}, the solid sample was placed in the oven depicted in Figure 1. The oven, which is ceramic and wrapped with heating wire, encloses a copper chamber containing the sample. The temperature of the sample was monitored by a chromel–tungsten thermocouple in direct contact with the sample chamber. When the sample was heated, its vapor escaped through a 0.1-mm-diameter hole in the top of the chamber and condensed on the cooled CsI window.

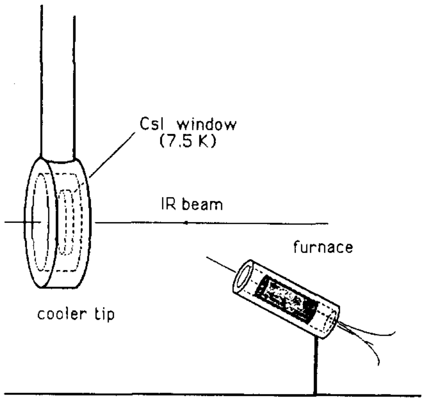

Figure 1. Arrangement of furnace inside cryocooler for preparing amorphous films of perfluoro-*n*-alkanes. The copper sample chamber, with a small hole in its top directed at the window, is contained inside the ceramic heater.

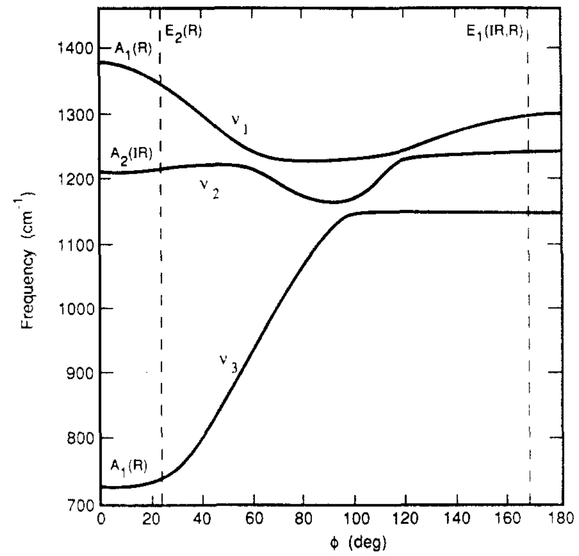

Figure 2. Dispersion curves, calculated by Boerio and Koenig,[6] for an isolated 15/7 helix of poly(tetrafluoroethylene) in the frequency region 1400–700 cm^{-1}. The zone-center fundamentals A_1, A_2, E_1, and E_2 are indicated.

For C_8, which has a higher vapor pressure, a simpler apparatus was used. In this case, vapor from the sample, which was held in its condensed state at room temperature outside the cryocooler, was transported into the cryocooler through a line whose end opened in front of the cooled CsI window. The vapor flow was controlled by adjusting the temperature of the external sample source. Both this technique and that involving the furnace gave films that were approximately of uniform thickness in the area sampled by the infrared beam.

III. Assignments

In interpreting the spectra of the perfluoro-*n*-alkanes, we have focused on the frequency region above 700 cm^{-1}. This region is less congested with vibrational modes than the region below 700 cm^{-1} and consequently is better understood. A guide to its understanding is provided by dispersion curves for the ordered helical poly(tetrafluoroethylene) (PTFE) chain. The structure of the crystalline perfluoro-*n*-alkanes is thought to be similar to that of PTFE.[5] A set of dispersion curves, which are those calculated by Boerio and Koenig[6] for the 15/7 helix, are shown in Figure 2. Similar curves were calculated by Rabolt and Fanconi.[7] We have noted from our own calculations that the dispersion curves are not very sensitive to the pitch of the helix. Nearly the same curves are obtained for the 15/7 and 13/6 helices for a given set of force constants.[8] The location of the zone-center funda-

Table II
Some Constant-Frequency Features in the 1400–700-cm^{-1} Region of the Infrared Spectra of Perfluoro-*n*-alkanes (n = 8, 14, 16, 20) and Their Correlation with the Zone-Center Fundamentals of the 15/7 Helix of Poly(perfluoroethylene)

		corresponding PTFE modes	
freq, cm^{-1}	int[a]	sym species[b]	descrip[c]
1375[d]	w	A_1 (ν_1)	antisym CF_2 stretch, CF_2 rock
1260–1200[e]	vs	E_1 (ν_2)	antisym CF_2 stretch, CF_2 rock
		A_2 (ν_2)	CC stretch, CCC bend
1150	s	E_1 (ν_3)	sym CF_2 stretch, CF_2 scissors
~730[f]	m	A_1 (ν_3)	sym CF_2 stretch, CF_2 wag

[a] w = weak, m = medium, s = strong, vs = very strong. [b] The symmetry species may be identified on the dispersion curves in Figure 2. [c] The descriptions of the vibrations are taken from ref 7. [d] ~1350 cm^{-1} for n-C_8F_{18}. [e] Not shown in our spectra. [f] Consists of a complex of bands in the case of the amorphous samples.

mentals and their infrared and Raman activity are indicated in Figure 2.

There are features in the infrared spectra that are common to all the perfluoro-*n*-alkanes. Most of the constant-frequency features that are to be found in the spectra of ordered and disordered perfluoro-*n*-alkanes are associated with (zone-center) fundamentals that have been previously assigned to PTFE chains in the crystal. These assignments are summarized in Table II.

The most intense infrared bands appear in the region 1260–1200 cm^{-1}. These bands, which because of their high intensity have not been included in our spectra, are associated with E_1 and A_2 fundamentals of helical PTFE. The less intense band at 1150 cm^{-1} is associated with another E_1 mode. A series of weak bands observed near 1300 cm^{-1} are probably related to a weak band that appears near 1300 cm^{-1} in the infrared spectrum of crystalline PTFE.[9] Since these latter assignments are less certain, they have not been included in Table II.

The two features near 1375 and 730 cm^{-1} observed in the spectra of the fluoro chains are associated with A_1 fundamentals of PTFE. The species A_1 is infrared inactive for the infinite chain. These modes, however, are allowed activity for finite chains.

We have not assigned infrared bands to modes associated with the CF_3 end groups since it is not obvious that there exist isolated bands in the infrared spectrum that are characteristic of these groups. The absence of such bands is presumably due to extensive coupling between CF_3 and CF_2 groups. In the case of the Raman spectrum, however, the assignment of specific bands to CF_3 modes for the perfluoro-*n*-alkanes has been discussed in refs 7 and 10.

From the standpoint of the analysis of conformational structure, by far the most informative region of the infrared spectrum is that lying between 1150 and 700 cm^{-1}. This frequency region contains vibrations that are associated with the ν_3 branch of the dispersion curve of conformationally ordered PTFE chains (Figure 2). This dispersion curve gives rise to a regular series of bands in the infrared and Raman spectra of conformationally ordered perfluoro-*n*-alkanes. The assignments and observed frequencies of these bands have been used to determine the ν_3 dispersion curve, which is shown in Figure 3. Rabolt and Fanconi[7] have used the Raman-active ν_3 modes to establish the shape of this dispersion curve. We have extended this analysis to include data derived from the infrared measurements. This will be discussed further in section V.A.1.

IV. Results

A. *n*-C_8F_{18}. The infrared spectrum of a film of n-C_8F_{18} deposited from the vapor at 7.5 K is shown in Figure 4. Also shown is a series of spectra of the film annealed and measured at higher temperatures. The highest attainable annealing temperature was 180 K, since, at a temperature slightly higher, the film evaporated from the window.

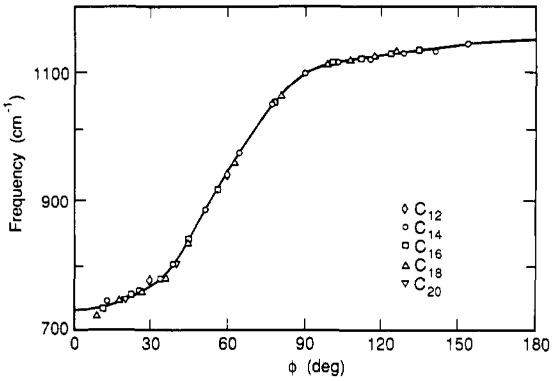

Figure 3. ν_3 dispersion curve of the ordered poly(tetrafluoroethylene) chain as represented by a plot of the frequencies of the infrared and Raman ν_3 bands of a series of crystalline perfluoro-*n*-alkanes (n = 12, 14, 16, 18, and 20) versus phase angles give by eq 1. The frequencies and assignments of these bands are listed in Table III.

The complexity of the spectrum of the amorphous film of n-C_8F_{18} in the 1100–700-cm^{-1} region indicates the presence of more than one conformer. This is readily established from the number of bands observed in the region 1110–800 cm^{-1}. The number of bands expected in this region for a single conformer is 3 (see section V.A.2), whereas the number found is clearly much larger.

Infrared and Raman spectra of solid n-C_8F_{18} have been reported by Compos-Vallette and Rey-Lafon (CR).[10] Their infrared spectra were measured with the sample in its lowest temperature phase (100 K) and in its intermediate solid phases (195 and 208 K) (see Table I). From their spectra, CR concluded that the low-temperature phase of n-C_8F_{18} consists of a single conformer and that the solid phases at higher temperatures consist of more than one conformer. They found the solid–solid transitions to be reversible.

In terms of general complexity, our infrared spectrum of the amorphous solid is most like that of the highest temperature solid reported by CR. Both our spectra and theirs indicate the presence of more than one conformer. A close comparison of the two spectra, however, reveals many differences.

The distribution of conformers in our amorphous film appears to change somewhat upon warming from 7.5 to 180 K. The spectral changes indicating this are small but significant. The changes in band shape are more pronounced than those normally associated with temperature change per se, that is, with the band-shape changes that are commonly observed in conjunction with temperature-induced changes in density and molecular mobility. There are also pronounced changes in the relative intensities of certain bands, especially in the 1100–700-cm^{-1} region (Figure 4B). The earlier results of CR[10] suggest that these changes are likely reversible.

B. *n*-$C_{14}F_{30}$. The infrared spectrum of an as-deposited film of C_{14} at 7.5 K is shown in Figure 5 along with representative spectra of the annealed film measured at the temperatures indicated. The highest annealing temperature attained before sublimation from the window was 150 K. The film that was annealed at the highest temperature, 150 K, was recooled to 8 K, and its spectrum was remeasured at that temperature. The 8 K spectrum was found to be essentially identical with the 150 K

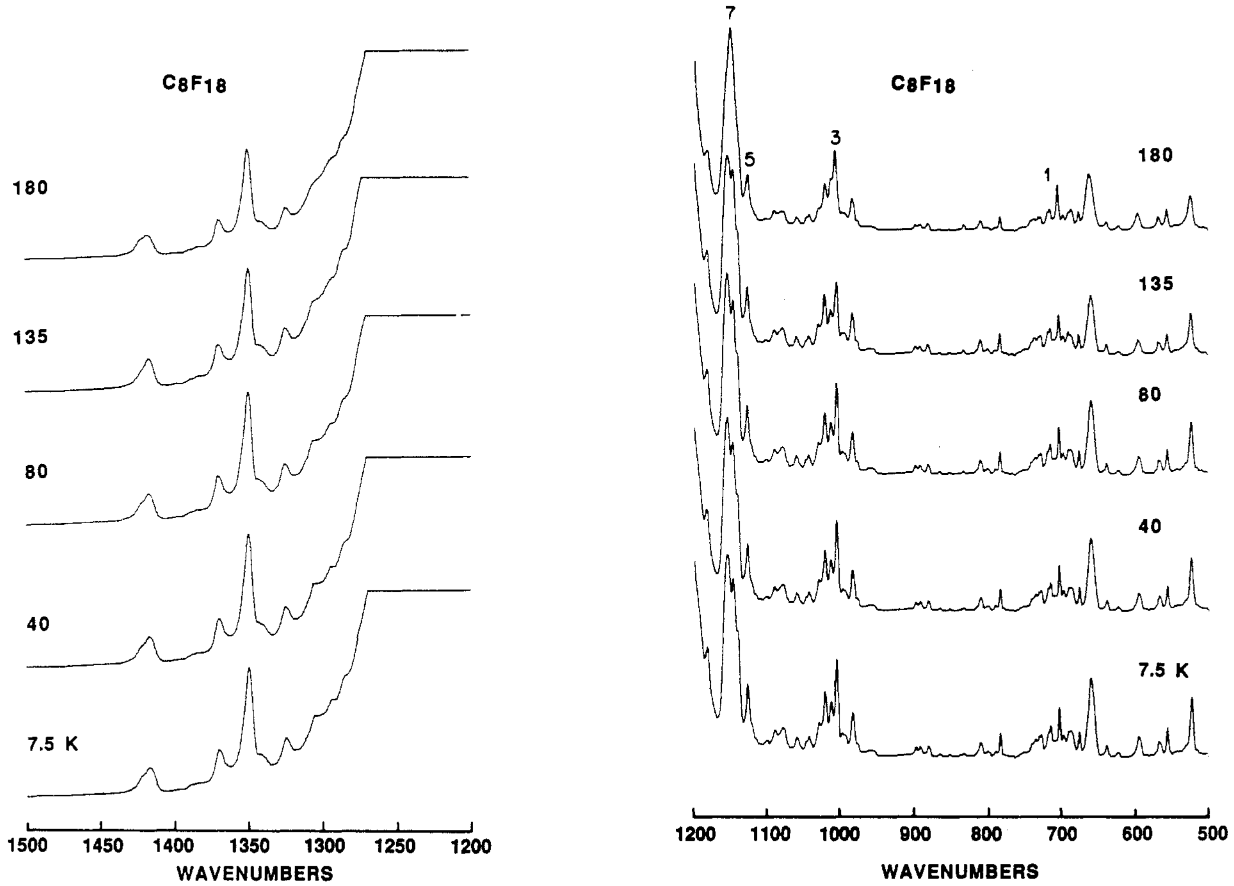

Figure 4. Infrared spectra of a film of n-C_8F_{18}: as-deposited at 7.5 K and annealed and measured at the temperatures indicated. The k-value numbers shown above the 180 K spectrum are in the vicinity of the frequencies of the infrared-active (k_{odd}) ν_3 modes of the trans conformer, as derived from the dispersion curve in Figure 3.

spectrum except that the bands in the 8 K spectrum are narrower.

The spectrum of the 150 K annealed film is very simple, indicating that most of the chains are ordered. Nearly all the bands in the 1150–700-cm^{-1} region of this spectrum can be assigned to modes associated with the ν_3 dispersion curve.

The spectrum of the as-deposited film (8 K) is much more complex than that of the film annealed at 150 K due to the many conformers that comprise the amorphous solid. A few of the bands observed in the spectrum of the 150 K annealed film also appear in the spectrum of the as-deposited film, albeit with much attenuated intensities. These bands are associated with conformationally ordered chains, and from their intensities it is possible to estimate the energy difference, E_g, between a gauche and a trans C–C bond. This will be discussed in section V.D.

Annealing from 8 to 150 K produces continuous, irreversible spectral changes (Figure 5), which consist mainly of the growth of bands associated with ordered chains and a concomitant diminution of the other bands. This behavior is similar to that observed in our earlier infrared study of the n-alkanes.

A few bands seemed to behave in an anomalous manner. These bands, several of which are marked with asterisks in Figure 5, at first increased in intensity in going to higher annealing temperatures and then decreased. A maximum intensity was reached near 52 K. While the intensity changes are not dramatic in magnitude, this phenomenon is noteworthy in that it appears to indicate the formation of an intermediate conformational state during the ordering process.

A crystallization of the n-$C_{14}F_{30}$ film is observed between 135 and 150 K. This is evident from the changes in the 1200–600-cm^{-1} region of the infrared spectra that occur between these temperatures. The spectrum of the sample at 150 K is different from the spectra measured at lower temperatures in that it has fewer bands. It is especially significant that the spectrum has a markedly sloping background, which increases in intensity in going to higher frequencies and that the bands in this spectrum have shapes that display significant asymmetry. Spectral features of this latter kind are known to be characteristic of polycrystalline samples in which the crystallites have dimensions comparable with the wavelength of the incident radiation. Another distinguishing characteristic of the 150 K spectrum is that the frequencies of the bands in the 1150–700-cm^{-1} region are consistently higher by a few wavenumbers than those of the corresponding bands in the spectra of the film at lower temperatures. At temperatures below 150 K, band frequencies were found to be essentially temperature independent.

C. n-$C_{16}F_{34}$. Spectra of as-deposited and annealed films of C_{16} are displayed in Figure 6. The highest annealing temperature attained was 210 K. The spectrum at this temperature is virtually indistinguishable from the 180 K spectrum. The appearance and the temperature behavior of the spectra are similar to those of the C_{14} case.

The spectra of the sample annealed at 180 and 210 K indicate that nearly all of the chains are ordered. All the intense bands in the 1150–700-cm^{-1} region are members of the ν_3 band progression. The remaining unassigned bands are weak and appear to represent a small fraction of disordered chains.

Conformational complexity in the as-deposited film is again indicated by the many bands in the 1150–700-cm^{-1} region. As in the C_{14} case, there are several weak bands associated with the conformationally ordered chains (see

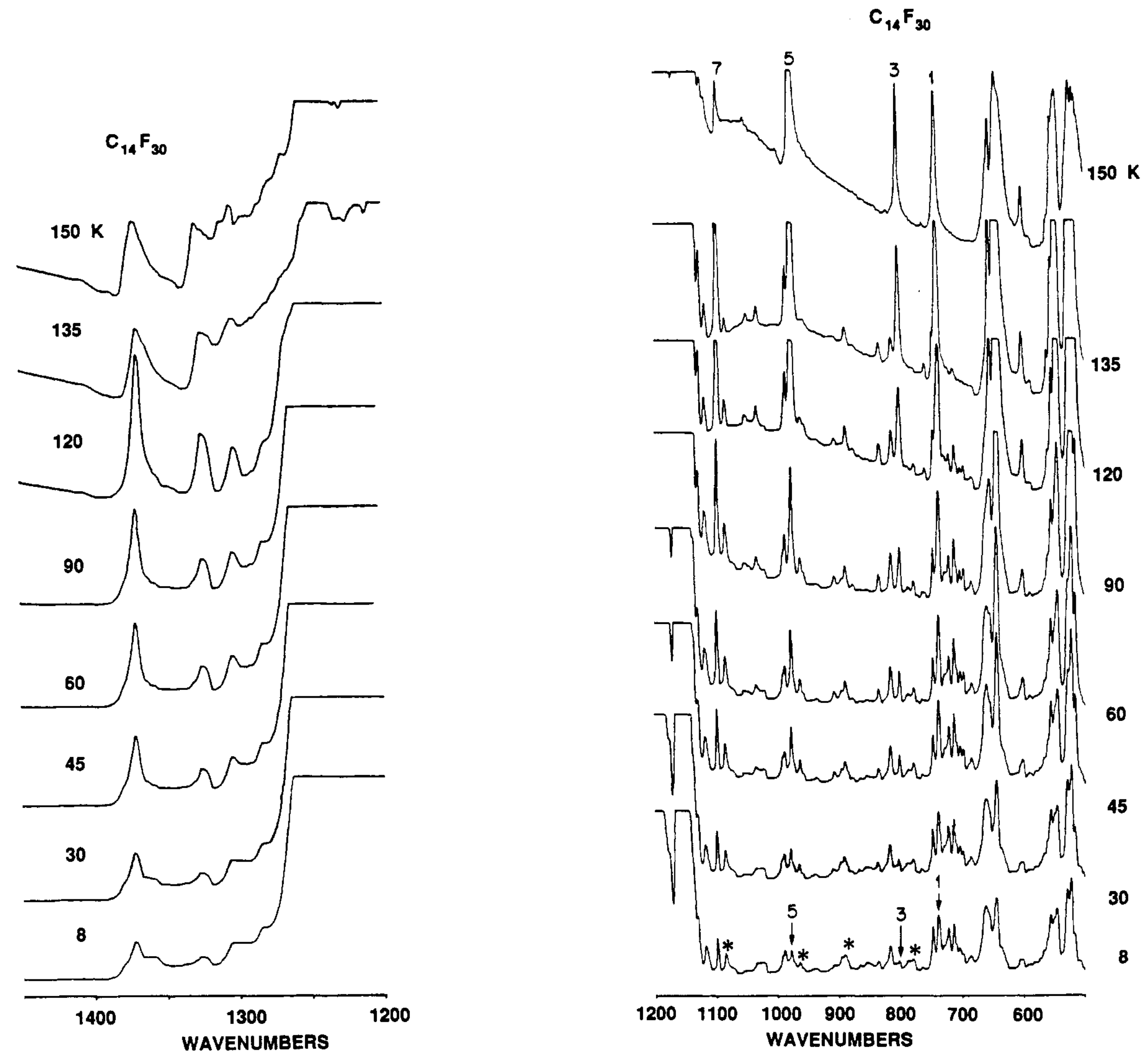

Figure 5. Infrared spectra of a film of n-$C_{14}F_{30}$: as-deposited at 7.5 K and annealed and measured at the temperatures indicated. Assignments (values of k) of the ν_3 bands that are associated with the all-trans conformer are marked on the 150 and 8 K spectra. Asterisks mark the bands in the 8 K spectrum that appear to first increase and then decrease in intensity upon annealing.

section V.D).

Again, as in the case of C_{14}, annealing at successively higher temperatures produces simpler spectra as a result of increased conformational ordering, and again there are a few bands, marked in Figure 6, that initially increase in intensity and then decrease as the annealing temperature is increased. The intensity of these latter bands reaches a maximum near 60 K.

The C_{16} (or C_{20}) chains in the most annealed films are less conformationally ordered than those for C_{14} at 150 K. In contrast to the C_{14} spectrum, it is not clear from the spectrum of C_{16} (or of C_{20}, which is considered next) at the highest annealing temperature that the film is polycrystalline. It may be that the crystallite sizes are too small to show the large background and band-shape effects observed for the C_{14} film upon crystallization.

D. n-$C_{20}F_{42}$. The infrared spectra of as-deposited and annealed films of C_{20} are shown in Figure 7. The highest annealing temperature was 250 K. These spectra and their interpretation follow the patterns described for C_{14} and C_{16}.

The film annealed at the highest temperature (250 K) consists predominantly of ordered chains, as indicated by the progression of intense bands in the 1150–700-cm^{-1} region. The as-deposited film consists of conformationally disordered chains that become ordered upon annealing the sample. Those few bands that first increase and then decrease in intensity as the annealing progresses reach maximum intensity around 65 K.

V. Discussion

A. The ν_3 Progression. 1. Ordered Chains. Rabolt and Fanconi (RF) have used the frequencies of the ν_3 bands observed in the Raman spectra of the n = 9, 10, 12, 14, 16, 18, and 20 perfluoro-n-alkanes in the crystalline state at 300 K to construct the ν_3 dispersion curve.[7] Following an approach used earlier to assign progression bands in the spectra of the crystalline n-alkanes,[11] these authors obtained the ν_3 dispersion curve by plotting the observed Raman frequencies, ν_k, against the phase angles, ϕ_k. The frequencies, ν_k, were assigned specific mode numbers, k (= 0, 2, 4, ...). The corresponding phase angles, ϕ_k, were obtained from k with the use of the empirically derived relation

$$\phi_k = \frac{k\pi}{N+2} \qquad k = 0, 1, 2, ..., N-1 \qquad (1)$$

where N is the number of CF_2 groups. The ν_3 dispersion curve obtained in this way was found to be in good agreement with that obtained from normal-coordinate calculations.[6,7]

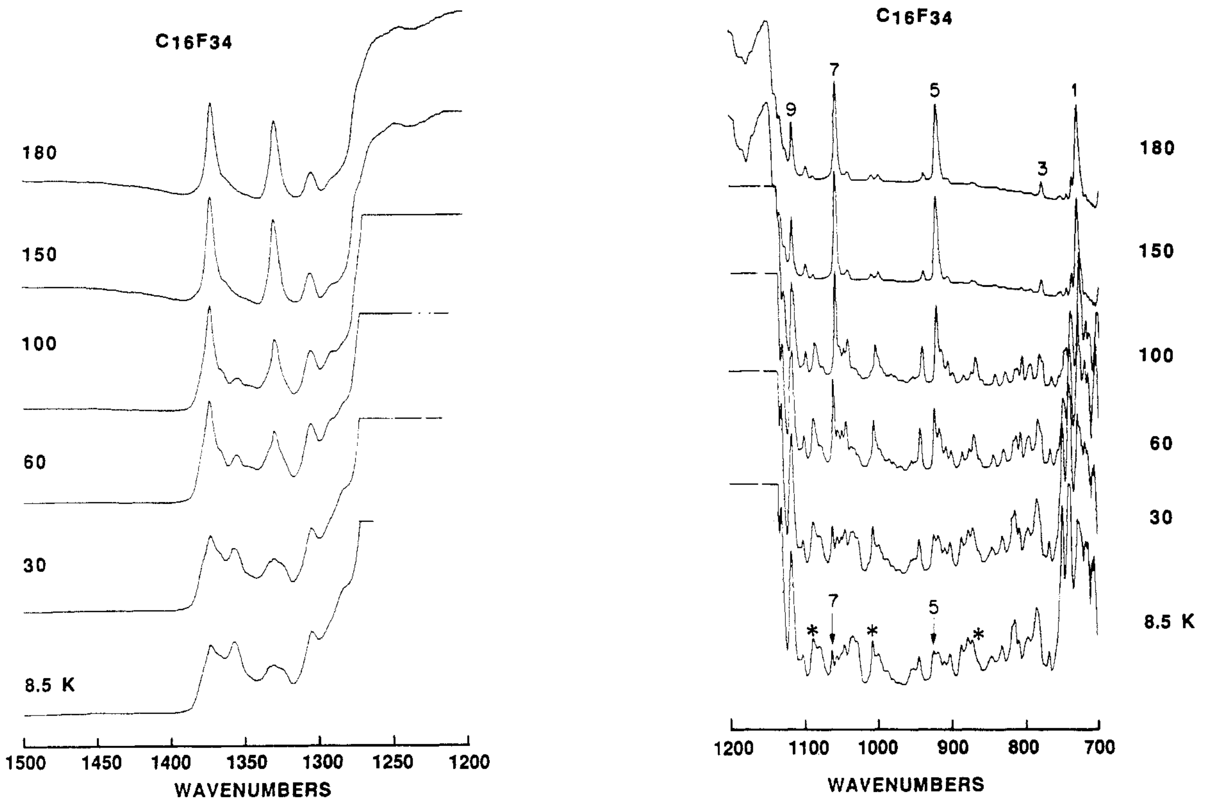

Figure 6. Infrared spectra of a film of n-$C_{16}F_{34}$: as-deposited at 7.5 K and annealed and measured at the temperatures indicated. Assignments (values of k) of the ν_3 bands associated with the all-trans conformer are marked on the 180 and 8.5 K spectra. Asterisks mark the bands in the 8.5 K spectrum that appear to first increase and then decrease in intensity upon annealing.

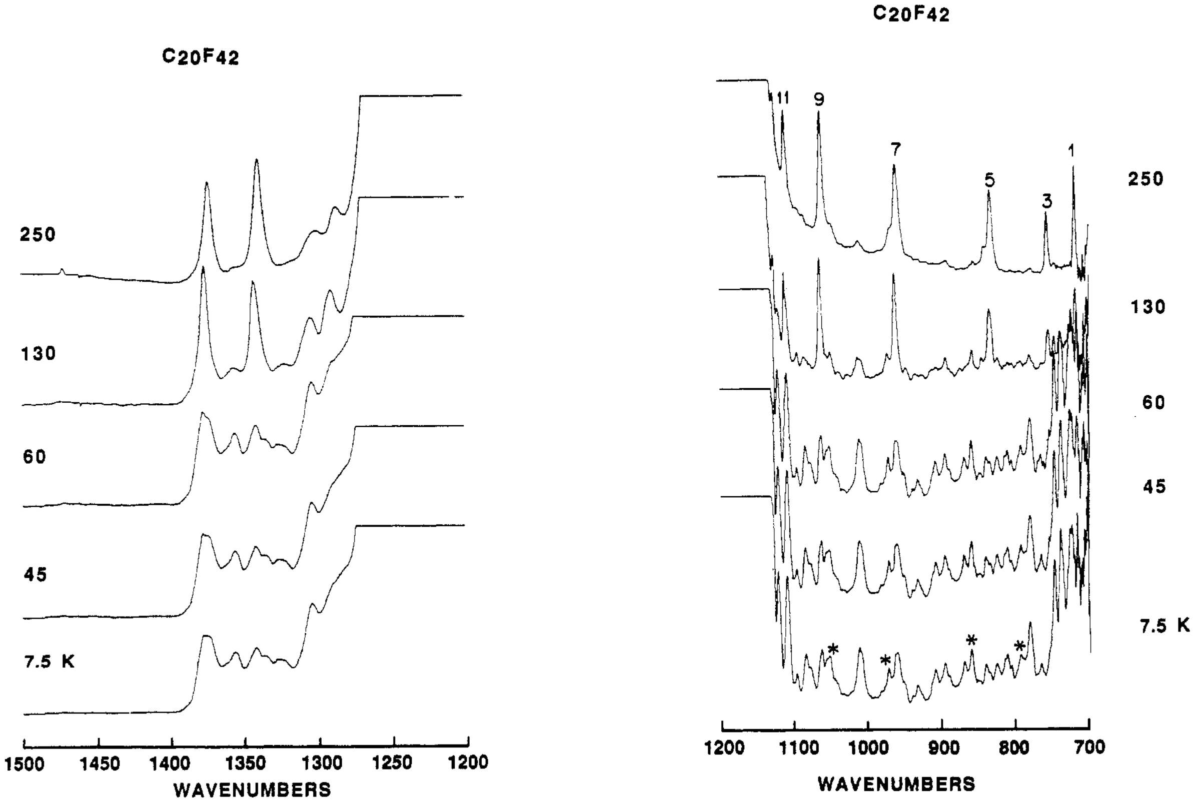

Figure 7. Infrared spectra of a film of n-$C_{20}F_{42}$: as-deposited at 7.5 K and annealed and measured at the temperatures indicated. Assignments (values of k) of the ν_3 bands associated with the all-trans conformer are marked on the 250 K spectrum. Asterisks mark the bands in the 7.5 K spectrum that appear to increase first and then decrease in intensity upon annealing.

However, the expression appropriate for an isolated system of N coupled oscillators is

$$\phi_k = \frac{k\pi}{N+1} \qquad k = 1, 2, 3, ..., N \tag{2}$$

The form of the empirically derived expression, eq 1, suggests the presence of some complicating factor. Most likely, this factor is vibrational coupling between the CF_2 groups and the CF_3 end groups, in which case the CF_3 groups would in effect augment the number of CF_2 groups.

Table III
Observed Frequencies and k Assignments of the ν_3 Progression Bands for Perfluoro-*n*-alkanes, n-C_nF_{2n+2}

	frequencies,[a] cm^{-1}						
k	$n = 9$	$n = 10$	$n = 12$	$n = 14$	$n = 16$	$n = 18$	$n = 20$
0	739	735	734	731	730	731	730
1	750	745		743	732		719
2	829	780	776	760	754	745	744
3				802	778		757
4	1076	1034	941	887	839	802	778
5				976	918		834
6				1051			
7				1096	1054		960
8				1114			
9				1121	1114		1062
10				1128	1121		
11				1133	1128		1111
12				1143	1135		1118
13							1124
14							1133

[a] The k_{even} frequencies below 1000 cm^{-1} are from Raman measurements on samples near 300 K reported in ref 7. All other frequencies are from our infrared measurements and are for samples near 300 K.

An analogous situation exists for the methylene rocking band progression for the crystalline *n*-alkanes. The methyl groups couple with the methylenes in a way that appears to increase the number of methylenes involved.[12]

We have constructed a ν_3 curve that is very similar to the curve of RF by combining our frequency data for the infrared ν_3 bands with those from the Raman used earlier by RF. The result is shown in Figure 3. The data displayed in this figure are given in Table III. Our band assignments (values of k) and our value for N (the number of oscillators) are the same as those used by RF. To check for uniqueness, we derived these values in a systematic way. The existence of a dispersion curve implies that $\nu_{k,N} = f(\phi_{k,N})$, where n is the number of oscillators. From this it follows that, if two ν_3 bands from different chains have the same frequency, then

$$\phi_{N,k} = \phi_{N',k'} \tag{3}$$

where the primes indicate the second chain. Since we know the value of $\Delta N = N' - N$ and of $\Delta k = k' - k$, the integer solution of the expression

$$\frac{k}{N+1} = \frac{k + \Delta k}{N + \Delta N + 1} \tag{4}$$

which follows from eq 3, provides a way of determining k and N. From Table III we find that C_{16} and C_{20} both have ν_3 bands at 839 cm^{-1}, so that the chain length difference gives $\Delta N = 4$ and band counting gives $\Delta k = 1$. The integer solution of eq 4 gives $k = 4$ and $N = 15$ for the 839-cm^{-1} band of C_{16} and $k = 5$ and $N = 19$ for C_{19}. This is the RF result derived from eq 1.

2. Disordered Chains. As we have stated earlier, the complex spectra of the conformationally disordered films in the ν_3 region (1150–700 cm^{-1}) are not understood in detail. It is of interest, however, to note that the bands in this region tend to form a pattern that is in a general way similar to the well-defined pattern of progression ν_3 bands observed for ordered chains. This pattern can be discerned by comparing the spectra in the annealing sequence, beginning with the spectrum of the most highly ordered sample (Figures 5–7). In general, in going from ordered to disordered chains, the intense k_{odd} bands tend to persist, while the k_{even} bands, which are generally weak or absent in the spectrum of the ordered chains, gain in intensity. Both the odd and even bands may acquire companions to form clusters. These clusters tend to remain located in the vicinity of the bands associated with the ordered chain. Thus, the observed spectrum of the disordered film appears to consist of a progression of clusters of approximately the same integrated intensity, each cluster being centered near the frequency of a ν_3 mode of the ordered chain. Unlike the situation for ordered chains, however, there is essentially no intensity distinction between even and odd k. The tendency for the bands in the infrared spectrum of an assembly of conformationally disordered perfluoro-*n*-alkane chains to form a regular pattern and the marked correlation of this pattern with that for an ordered chain is depicted in Figure 8 for C_{14}, C_{16}, and C_{20}. While the correlation is by no means perfect (the patterns appear out of register with each other at ca. 820 and 1050 cm^{-1}), the trend is clearly evident.

We have recently considered the possibility that band progressions can exist in the infrared spectrum of an assembly of conformationally disordered chains.[13] This was shown to be the case for an ensemble of model chains whose skeletal bonds could have either a trans or cis conformation. The sole effect on the spectrum in going from ordered chains (all-trans) to disordered chains (random placements of trans and cis bonds) is a redistribution of intensity so that intensity is more evenly divided among the various modes. If gauche bonds rather than cis bonds are involved, the same type of intensity redistribution will occur. In this case, however, the single bands will be replaced by band clusters in the disordered system.[14]

The situation for the ν_3 modes of the perfluoro-*n*-alkanes is in some ways quite similar to that for the modes of the model chains. The ν_3 dispersion curve associated with the ordered perfluoro-*n*-alkane chains is isolated in being removed in frequency from the other dispersion curves, and so it resembles the dispersion curve of the model chain. The perfluoro chain has trans and gauche bonds. As we have noted, the main effect on the spectrum of introducing disorder into the perfluoro chain is to make both k_{odd} and k_{even} bands equally intense and to develop band clusters that tend to occur near the frequencies for the ordered chain, in accordance with the predictions of the model.

A practical consequence of the tendency of the frequency of a ν_3 band to be insensitive to conformation is that we can assume to a first approximation that the number and frequency of ν_3 bands will be the same for each conformer, justifying our earlier contention that for C_8 the number of infrared bands expected per conformer in the region 1110–800 cm^{-1} was 3. The number 3 is simply the number of modes that occurs in this frequency region for the one

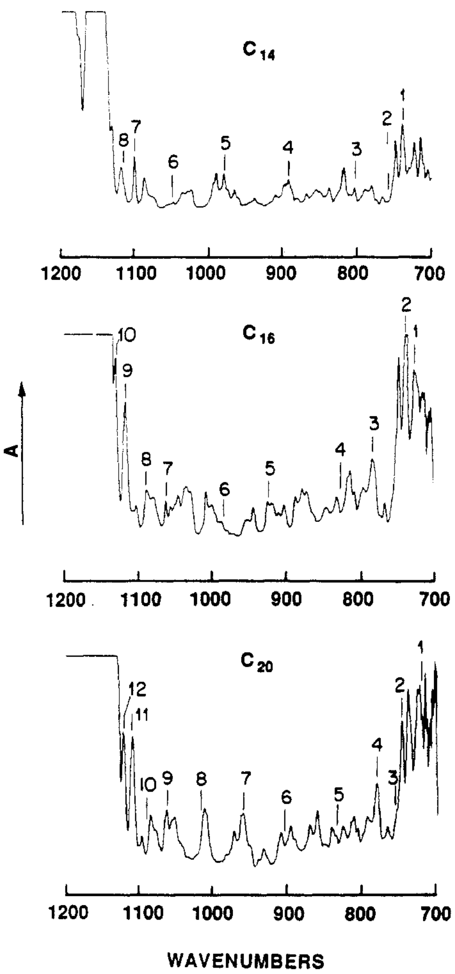

Figure 8. Infrared spectra of as-deposited, amorphous n-$C_{14}F_{30}$, n-$C_{16}F_{34}$, and n-$C_{20}F_{42}$ at 8 K in the ν_3-band region. The frequencies of the ν_3 bands observed for the *ordered* chains are indicated.

conformer, the all-trans conformer, that can be determined. The determination for this conformer is easily made from the ν_3 dispersion curve (Figure 3) assuming $\phi_k = k\pi/8$.

B. Structure and Spectra of the Annealed (Ordered) Perfluoro-*n*-alkane Films. The infrared spectra of films of C_{14}, C_{16}, and C_{20} that have been annealed at the highest temperature possible in our experiments indicate that these chains are in large part conformationally ordered and have a conformational structure that is near that of PTFE. This follows because all the intense infrared and Raman bands in the frequency region 1150–700 cm^{-1} can be assigned to bands associated with the ν_3 dispersion curve for PTFE. The preciseness with which the bands observed for the chains $n = 12$–20 fall on this curve (Figure 3) affirms the fact that these perfluoro-n-alkanes are conformationally isostructural. Although the details of the structure are not known, the X-ray studies of Bunn and Howells[5] on C_{16}, Strobl et al.[15] on C_{20}, and Starkweather[16] on C_{12}, C_{16}, C_{20}, and C_{24} all indicate a helical structure similar to that found for PTFE. Both Strobl et al.[15] and Starkweather[16] note that the X-ray scattering traces of the perfluoro chains are similar to the trace of PTFE in its disordered phase ($T > 30$ °C). A recent review by Wunderlich et al.[16a] provides a more complete summary of what is currently known about the structure and dynamics of the solid perfluoro-n-alkanes and the relation between these chains and PTFE.

The infrared spectra of C_{16} and C_{20} films annealed at the highest temperature and of C_{14} annealed at 135 K reveal a significant degree of conformational disorder, which is manifest in the presence of a number of weak bands that cannot be assigned to ν_3 modes. Since the normal-coordinate analyses on the ordered chains[6,7] show that only ν_3 modes are present in the 1150–700-cm^{-1} region, the anomalous bands are likely to be associated with conformational disorder. While these bands are absent from the spectrum of C_{14} annealed at 150 K, they are present in the spectra of perfluoro-n-alkanes in KBr pressed disks.

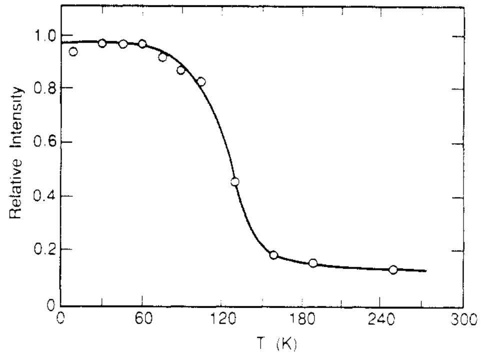

Figure 9. Fraction of conformationally disordered chains (expressed as relative intensity) plotted against annealing temperature for a deposited film of n-$C_{20}F_{42}$. The value for the disordered fraction was estimated from the intensities of the bands at 1357, 1085, 794, 781, and 740 cm^{-1}, which are associated with conformationally disordered chains. The intensity of each band was normalized by its maximum value. The value for the disordered fraction is the average of the normalized intensities for all bands.

The concentration of disorder is essentially independent of temperature in that recooling the annealed films does not appear to affect the intensity of the disordered bands. Invariance of disorder to temperature was also recently reported for the orthorhombic n-alkanes.[17] In the latter case, a low but constant concentration of gauche bonds was observed from 8 K to either the onset of premelting or the onset of the hexagonal-phase transition. For the perfluoro-n-alkanes, unlike the n-alkanes, the disorder appears to be chain length dependent. It is greater for C_{14} than for C_{20}. We can speculate that the chain length dependence may be related to difficulties in matching interlamellar chain-end contacts for chains whose lengths deviate from the translational repeat unit. Thus, matching might be easier for C_{14} than for C_{20}, since the length of the C_{14} chain is about one translational repeat unit of the 13/6 helix.

C. Conformational Ordering upon Annealing. The conformational transformation that occurs upon warming the amorphous film was measured quantitatively for C_{20}. In Figure 9, the overall concentration of disordered chains of C_{20}, as measured by the peak heights of a number of bands that we known to be associated with disordered conformers, is plotted as a function of the annealing temperature. We note that there are bands in the 1400–1350-cm^{-1} region for C_{14}, C_{16}, and C_{20} that change in intensity between 8 and 30 K. The relation between these bands and conformational order is not known.

The temperature, T_{beg}, at which conformational ordering appears to begin, is found to be around 65 K. The temperature, $T_{1/2}$, at which the process is half completed, is around 130 K.

It is of interest to compare the values of T_{beg} and $T_{1/2}$ found for $C_{20}F_{42}$ with the values found earlier for an n-alkane of comparable length.[4] For $C_{21}H_{44}$, T_{beg} is ca. 60 K and $T_{1/2}$ ca. 107 K. For a more precise comparison with $C_{20}F_{42}$, we need these values for $C_{20}H_{42}$ rather than for $C_{21}H_{44}$. The required values can be estimated by using the chain-length dependence of T_{beg} and $T_{1/2}$, which was

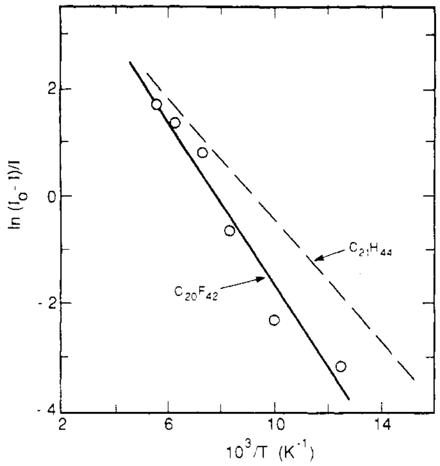

Figure 10. Plot of ln $(I_0 - I)/I$ versus T^{-1} for n-$C_{20}F_{42}$. The quantity $(I_0 - I)/I$ is taken as a measure of the ratio of the concentration of ordered to disordered chains. The quantity I is the relative concentration of the amorphous component as given in Figure 9. The temperature T is the annealing temperature. The dashed line represents a similar plot for n-$C_{21}H_{44}$ reported in ref 4.

determined in our earlier study.[4] This leads to values of 58 and 103 K, respectively, for $C_{20}H_{42}$, to be compared with 65 and 130 K for $C_{20}F_{42}$. Thus, for both T_{beg} and $T_{1/2}$ the perfluoro-n-alkane value is larger.

An additional and perhaps more physically significant basis for comparison is the activation energy, E^*, associated with conformational ordering. A measure of this quantity can be derived from the slope of a plot of ln (x_{ord}/x_{dis}) against $1/T_{an}$, where x_{ord} and x_{dis} refer to the mole fraction of conformationally ordered and disordered chains and T_{an} is the annealing temperature. Values of x_{ord} and x_{dis} may be estimated from the data in Figure 9. Figure 10 is plotted with $I = x_{dis}$ and $T = T_{an}$.

The value of E^* for $C_{20}F_{42}$ derived from Figure 10 is 1.4 ± 0.1_5 kcal/mol, which may be compared with a value of 1.1 ± 0.1 kcal/mol found earlier for $C_{21}H_{44}$.[4] Thus E^* is somewhat larger for $C_{20}F_{42}$ than for $C_{20}H_{42}$. Since the gauche–trans free energy difference for a C–C bond in a perfluoro-n-alkane is at least twice that for an n-alkane, it is clear that the determining factor for conformational ordering is not the gauche–trans energy difference. If we associate E^* with the intramolecular barrier in going from a gauche bond to a trans bond, the higher value of E^* found for $C_{20}F_{42}$ is understandable in that calculations indicate that this barrier is above 10 kcal/mol[18] for the perfluoro chains but is around 4 kcal/mol[19] for the n-alkanes.

For the perfluoro-n-alkanes, there is systematic chain-length dependence of T_{beg} and $T_{1/2}$ that parallels that found for the n-alkanes. In general, we find that the conformational organization process occurs at lower temperatures for shorter chains. Increasing the temperature of the as-deposited films of $C_{14}F_{30}$ and $C_{16}F_{34}$ from 8 to 30 K results in some significant conformational ordering, so that, although data for these chains are unavailable at temperatures intermediate between 8 and 30 K, we know that $T_{beg} < 30$ K. The values of T_{beg} for C_{14} and C_{16} are thus lower than that for C_{20}. A similar situation exists for $T_{1/2}$ in that for C_{14} and C_{16} the values of $T_{1/2}$ for these chains are lower than that for C_{20}. It thus appears that T_{beg} and $T_{1/2}$ for the perfluoro-n-alkanes are dependent on chain length in essentially the same way as in the n-alkane case.[4] The shortest perfluoro chain, C_8, is an exception. The as-deposited film of C_8 undergoes much less conformational change between 8 and 180 K than the corresponding films of the longer chains.

The intensities of different infrared bands of the disordered perfluoro-n-alkanes C_{14}, C_{16}, and C_{20} may behave differently upon annealing. This phenomenon was not observed for n-alkanes.[4] A striking example has already been mentioned: the intensities of some bands associated with disordered chains *increase* in the initial stages of annealing. The intensity reaches a maximum at quite a low temperature that appears to be dependent on chain length. For C_{14}, C_{16}, and C_{20}, this temperature is estimated to be 52 ± 8, 60 ± 5, and 65 ± 5 K, respectively. These values are just above T_{beg}.

Although the intensities of most bands decrease or increase monotonically with increasing temperature, some bands vanish while the sample is still at relatively low temperatures, while others persist over a wide temperature range.

The crystallization process for the perfluoro chains probably proceeds in the same manner as for the n-alkanes. In our study on amorphous C_{21}, we interpreted our spectral data to support a process in which microdomains of conformationally ordered chains were formed in a matrix of the disordered phase. The distribution of conformers in the disordered fraction appeared to remain unchanged.[4] This could not be ascertained with certainty, however, since the bands upon which the measurements were based are associated with specific kinds of *short* conformational sequences rather than with individual conformers as in the perfluoro chain case. During the annealing process, the intensities of the n-alkane bands associated with conformational disorder maintained their relative intensities while their overall intensity diminished. Thus, we concluded that the relative concentrations of the various kinds of short conformational sequences did not change significantly. We would allow, however, that the distribution of conformers in the amorphous n-alkane samples could change in some small degree, as appears to be the case for the perfluoro-n-alkanes, without having a detectable effect on the average local conformational statistics.

D. Conformational Disorder and the Value of the Gauche–Trans Energy Difference. Relatively few spectroscopic studies concerning the extent of conformational isomerism in perfluoro-n-alkanes have been reported, and these have not always been in accord. Early infrared studies by Szasz[20] on the C_5, C_6, and C_7 chains indicated the existence of various conformers in the liquid state. More recently, Rabolt and Fanconi,[21] in a low-frequency Raman study, emphasized that in the liquid state chains shorter than C_{12} exist mainly as rigid rods, that is, as extended helices. However, most recently, the infrared and Raman studies by Campos-Vallette and Rey-Lafon (CR)[10] show evidence for extensive conformational disorder in both the liquid and amorphous states.

The quantity that in large part determines the average extent of conformational disorder in the perfluoro-n-alkane chains is, of course, the gauche–trans energy difference E_g. An estimate of E_g can be derived from the concentration of the ordered conformer in the as-deposited film, since the concentration of this conformer depends on E_g and can be calculated as a function of E_g with the use of the rotational isomeric state model. The concentration of the ordered conformer can be determined experimentally from the ratio of the intensity of a band associated with this conformer in the as-deposited film to that for an annealed film, since the latter consists almost entirely of all-trans chains. A key assumption is that the distribution of conformers in the as-deposited film is the same as that in the vapor before condensation. Our earlier

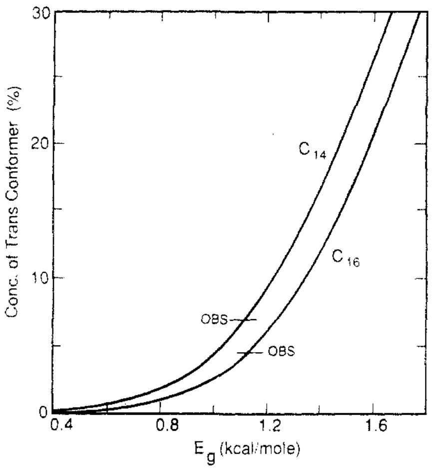

Figure 11. Concentration of the trans conformer of n-$C_{14}F_{30}$ and n-$C_{16}F_{34}$ calculated from the rotational isomeric state model plotted against the assumed value of the gauche-trans energy difference. The observed values of the concentration of the trans conformer are indicated. (See text.)

studies on similarly deposited n-alkane films indicate this is indeed the case for chains longer than about C_{10}.[4]

We have determined E_g values from the $k = 3$ and $k = 5$ bands of C_{14} at 805 and 980 cm^{-1} measured at 8 K and at 135 K and the $k = 7$ band of C_{16} at 1057 cm^{-1} measured at 8 K and at 180 K. These bands are indicated on Figures 5 and 6.

From the integrated areas of these bands, we find that the concentration of ordered chains in the as-deposited films (8 K) is for C_{14} 7.0 and 7.2% based on the 805- and 980-cm^{-1} bands, respectively, and for C_{16} 4.5% based on the 1057-cm^{-1} band. These experimentally determined concentrations can be related to the value of E_g though Figure 11, which shows the calculated value of the concentration of ordered chains plotted as a function of E_g. (The calculation is based on an isomeric state model[1] in which pentane-type interactions, gg′ pairs, are excluded.)

This procedure yields values for E_g of 1.12 and 1.13 kcal/mol for C_{14} and C_{16}, respectively. Estimating an experimental error of 30% in the measured value of the ordered-chain concentrations, we assign a value of 1.1 ± 0.1 kcal/mol for E_g. This value is near that 1.05 kcal/mol that we determined earlier from the frequencies of the D-LAM bands in the Raman spectra of liquid perfluoro-n-alkanes[22] and is slightly lower than the 1.4 ± 0.4 kcal/mol that Bates and Stockmayer reported from dipole measurements.[3]

VI. Summary

We have prepared totally amorphous films of n-C_8F_{18}, n-$C_{14}F_{30}$, n-$C_{16}F_{34}$, and n-$C_{20}F_{42}$ by vacuum deposition of the vapor onto a CsI window maintained at 8 K and, by means of infrared spectroscopy, have studied the conformational structure of the perfluoro-n-alkane chains in the amorphous state and the evolution of the conformational changes that are induced by annealing. The spectral region 1150–700 cm^{-1} was found to be a particularly useful diagnostic for the determination of conformation. This region had been previously analyzed for ordered perfluoro-n-alkane chains.[7]

The spectra of the amorphous, as-deposited films are very complex as a result of extensive conformational disorder involving gauche bonds. Annealing the films at successively higher temperatures resulted in simpler and simpler spectra due to the diminution of the conformational disorder. The annealing behavior of C_{14}, C_{16}, and C_{20} is similar in that disorder diminishes continuously over a wide range of increasing temperature. At the highest annealing temperature that was attainable in our experiments, the chains are highly ordered, and the spectra of the films are very similar to those observed for the crystalline perfluoro-n-alkanes at room temperature.

Quantitative annealing measurements were carried out on C_{20}. We found that conformational ordering commenced around 65 K and was half-completed near 130 K. These temperatures are somewhat higher than the values (58 and 103 K) estimated from our earlier study on amorphous films of n-alkanes of essentially the same length.[4]

The onset of conformational ordering begins at lower temperatures for shorter chains. This is also true for the n-alkanes.[4]

An activation energy for conformational ordering was estimated to be 1.4 ± 0.1_5 kcal/mol for C_{20}. This value is greater than the 1.1 ± 0.1 kcal/mol determined earlier for an n-alkane of the same length.[4] Clearly then, the activation energy for chain ordering is not lowered by an increase in the gauche–trans energy difference, since this difference for the perfluoro-n-alkanes is at least twice that for the n-alkanes.

Our spectra enable us to determine the gauche–trans energy difference E_g for the perfluoro-n-alkanes in a new way. The determination is based on the spectrally derived value for the concentration of ordered chains in the as-deposited amorphous film. This leads to a value for E_g of 1.1 ± 0.1 kcal/mol, which is in keeping with the values that have been reported earlier for this chain from dipole moment[3] and Raman[22] measurements.

The annealed films of C_{14}, C_{16}, and C_{20} consist of chains that are conformationally ordered or nearly so. Analysis of the spectra of these samples in the ν_3 region, 1150–700 cm^{-1}, shows that chains are conformationally isostructural.

There remains, however, a small but significant degree of conformational disorder in the films of C_{16} and C_{20} annealed to the highest temperature possible in our experiment. This disorder occurs also for C_{14} annealed at 135 K but not at 150 K, in which case the film appears to be a crystalline solid with highly ordered chains. The conformational disorder is indicated by a number of weak bands in the 1150–700-cm^{-1} region that are not members of the progression of ν_3 bands associated with the conformationally ordered helix. These "extra" bands appear in the spectra of the perfluoro-n-alkanes at room temperature, indicating the ubiquitous nature of the disorder. The concentration of disorder in the crystalline state appears to be nearly temperature independent from 8 K to above room temperature and is greater in C_{20} than in C_{14}.

We have relied mainly on the bands in the 1150–700-cm^{-1} ν_3 region to analyze conformational disorder. Our infrared spectra of the ordered chains have enabled us to increase the frequency range and frequency accuracy of the previously available dispersion curve. However, an even partial realization of the wealth of conformational detail that is potentially available from a vibrational analysis of the rich infrared spectra of the amorphous films must await the development of a vibrational force field that is applicable to perfluoro-n-alkane chains in which both trans and gauche bonds can exist.

There exists in the 1150–700-cm^{-1} region of the infrared spectra of the amorphous films an intriguing pattern of band clusters that can be understood in a general way. The bands or band clusters tend to be located near the frequencies of the modes associated with the ν_3 bands of the ordered chain. The fact that band progressions can occur in the infrared spectrum of an assembly of conformationally disordered chains is indicated from the spectrum calculated for an ensemble of simple model chains that exhibit conformational disorder.[13,14]

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References and Notes

(1) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969.
(2) Scherer, J. R.; Snyder, R. G. *J. Chem. Phys.* **1980**, *72*, 5798–5808 and references therein.
(3) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 12–17.
(4) Hagemann, H.; Strauss, H. L.; Snyder, R. G. *Macromolecules* **1987**, *20*, 2810–2819.
(5) Bunn, C. E.; Howells, E. R. *Nature* **1954**, *174*, 549–551.
(6) Boerio, F. J.; Koenig, J. L. *J. Chem. Phys.* **1970**, *52*, 4826–4829.
(7) Rabolt, J. F.; Fanconi, B. *Macromolecules* **1978**, *11*, 740–745.
(8) Bohan, S. P. Dissertation, University of California, Berkeley, 1988.
(9) Masetti, G.; Cabassi, F.; Morelli, G.; Zerbi, G. *Macromolecules* **1973**, *6*, 700–707.
(10) Compos-Vallette, M.; Rey-Lafon, M. *J. Mol. Struct.* **1983**, *101*, 23–45.
(11) Snyder, R. G. *J. Mol. Spectrosc.* **1960**, *4*, 411–434.
(12) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1963**, *19*, 85–116.
(13) Snyder, R. G. *Macromolecules* **1990**, *23*, 2081–2087.
(14) Snyder, R. G., to be published.
(15) Strobl, G. R.; Schwickert, H.; Trzebiatowski, T. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 274–279.
(16) Starkweather, H. W. *Macromolecules* **1986**, *19*, 1131–1134. (a) Wunderlich, B.; Möller, M.; Grebowicz, J.; Baur, H. *Adv. Polym. Sci.* **1988**, *87*, 50.
(17) Soo, Yesook; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1989**, *93*, 7520–7526.
(18) Banerjea, A.; Taylor, P. L. *J. Appl. Phys.* **1982**, *53*, 6532–6535.
(19) De Santis, P.; Giglio, E.; Liquori, A. M.; Ripamonti, A. *J. Polym. Sci., Part A* **1963**, *1*, 1383–1404.
(20) Szasz, G. J. *J. Chem. Phys.* **1950**, *18*, 1417.
(21) Rabolt, J. F.; Fanconi, B. *Polymer* **1977**, *18*, 1258–1264.
(22) Snyder, R. G. *J. Chem. Phys.* **1982**, *76*, 3921–3927.
(23) Twieg, R. J.; Rabolt, J. F. *Macromolecules* **1988**, *21*, 1806–1811.