A Spectroscopic Analysis of the Structure of a Hexafluoroisobutylene–Vinylidene Fluoride Copolymer

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ABSTRACT: An analysis of the vibrational spectrum of the 1:1 hexafluoroisobutylene and vinylidene fluoride (HFIB/VF_2) copolymer is reported. On the basis of the CH and CD stretching region of the spectra of several model polymers containing either isolated CH_2 (or CD_2) groups or isolated CH_2CH_2 (or CD_2CD_2) groups and upon evaluation of the bending region we conclude that this copolymer has the head-to-tail structure, i.e., $-(C(CF_3)_2CH_2CF_2CH_2)_n-$. Our vibrational analyses suggest that there is more than one monomer per repeat unit.

Fluoropolymers are important in the plastics industry. They display a broad combination of useful properties. In general, they are chemically inert and thermally stable with high electrical resistance, and a very low surface tension. A copolymer of hexafluoroisobutylene and vinylidene fluoride (HFIB/VF_2) has been developed which exhibits these characteristics. In addition it is hard and rigid and can be melt-processed by conventional methods.[1]

Dielectric, dynamic mechanical, and NMR relaxation studies have been reported for this copolymer.[2,3] To understand more fully the cause of the extremely high T_g observed (405 K) for this copolymer, as well as its macroscopic properties, we have used vibrational spectroscopy to analyze the chain configuration and conformation. There are two principal questions of special interest: Is the copolymer completely alternating? Are the monomer units arranged head-to-tail to give a copolymer structure

$$-(C(CF_3)_2CH_2CF_2CH_2)_n-$$

or are they head-to-head to give the structure

$$-(C(CF_3)_2CH_2CH_2CF_2)_n-$$

To help answer these questions, we have compared the characteristic CH stretching mode vibration of HFIB/VF_2 copolymer with the analogous vibrations observed in the infrared and Raman spectra of the ethylene and tetrafluoroethylene copolymer, $-(CH_2CH_2CF_2CF_2)_n-$, of the ethylene–monochlorotrifluoroethylene copolymer, $-(CF_2CH_2CH_2CFCl)_n-$, and of different phases of poly(vinylidene fluoride), $-(CH_2CF_2)_n-$. In addition, we have also examined this spectral region for two samples of polyethylene, one containing isolated CD_2 groups and another containing isolated CD_2CD_2 groups.

Because of their high frequencies (normally in the region 2800–3200 cm^{-1} (CH) and 2000–2100 cm^{-1} (CD)), stretching vibrations are largely decoupled from other vibrations. This enables us to examine the local environment of the CH_2 units in a polymer chain. We have tested this approach on model systems and used it to distinguish between one CH_2 group or two adjacent CH_2 groups such as exist in the head-to-tail and head-to-head HFIB/VF_2 copolymer, respectively. Although the CH_2 bending modes are not decoupled from other vibrations to the extent of CH stretching modes, a similar approach is possible here also. We have also measured the infrared polarization of a uniaxially oriented sample and have used these data to help determine the conformation of the chain. These results will now be reported.

Experimental Section

Samples of hexafluoroisobutylene (HFIB) and vinylidene fluoride (VF_2) copolymers containing different amounts of vinylidene fluoride were available. The copolymer studied was a suspension-polymerized material. This sample has been shown by elemental analysis to contain HFIB/VF_2 in a molar ratio of 1:1. The material we studied did not contain $-(CH_2CF_2)_n-$ blocks. This point will be amplified in the Discussion section. The melting point of this sample is 329 °C. Its DSC curve is shown in Figure 1. The melt flow index is 15 (350 °C/2160 g load). Molecular weight of the sample was not determined since this copolymer does not dissolve in any solvent. HFIB/VF_2 copolymer does swell in ethyl acetate.

Infrared spectra were measured using a Nicolet 7199 Fourier transform spectrometer and a Beckman Model 12 spectrometer. Raman spectra were measured using a Spex Ramalog spectrometer equipped with holographically ruled gratings (1800 grooves/mm). The HFIB/VF_2 copolymer showed little fluorescence when the 6471-Å line of the Krypton laser was used.

A sample cell was built which permitted Raman and infrared spectra to be measured at temperatures between −196 and 450 °C. A zero crossing proportional temperature controller enabled a given temperature to be maintained to within 1 °C.

Infrared spectra of a compression molded film of (50 ton of pressure at 350 °C) HFIB/VF_2 copolymer (7.6×10^{-3} mm thick) are shown in Figure 2. Spectra taken at low temperature (77 K) are shown in Figure 3. A film drawn at 300 °C to only 200% elongation showed a high degree of dichroism. Polarized infrared spectra of this film are shown in Figure 4. Raman spectra of the HFIB/VF_2 copolymer at room temperature are shown in Figure 5. Frequencies and polarizations of the observed infrared bands are tabulated in Table I.

Discussion

Degree of Block Formation. We have concluded that the copolymer studied here has a high degree of alternation since we found no spectral evidence for $-(CH_2CF_2)_n-$ block formation. This conclusion is based on the following: (1) There is an intense band in the infrared and Raman spectrum of the copolymer at 3039 ± 1 cm^{-1} which is probably the CH_2 antisymmetric stretching vibration. On the other hand, there is a band at 3020 ± 3 cm^{-1} in the spectra of all three forms of poly(vinylidene fluoride) which has been assigned to the same fundamental.[4-6] There is no evidence of this poly(vinylidene fluoride) band in the spectrum of the 1:1 HFIB/VF_2 copolymer. (2) We have employed digital subtraction methods to compute the difference between the infrared spectrum of an emulsion polymerized copolymer containing higher vinylidene

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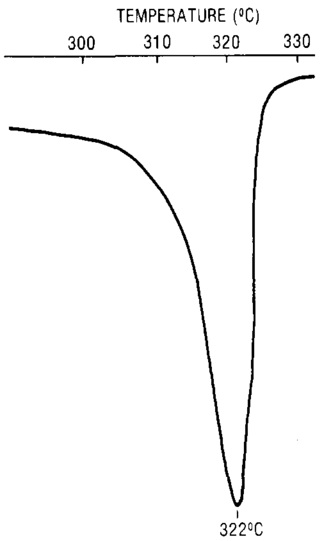

Figure 1. Thermogram of HFIB/VF$_2$ copolymer as polymerized. DuPont 990 DSC in Argon 10 °C/min heating rate.

fluoride content and a spectrum of our copolymer. The result was a spectrum characteristic of poly(vinylidene fluoride): the difference spectrum which showed strong bands at 3020, 2980, 1405, 1180, 880, and 840 cm^{-1} is essentially that of poly(vinylidene fluoride).[4-6] (3) One of the strongest bands in the infrared spectrum of PVF$_2$ is near 1400 cm^{-1} and has parallel polarization.[6] The HFIB/VF$_2$ copolymer of interest has a band at medium to weak intensity at 1407 cm^{-1}. However, this band has perpendicular polarization and therefore cannot have its origin in PVF$_2$ blocks. In addition, the infrared spectra of PVF$_2$ exhibits a band near 1430 cm^{-1} assignable to the CH$_2$ deformation motion.[4] The infrared spectrum of the sample studied showed strong absorptions at 1453 and 1407 cm^{-1} only.

This latter argument rests on the reasonable assumption that a $-(CH_2CF_2)_n-$ chain would assume the same conformation, i.e., either planar zigzag or TGTG′, that it assumes in the homopolymer. In either case, the 1400-cm^{-1} band is observed to have parallel dichroism.

The existence of a very stiff polymer backbone has been invoked to explain the high glass transition measured (~405 K).[2] This stiffness appears to result from steric hindrance and electronic repulsions of the CF$_3$ and CF$_2$ units of the copolymer chain. The infrared spectrum of this copolymer quick-quenched in ice water from the melt was compared to the spectrum of a sample "slow cooled" from the melt. No new bands appeared in either spectrum, although some intensity differences were found. Bands at 3040, 2985, 972, 860, 802, 535, and 488 cm^{-1} were more intense for the slow-cooled sample, while the bands at 1407 and 1372 were less intense. The similarity of the spectra of these two samples, which have a quite different thermal history, suggests that conformational freedom of the chain of this copolymer is constrained. Furthermore, the infrared spectrum obtained at low temperature is essentially identical to the one obtained at room temperature. The similarity of the two spectra is consistent with a stiff chain.

Chain Configuration. An important question in characterizing the HFIB/VF$_2$ copolymer concerns the structure of the chain: does HFIB/VF$_2$ polymerize in the head-to-tail fashion

$$-(C(CF_3)_2CH_2CF_2CH_2)_n-$$

or in the head-to-head fashion

$$-(C(CF_3)_2CH_2CH_2CF_2)_n-$$

Table I
Observed Frequencies of HFIB/VF$_2$ Copolymer

infrared[a]			Raman[a]
room temp	77 K	polarization	room temp
3040	3040 (m)	π	3040 (m, s)
2985	2985 (m)	π	2984 (s)
2968	2968 (w)	π	
			2824 (m)
1453	1453 (s)	σ	1450 (m)
1407	1410 (m)	σ	
1374	1374 (m)	σ	
1344	1344 (s)	π	1345 (w)
1280	1280 (vs)	σ	1275 (m)
			1260 (m)
1234	1234 (s)	?	1236 (w)
			1220 (w)
1206	1206 (vw)	?	
			1170 (w)
			1155 (m)
1146	1146 (vs)		
			1130 (w)
1118	1118 (vs)		
			1035 (w)
1027	1029 (sh)	π	
1009	1014 (s)	σ	
972	973 (w)	σ	
964	966 (m)	π	
920	920 (vvw)		
			895 (w)
886	886 (vw)	π?	
869	871 (w)	σ	873 (m)
859	860 (w)	σ	
824	826 (w)		
			813 (m)
801	802 (m)	σ	
			795 (vvs)
755	755 (m)	σ	
742	743 (w)	σ	742 (w)
			715 (m)
697	698 (s)	σ	
670	670 (sh)		672 (vw)
660	660 (w)	σ	659 (vvw)
638	637 (s)	σ	640 (w)
			622 (vvw)
605	607 (w)	σ	603 (w)
568	568 (w)		570 (w)
542	542 (m)	π	540 (s)
535	535 (sh)	σ	
509	507 (m)	σ	
489	488 (m)	σ	
464	463 (m)	σ	
432	432 (w)	π	
325 (w)			
310 (vw)			
283 (s)			
250 (s)			
236 (s)			
185 (vs)			
150 (w)			
117 (vw)			

[a] vs, very strong; m, medium; w, weak; π, polarization parallel to the draw axis; σ, polarization perpendicular to the draw axis.

To answer this question, we have compared the CH stretching vibrations of this copolymer with the corresponding vibrations in poly(vinylidene fluoride), $-(CF_2CH_2)_n-$, a copolymer of ethylene and tetrafluoroethylene, $-(CH_2CH_2CF_2CF_2)_n-$, a copolymer of ethylene–monochlorotrifluoroethylene, $-(CF_2CH_2CH_2CFCl)_n-$, and polyethylene containing in one case isolated CD$_2$ groups and in another case isolated CD$_2$CD$_2$ groups.

In the HFIB/VF$_2$ copolymer, we observed two intense Raman bands at 2984 and 3040 cm^{-1}, and a third less intense band at 2824 cm^{-1}. In the infrared spectrum, there

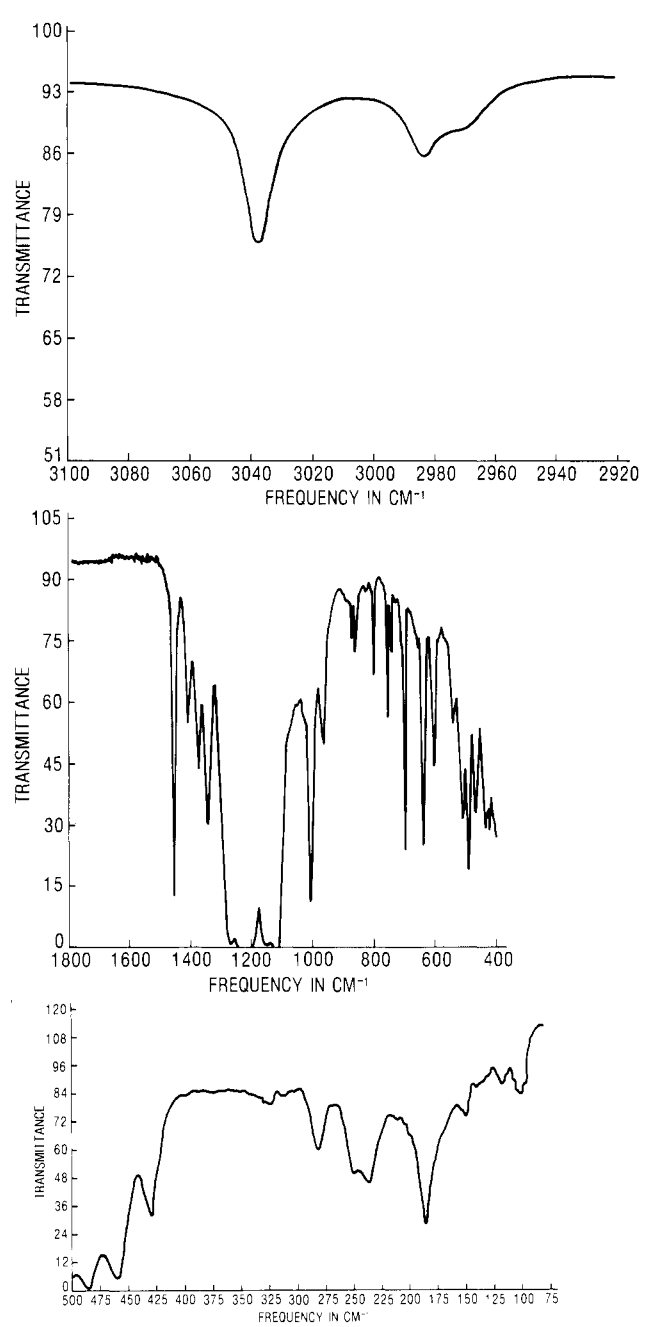

Figure 2. Infrared spectra of HFIB/VF$_2$ film; room temperature; 1 cm^{-1} resolution; (a, top) 3100–2920-cm^{-1} region; (b, middle) 1800–400-cm^{-1} region; (c, bottom) 400–50-cm^{-1} region.

are two intense bands at 2985 and 3040 cm^{-1} and a less intense component at 2968 cm^{-1}. In addition, weaker features at 2795, 2850, 2870, and 2920 cm^{-1} were observed at room temperature. We have assigned the 2984- and 3040-cm^{-1} bands, observed in both infrared and Raman, to the symmetric and antisymmetric methylene CH stretching vibrations. The frequency coincidences between the infrared and Raman spectra, and the relative simplicity of these spectra, support the head-to-tail structure rather than the head-to-head structure for the following reasons.

For either structure, the CH stretching modes by virtue of their high frequencies are to a good approximation uncoupled from all other vibrational modes, and thus can be treated as independently vibrating systems.

In the case of the head-to-tail structure, the CH$_2$ groups are separated from each other by CF$_2$ or C(CF$_3$)$_2$ units. Consequently the two CH stretching modes of a given CH$_2$ group are nearly uncoupled from the CH stretching modes of other CH$_2$ groups. The result is a near degeneracy of the frequencies of all antisymmetric CH stretching vibrations and likewise of all the symmetric CH vibrations. In the limit of total noninteraction, two well-separated bands will appear in the infrared. Analogous bands will also appear in the Raman at the same frequencies observed in the infrared. This is essentially what is found for the HFIB/VF$_2$ copolymer.

For the head-to-head structure CH$_2$ groups occur in adjacent pairs, each pair being flanked by a CF$_2$ group on one side and a C(CF$_3$)$_2$ group on the other. For the moment we will ignore the fact that the two flanking groups are different and will consider all methylenes to be chemically identical. The C–H stretching vibrations of adjacent CH$_2$ groups will couple to give four modes and each will have a different frequency. Two modes are antisymmetric stretches and two are symmetric. Which of these appear in a spectrum will be determined in large part by the conformation of the CC bond connecting the CH$_2$CH$_2$ pair. If the bond is gauche, all four are allowed

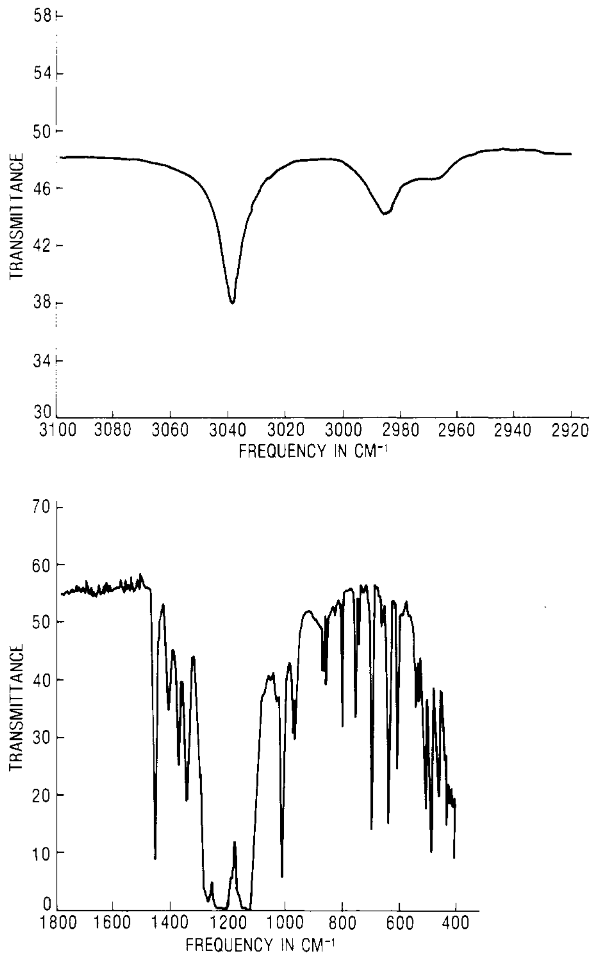

Figure 3. Infrared spectra of HFIB/VF$_2$ film; 77 K; 1-cm^{-1} resolution; (a, top) 3100–2920-cm^{-1} region; (b, bottom) 1800–400-cm^{-1} region.

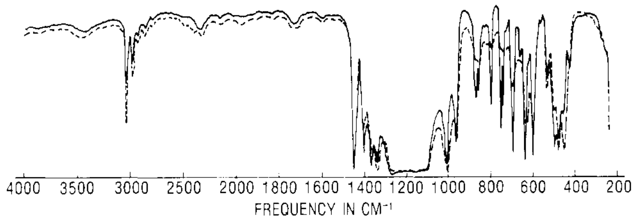

Figure 4. Oriented film of HFIB/VF$_2$ copolymer; 200% elongation at 300 °C; (---) electric field parallel to the draw direction; (—) electric field perpendicular to the draw direction.

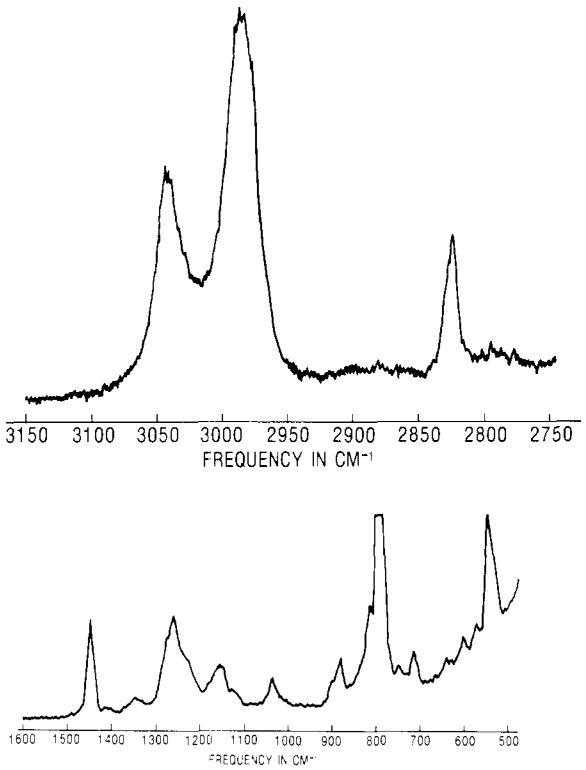

Figure 5. Raman spectra of HFIB/VF_2 film: room temperature; 6471-Å excitation; laser power, 100 mW; band pass, 3 cm^{-1}; (a, top) 3150–2750-cm^{-1} region; (b, bottom) 1650–450-cm^{-1} region.

to appear in both the infrared and Raman; if the bond is trans, two (one antisymmetric mode and one symmetric mode) will appear in the infrared while the other two will appear in the Raman. In summary, if the CC bond is trans, two bands will appear in both the infrared and Raman, but their frequencies will not coincide (in contrast to the head-to-tail case), while on the other hand if the CC bond is gauche, four bands will appear in both the infrared and Raman, and the frequencies of the bands will be the same in both spectra.

There are two factors, so far ignored, which tend to make the spectra predicted from these simple considerations somewhat more complicated.

If there is more than one monomer[19] in the translational repeat unit, any coupling between the CH_2 groups of different monomers will cause the CH stretching bands to be slightly displaced in frequency from their values for a single monomer unit and may result in some additional structure in the spectra. This complicating factor is most important for simple polymers such as PVF_2.

The origin of "extra" bands in this region is, however, more commonly the result of Fermi resonance interaction between the C–H stretching modes and overtones and combinations of hydrogen bending modes (predominantly the CH_2 scissor modes in the present case). This phenomenon is nearly always manifest in the CH stretching region even for the simplest molecules, and for polymers it can lead to complex band structure.[9]

To illustrate the method of inferring structure from an analysis of CH stretching vibrations, we have recorded the spectra of two samples of polyethylene, one containing isolated CD_2 groups and another containing isolated $-CD_2CD_2-$ groups.[10] The CD stretching modes are essentially uncoupled from both the CH stretching modes and from all other modes and can thus be treated as an independent system. The 1900–2200-cm^{-1} regions of the infrared and Raman spectra are shown on Figures 6 and 7.

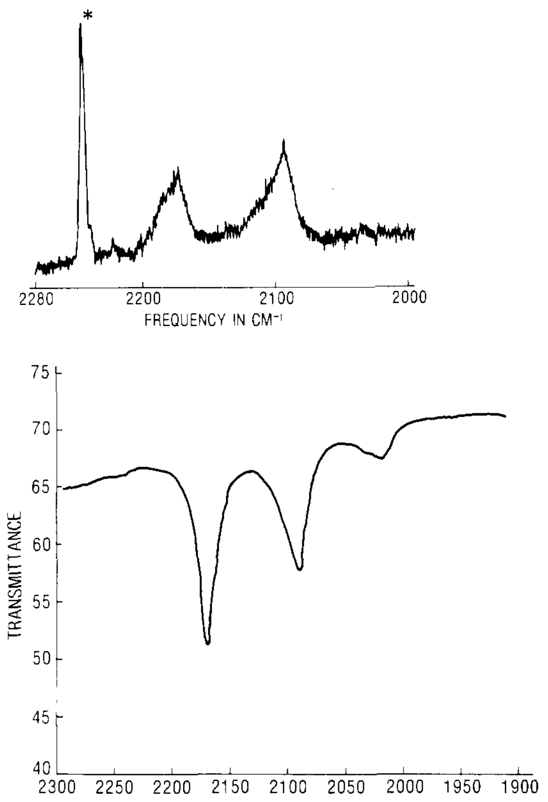

Figure 6. CD stretching region of polyethylene chain containing one CD_2 group. (a, top) Raman, 2280–2000 cm^{-1}; 6471-Å excitation; laser power, 100 mW; band pass, 3 cm^{-1}. Laser emission line; (b, bottom) infrared, 2300–1900 cm^{-1}; 2-cm^{-1} resolution.

For an isolated CD_2 group, we observe, as expected, a coincidence of CD stretching vibrations in the infrared and Raman spectra. The bands at 2090–2091 (IR; Raman) and 2170–2171 cm^{-1} (IR; Raman) for $-(CH_2)_mCD_2(CH_2)_n-$ may be assigned to the symmetric and antisymmetric stretching vibrations, respectively.

For the system $-(CH_2)_n(CD_2)_2(CH_2)_m-$, we observed infrared bands at 2020 (w), 2079 (s), 2122 (w), and 2180 cm^{-1} (s) and Raman bands at 2059 (vvw), 2097 (s), 2135 (w), 2144 (w), and 2179 cm^{-1} (m). Although the spectrum in this region displays complications due to Fermi resonance interactions, it is clear in this case that due to the local interactions between the CD_2CD_2 group, general coincidences between infrared and Raman observations are no longer present. Thus the complexity of the spectra combined with the absence of coincidence indicates two adjacent CD_2 groups connected by a trans CC bond.

We have also examined the CH stretching vibrations of other model systems in order to differentiate the head-to-head structure from the head-to-tail one. Poly(vinylidene fluoride) (PVF_2), $-(CH_2CF_2)-$, is such a model. PVF_2 has been reported to exist in three forms.[6,11,12] Again regardless of the overall conformation of the chain, we expect the CH stretching vibrations of the CH_2 group to be decoupled from other normal vibrations of much lower energy. For this isolated CH_2 unit in PVF_2, the infrared and Raman active CH stretching frequencies should coincide and this is observed for the planar zigzag forms,[4-6,13,14] since these have one monomer per repeat unit. The nonplanar form, however, has a TGTG′ conformation with two monomers per repeat unit. For the reasons discussed earlier, this results in a slightly more complex CH stretching spectrum than for the planar forms.

The antisymmetric and symmetric CH stretching frequencies for all these conformations of PVF_2 are found at

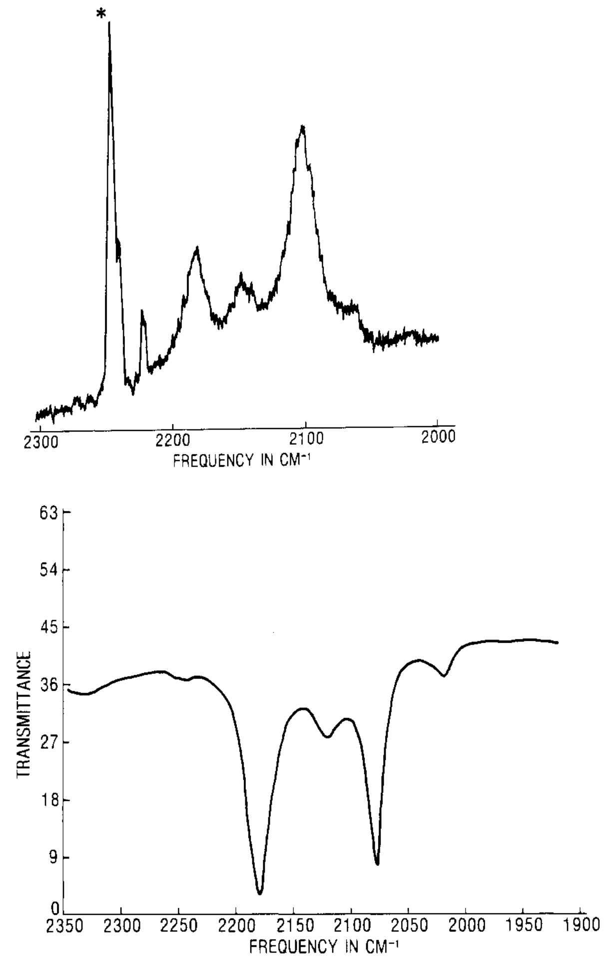

Figure 7. CD stretching region of polyethylene chain containing two CD_2 groups in sequence. (a, top) Raman, 2000–2300 cm^{-1}; 6471-Å excitation; laser power, 100 mW; band pass 3 cm^{-1}. Laser emission line; (b, bottom) infrared, 1900–2350 cm^{-1}; 2-cm^{-1} resolution.

3020 and 2984 cm^{-1}, respectively.[4–6,13,14] These observations provide strong support for the assumption that CH stretching vibrations are not only decoupled from other normal modes but that their frequencies are relatively insensitive to chain conformation.

For the ethylene and tetrafluoroethylene copolymer, $-((CH_2)_2-(CF_2)_2)_n-$, the CH_2 groups have been postulated to exist in a trans conformation,[15] i.e., there is a local inversion center. In this case, although the symmetric and antisymmetric CH stretching vibrations of the two CH_2 units are decoupled from other motions, they interact with each other. However, as we noted earlier, the presence of a trans C–C bond between the CH_2 groups prevents coincidences between infrared and Raman frequencies. The bands assignable to the CH_2 antisymmetric stretching vibrations are 3005 cm^{-1} (R; s) and 2956 (IR; w). Bands at 2979 cm^{-1} (R; vs) and 2975 cm^{-1} (IR; w) have been assigned to the CH_2 symmetric stretching vibrations.[4] In this case, the observations are consistent with the selection rules associated with such a structure. A final example is the "kinked" structure suggested by Sibilia et al.[7,8] for the ethylene–monochlorotrifluoroethylene copolymer, $-(CF_2CH_2CH_2CFCl)_n-$. The CH_2 groups are also connected by a trans CC bond. In this case, we observed medium to strong Raman bands at 2960 and 2991 cm^{-1} while we observed the infrared absorption bands associated with the CH_2 groups in this copolymer at 2975 cm^{-1} (vs) and 2875 cm^{-1} (m).[7,8]

The arguments which lead us to believe the HFIB/VF_2 copolymer exists in a head-to-tail structure (isolated CH_2 groups) rather than a head-to-head structure (isolated CH_2CH_2 groups) can now be summarized.

The simplicity of the CH stretching region observed for this copolymer suggests in itself the presence of isolated CH_2 groups. In order for the spectrum of a CH_2CH_2 group to be this simple a trans CC connecting bond is required. However, the presence of a trans bond does not allow coincidences in band frequencies between the infrared and Raman spectra. Since coincidences are indeed observed, this structure is ruled out.

A second argument against the head-to-head structure is based on the observed frequencies of the CH stretching bands. In the head-to-head structure one CH_2 group exists in an essentially saturated hydrocarbon environment since it is flanked by a CH_2 group and a $C(CF_3)_2$ group. Consequently the CH stretching frequencies would be expected to be in the range 2930–2840 cm^{-1}. The observed frequencies, 3040 and 2984 cm^{-1}, are considerably higher. These higher values are consistent only with the head-to-tail structure since it has been observed for PVF_2 and for the copolymer $-((CH_2)_2(CF_2)_2)_n-$ that the influence of a CF_2 group adjacent to a CH_2 is to raise the values of the frequencies of the CH stretching modes into the frequency region above 2980 cm^{1}.

The HCH bending (scissors), 1480–1420 cm^{-1}, region provides additional support for the head-to-tail structure. Analysis of this region can be more difficult than for the stretching region because there can be mixing with other modes. In general, however, these vibrations are predominantly methylene scissors.

In the head-to-head structure the $-CH_2-$ groups are always flanked on one side by another CH_2. On the other side, however, the neighboring group is either a CF_2 group or a $C(CF_3)_2$ group. The result is two chemically nonequivalent CH_2 groups. The inductive forces due to adjacent groups are thus slightly different. As a consequence the HCH bending force constants will be different as will be the frequency of the two CH_2 bending modes.

On the other hand, in the head-to-tail structure all methylene units have exactly the same chemical environment. Each CH_2 is neighbored by a CF_2 and a $C(CF_3)_2$ group. The CH_2 groups in this structure will therefore have the same force constant for bending. In Figure 3b the CH_2 bending mode appears in the infrared as a very sharp single band at 1453 cm^{-1}. The presence of the single sharp band further supports the head-to-tail structure deduced from the –CH– stretching region.

Chain Conformation. Having established the most probable structure of the copolymer, we now consider its conformation. Certain bands in the spectra suggest that there is more than one monomer per repeat unit, and infrared polarization data indicate that the CH_2 groups are tilted on the average in such a way that both the symmetric and antisymmetric CH stretching mode transition moments form angles less than 54° with the chain axis.[7]

The weak unassigned infrared band at 2968 cm^{-1} (which may also be present in the Raman, hidden under the intense and broad band at 2984 cm^{-1}) may be due either to Fermi resonance or alternatively to a complex repeat unit. As pointed out earlier, there is some detail in the spectrum of the nonplanar form of PVF_2 that is not present in the spectrum of the planar form. The unassigned Raman band of medium intensity at 2824 cm^{-1} is probably due to Fermi resonance between the overtone of the 1407-cm^{-1} fundamental and the symmetric CH stretching fundamental at 2984 cm^{-1}. Normally, strong resonance occurs when the overtone is associated with a

CH_2 scissors mode. However, the 1407-cm^{-1} fundamental has a frequency appropriate to a methylene wagging mode, but because its overtone enters into Fermi resonance with the C-H symmetric stretch, it probably has a scissors component. This in turn indicates a nonplanar structure since only in that case can scissors and wagging modes mix.

Further evidence for mixing of CH_2 scissors and wagging modes is found in the region 1500–1300 cm^{-1} of the infrared spectrum. Four bands of medium intensity are spread throughout this region. If the copolymer were planar, the two equivalent CH_2 groups would lead to two pairs of bands, one pair near 1440 cm^{-1} and the second near 1390 cm^{-1}. No other bands should appear. Thus the complexity in this region points to a nonplanar structure.

One interesting spectral property of the HFIB/VF_2 copolymer is the infrared polarization of the (CH_2) stretching modes. Both the ~3038-cm^{-1} and the 2985-cm^{-1} bands are parallel polarized. In PVF_2 and polyethylene these modes are both perpendicular[6,16] as expected from their structures. On the other hand, the parallel dichroism observed in HFIB/VF_2 indicates that the symmetric and antisymmetric CH stretching mode transition moments form angles less than 54° with the chain (draw) axis.[7]

The perpendicularly polarized 1453-cm^{-1} frequency can be assigned to a mode which is predominantly bending. From intensity and position considerations, we have assigned the perpendicularly polarized 1407 cm^{-1} peak in infrared to be the CH_2 wagging motion.[6] From bond polarizability considerations, it has been postulated that CH_2 wagging modes are weak in the Raman.[17] Even under high sensitivity, we could not clearly observe in the Raman (Figure 5) the 1407-cm^{-1} band, which is prominent in the infrared spectrum.

The origins of the unexpected polarization data associated with the 1453- and 1407-cm^{-1} bands are not clearly understood at this moment. However, if the CH_2 groups are significantly tilted with respect to the chain axis as expected in a helix, we would expect CH_2 stretching and CH_2 bending motions to have the same parallel polarization and the CH_2 wagging motions to have the perpendicular polarization. We have carried out a normal vibrational analysis of the HFIB/VF_2 copolymer in order to obtain a quantitative description of these modes, i.e., the degree of "purity" associated with these bending and wagging motions in the presence of CF_2 and $C(CF_3)_2$ groups. We are analyzing the transition moments associated with such coupled motions and will report the results elsewhere.[18]

Conclusions

We have obtained the characteristic CH stretching vibrations associated with ethylene–tetrafluoroethylene, poly(vinylidene fluoride), and ethylene–chlorotrifluoroethylene. We have used this information together with the characteristic CD stretching vibrations in $-(CH_2)_nCD_2(CH_2)_n-$, $-(CH_2)_n(CD_2)_2(CH_2)_m-$, and HFIB/$VF_2$ copolymer. Our observations provide a strong support for the assumption that its CH stretching vibrations are not only decoupled from other normal modes but that their frequencies are relatively insensitive to chain conformation. In addition, we established that Raman and infrared observations should coincide for an "isolated" CH_2 unit on a polymer chain. These analyses have led us to conclude that the HFIB/VF_2 copolymer exists in a head-to-tail structure. An evaluation of the CH_2 bending region supports this conclusion. Our vibrational analysis suggests that there is more than one monomer per repeat unit. Infrared polarization data indicate that the CH_2 groups are tilted on the average in such a way that both the symmetric and antisymmetric CH stretching mode transition moments form angles less than 54° with the chain (drawn) axis.

References and Notes

(1) P. S. Minhar and F. Petrucelli, *Plast. Eng.*, 60 (1977).
(2) J. M. Pochan, D. F. Hinman, M. F. Froix, and T. Davidson, *Macromolecules*, **10**, 113 (1977).
(3) M. F. Froix, A. O. Goedde, and J. M. Pochan, *Macromolecules*, **10**, 778 (1977).
(4) M. Kobayashi, K. Tashiro, and H. Tadokoro, *Macromolecules*, **8**, 158 (1975).
(5) S. Enomoto, Y. Kawai, and M. Sugita, *J. Polym. Sci., Part A2*, **6**, 861 (1968).
(6) G. Cortelli and G. Zerbi, *Spectrochim. Acta, Part A*, **23**, 285 (1967).
(7) J. P. Sibilia, L. G. Roldan, and S. Chandrasekaran, *J. Polym. Sci., Part A2*, **10**, 549 (1972).
(8) J. P. Sibilia, R. J. Schaffhauser, and L. G. Roldan, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1021 (1976).
(9) R. G. Snyder, S. L. Hsu, and S. Krimm, *Spectrochim. Acta, Part A*, **34**, 395 (1978).
(10) R. G. Snyder and M. W. Poore, *Macromolecules*, **6**, 708 (1973).
(11) R. Hasegawa, M. Kobayashi, Y. Chatani, and H. Tadokoro, *Polym. J.*, **3**, 591 (1972).
(12) R. Hasegawa, Y. Takahashi, Y. Chatani, and H. Tadokoro, *Polym. J.*, **3**, 600 (1972).
(13) F. J. Boerio and J. L. Koenig, *J. Polym. Sci., Part A-2*, **9**, 1517 (1971).
(14) G. L. Cessac and J. G. Curio, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 695 (1974).
(15) F. C. Wilson and H. W. Starkweather, Jr., *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 919 (1973).
(16) S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).
(17) R. G. Synder, *J. Mol. Spectrosc.*, **23**, 224 (1967).
(18) S. L. Hsu and J. P. Sibilia, to be published.
(19) A monomer unit for the copolymer would correspond to HFIB monomer + VF_2 monomer.