seen that the rate of degradation in the transcrystalline film (no filler) is in fact more rapid than in the control. These results then indicate that in order to improve the photooxidative stability of polyethylene, a filler, in addition to being a light shield, should preferably have a low surface energy.

To further support this hypothesis, the high surface energy fillers, graphite and diamond, which originally contributed to a high rate of photooxidation on exposure (Figure 1) were converted into low surface energy materials by direct fluorination with fluorine gas for 1 hr at ambient conditions. Since polymers have been known to convert their surface layers into perfluorinated species,[13] the increase in hydrophobicity of the diamond and graphite is believed to result from partial fluorination of their respective surfaces.

In Figure 1, comparison of the PE films containing the fluorinated graphite and fluorinated diamond with the original "PE + graphite" and "PE + diamond" films reveals the increased protection afforded by the now lower surface energy graphite and diamond fillers. The observed increase in protection to photooxidation is believed to result from a combination of light shielding and a decrease in the highly structured region around the filler particles.

The results of Eby[10] support the hypothesis that a layer of lamellar oriented normal to the surface augments diffusion into the polymer. Eby obtained a value of 3.6×10^{-8} cm^2 sec for the diffusion constant of ethane into a transcrystalline region and a value of 1.7×10^{-8} cm^2 sec for the bulk (spherically symmetrical spherulites). Michaels and Bixler[14] have demonstrated quite clearly that diffusion of oxygen into a high density linear polyethylene is one order of magnitude greater than ethane (diffusion constant = 17.0×10^{-8} cm^2/sec) and that the diffusion is extremely sensitive to crystallinity. Michaels and Bixler[14] estimate that the diffusion constant of oxygen in amorphous polyethylene would be 173×10^{-8} cm^2/sec, or ten times that of linear high density polymer (77% crystalline). Since the boundary between neighboring spherulites is considered to be relatively amorphous,[10] it then becomes apparent why the transcrystalline regions are more susceptible to oxidative photodegradation. In the transcrystalline morphology, considerably more boundary regions exist, permitting greater access of excited oxygen[15] to the polymer resulting in the observed degradation.

It is possible that other factors may be involved in determining the polymer photooxidative stability of composites, but it appears that the influence of fillers on the morphology of the polymer matrix should be considered extremely important. A more detailed report concerning other physical and chemical effects associated with polymer–filler composites is in preparation.

Acknowledgment. The authors are indebted to Mr. F. W. Ryan for his valuable assistance in the course of this work and to Dr. P. K. Gallagher and Mr. F. Schrey for their cooperation in the fluorination of the fillers.

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Fold Structure of Polyethylene Single Crystals

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ABSTRACT: Using model compounds we have observed infrared absorptions which can be attributed to the folding and bending conformations in *n*-hydrocarbons. Comparison of the crystalline and melt spectra of *n*-hydrocarbons and tightly folded cyclic $C_{34}H_{68}$ provides evidence that an absorption at 1340 cm^{-1} is associated with folding or bending in a hydrocarbon chain. Our results also corroborate the assignment of the 1350-cm^{-1} band to *gauche* conformation in *n*-hydrocarbons. Based on a comparison of the relative intensities of the 1340/1350-cm^{-1} bands in the spectrum of polyethylene single crystal aggregates it appears that the fold structure is not that of a tight fold with adjacent reentry.

Chain folding in polyethylene single crystals is an accepted phenomenon.[1] However, the nature of the fold structure, whether there is adjacent reentry,[2] switchboard-type folding,[3] a loosely looped fold model (essentially amorphous),[4] or any combination of the above, is an active area of research.[5]

Krimm and Bank[6,7] have recently concluded, based on an infrared study of the 71-cm^{-1} absorption in polyethylene single crystals consisting of a mixture of normal and deuterated hydrocarbons, that there is adjacent reentry. Okada and Mandelkern[8] report that their studies of the fold structure of polyethylene single crystals using infrared spectroscopy support the concept of a disordered surface region in the crystals that are formed from xylene. The results of Okada and Mandelkern are in accord with other measurements such as wide-angle X-ray,[9] broad-line nmr,[10] and selective oxi-

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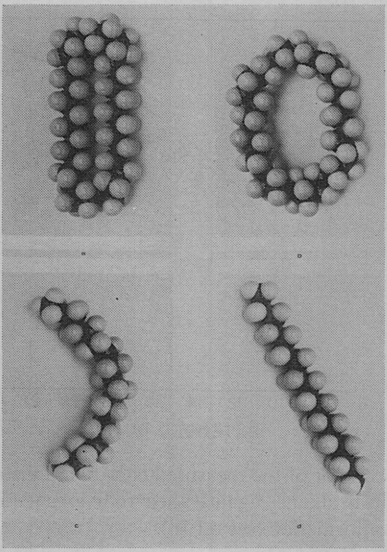

Figure 1. (a) Conformation of crystalline cyclic saturated hydrocarbon ($C_{34}H_{68}$). (b) Cyclic hydrocarbon ($C_{34}H_{68}$) in melt. (c) *n*-Hydrogarbon ($C_{17}H_{38}$) in melt. (d) *n*-Hydrocarbon ($C_{18}H_{38}$) in crystal.

dation.[11,12] Kawai, Goto, and Maeda[13] support the adjacent reentry model based on a study of the molecular weight dependence of crystallinity and surface structure. Bassett[14] has suggested that adjacent reentry probably occurs in crystals grown from dilute solution but that it may not always be detectable in Moiré patterns of single crystal aggregates because of inadequate lamellae contact.

A number of infrared absorption bands have been studied[15,16] to determine their possible connection with the fold structure. We will report here our conclusions based on infrared data using model compounds. In this study we will consider a chain fold to be as shown in Figure 1a and chain bending as shown in either Figure 1b or 1c.

Using normal and cyclic saturated hydrocarbons, our results indicate that the presence of an absorption band at 1340 cm^{-1} is associated with the fold structure. Our further observations agree with those of Nielsen and Holland[17] which suggest that the absorption at 1350 cm^{-1} may be attributed to *gauche* conformation in the polymer chain. Crystalline normal hydrocarbons which are free of amorphous regions and defects do not exhibit an absorption at 1340 cm^{-1}. The band is also apparently independent of crystal structure since we have examined a variety of both odd and even *n*-hydrocarbons from C_6 to C_{94} which do not exhibit this band. These results are corroborated by independent X-ray[18] and nmr studies.[19]

Experimental Section

The infrared spectra were recorded on a Model 421 Perkin-Elmer spectrophotometer. A Beckman variable-temperature infrared cell was used for studies of the samples as a function of temperature. The liquid samples (C_6 to C_{12}) were run in a sealed cell of 0.05-mm path length.

The *n*-hydrocarbons were spectroscopically pure and were further purified to better than 99 mol % by zone refining. The sample of $C_{94}H_{190}$ was obtained from the National Bureau of Standards and was used without further purification. The cyclic hydrocarbon $C_{34}H_{68}$ was kindly furnished by Dr. E. Wasserman, Bell Telephone Laboratories, Inc., in a highly purified state. The polyethylene single crystal aggregates were prepared by Bair, Huseby, and Salovey[20] and used in the form of thin mats.

Results and Discussion

Since it was believed that the conformation of the backbone at a fold, in a saturated long chain hydrocarbon, would have some effect on the $-CH_2-$ deformation mode near 1350 cm^{-1}, we chose a number of crystalline low molecular weight *n*-hydrocarbons, with no fold structure, and for comparison a cyclic saturated hydrocarbon $C_{34}H_{68}$ which has a tight fold (adjacent reentry) in the crystal.[21]

Newman and Kay[21] have suggested recently that an infrared study of the cyclic saturated hydrocarbon $C_{34}H_{68}$ should reveal details about *gauche*-bond motions since 8 of the 34 methylene groups are in the *gauche* conformation in the fold (Figure 1a). Since the cyclic hydrocarbon $C_{34}H_{68}$ has been shown by Newman and Kay[21] to be organized in the crystal in a tight fold structure (*i.e.*, adjacent reentry) we hoped to observe the appearance of absorptions related to the fold structure which would be absent in crystalline low molecular weight *n*-hydrocarbons. Infrared absorption bands related to a fold structure would be expected to possess the following characteristics.

a. They should be absent in crystalline *n*-hydrocarbons (Figure 1d) but may be present in the melt (or amorphous regions) (Figure 1c).

b. They should be more intense in the crystalline form of a cyclic hydrocarbon such as $C_{34}H_{68}$ (having the tight fold structure) (Figure 1a) and less intense in the liquid state (Figure 1b).

In the *n*-hydrocarbon crystals, no fold structure should be expected since the chains in the crystal are fully extended and no folds exist. Of course this is only true in an ideally crystalline material, since in a real crystal there usually are defects or noncrystalline regions present. This may give rise to absorptions not representative of the crystal. When the crystalline *n*-hydrocarbons are melted, infrared absorptions which are representative of the folding or bending may be observed. Folding or bending effects have been observed in *n*-hydrocarbon melts by X-ray[18] and nmr techniques.[19] In the cyclic hydrocarbon crystal, the conformation is that of a fully collapsed hoop having tight folds char-

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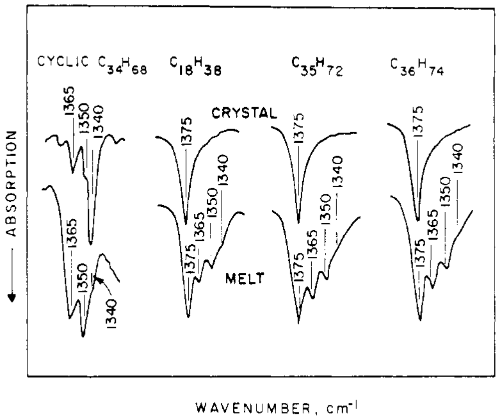

Figure 2. Spectra of cyclic ($C_{34}H_{68}$) and normal hydrocarbons (C_{18}, C_{35} and C_{36}), melt and crystal forms, in the 1400–1300-cm^{-1} region.

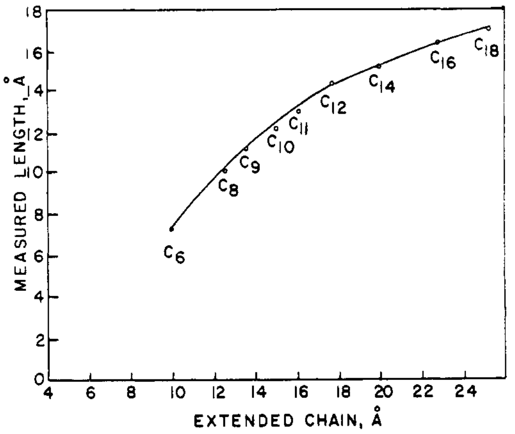

Figure 3. A plot of the measured end-to-end distances of a series of linear alkanes against their fully extended length in the *trans* conformation (see ref 18).

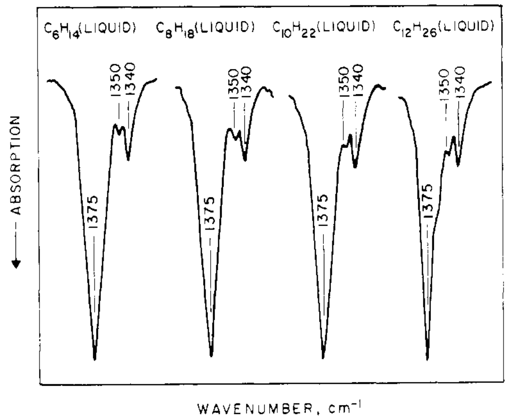

Figure 4. Spectra of *n*-hydrocarbons (C_6, C_8, C_{10} and C_{12}) melts in the 1400–1300-cm^{-1} region.

acteristic of adjacent reentry. For this type of fold a *ggtgg* sequence is required (where g = *gauche* and t = *trans* conformation). In this instance, if there are absorptions in the infrared which are due to the fold structure, their infrared intensities may be reduced upon melting of the cyclic hydrocarbon since the molecule expands and assumes the conformation of an expanded hoop (Figure 1b).

Comparison of the spectra of the melted and crystalline normal and cyclic hydrocarbons reveals a number of differences in the 1300–1400-cm^{-1} region (Figure 2). In particular, two absorptions bands, at 1340 and 1350 cm^{-1}, appear in the melt *n*-hydrocarbon spectra but are virtually absent in the corresponding crystalline spectra. In the cyclic hydrocarbon spectra (crystal and melt) both the 1340- and 1350-cm^{-1} bands appear. However they differ significantly in their relative intensities in the crystal and the melt.

The 1340-cm^{-1} absorption satisfies the criteria mentioned earlier for an infrared absorption band related to the presence of bending or folding.

The presence of a 1340-cm^{-1} absorption in the *n*-hydrocarbon melt is understood in light of the work of Brady, *et al.*,[18] and Liu.[19] Brady, *et al.*,[18] using X-ray techniques to examine the most probable end-to-end distance in *n*-hydrocarbons with brominated terminal groups, for ease in identification, have concluded that there is a shortening of the end-to-end distance of the chains on melting (Figure 3). The data of Brady, *et al.*, indicate that bending occurs (Figure 1c) in molecules of *n*-hexane and higher members of the homologous series and is independent of whether or not they are odd or even. A similar effect has been observed by Liu[19] using nmr techniques. Liu has suggested that in *n*-hydrocarbons greater than n = 16, there is the probability of folding (or bending) of the chains.

Since we propose that the 1340-cm^{-1} absorption is related to a moderate bending or folding being present in the *n*-hydrocarbon molecule in the melt, we would expect, based on the data of Brady, *et al.*, that from C_6 to C_{12} the intensity of this absorption would be relatively constant. This is precisely what is observed (Figure 4). From C_{12} to C_{18}, Brady, *et al.*,[18] have found that the slope of mean end-to-end distance *vs.* chain length decreases as chain length increases, indicating more bending or folding. This should be reflected in an increase in the 1340-cm^{-1} absorption. Beyond C_{18} (*n*-hydrocarbons) we find an increase in the intensity of the 1340-cm^{-1} absorption (Figure 2), as expected. There does not appear to be any significant differences in the intensity of the 1375-cm^{-1} band from C_6 to C_{12}.

It was previously suggested that the 1350-cm^{-1} band in polyethylene is attributable to *gauche* conformation of $-CH_2-$ groups as a result of rotational isomerism.[17]

In the *n*-hydrocarbon liquids, the 1350-cm^{-1} absorption increases with increasing number of methylene groups introduced into the chain. If the 1350-cm^{-1} absorption relates to the presence of *gauche* conformation then part of its intensity increase could be due to the additional $-CH_2-$ groups in the chain and part due to more *gauche* conformation. In the cyclic hydrocarbon we can understand the variation in the 1340- and 1350-cm^{-1} absorption in going from the crystal to the melt if we assign the 1340-cm^{-1} absorption to folding (or bending) and the 1350-cm^{-1} absorption to *gauche* conformation. Upon melting of the cyclic hydrocarbon, $-CH_2-$ groups which were associated with the extended portion of the molecule (not those in the fold structure which are already *gauche*) are permitted to rotate freely upon expansion of the molecule (forming a hoop) (Figure 1b) and assume *gauche* conformations.

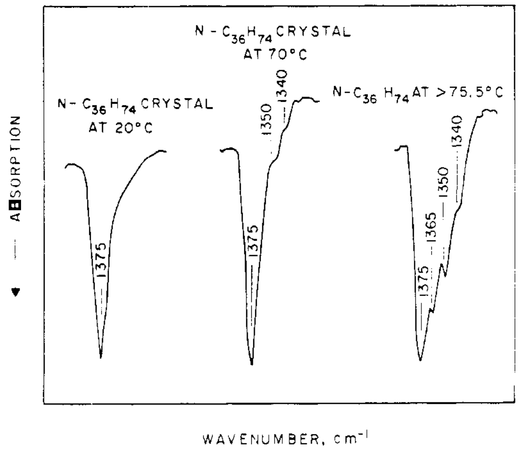

Figure 5. Spectra in 1400–1300-cm^{-1} region of n-$C_{36}H_{74}$ at 70°, crystalline form (20°), prior to the onset of the rotational transition (73.5°), and in the melt (>75.5°).

Therefore the 1340-cm^{-1} intensity is reduced since the *ggtgg* sequence is disrupted and the 1350-cm^{-1} absorption increases in intensity (most of the $-CH_2-$ groups may now assume *gauche* conformation). This is apparently the reason why, in the normal hydrocarbon melts, the 1350-cm^{-1} absorption is such a relatively strong absorption (Figure 2).

These results would indicate that in melt-crystallized polyethylene, where one normally has a sizable amorphous fraction, with many possibilities for *gauche* conformation, the 1350-cm^{-1} contribution far outweighs any possible 1340-cm^{-1} contribution. In reality the 1340-cm^{-1} band may exist but is probably masked by the 1350-cm^{-1} absorption.

To obtain additional evidence with respect to the assignment of the 1340-cm^{-1} absorption to fold structure and 1350-cm^{-1} absorption to *gauche* conformation, not in a fold, we followed the temperature dependence of the 1340- and 1350-cm^{-1} bands in n-hexatriacontane which undergoes a rotational transition prior to melting.[22] We would expect that below the melting point no 1340-cm^{-1} band should be observed due to the absence of significant folding. The crystal begins to undergo a change in the specific volume at about 70°. A solid–solid transition from orthorhombic to hexagonal occurs at 73.5°. Since the chains, in the melt, apparently rotate freely while still extended, relatively little bending should be noted while considerable *gauche* conformation is possible. This again is consistent with what we observe (Figure 5). There is essentially no evidence of absorptions at 1340 and 1350 cm^{-1} below 70°. Beginning at 70°, the 1350-cm^{-1} band becomes more prominent with an intensity increase at the solid–solid transition temperature. Throughout this increase in temperature little or no 1340-cm^{-1} absorption is noted. At the melting temperature, however, there is an increase in the 1340-cm^{-1} absorption as well as the 1350-cm^{-1} absorption due to the rotational isomerism permitting *gauche* conformation and some folding of the chains of the type shown in Figure 1c. Cooling the specimen below 70° results in the loss of both the 1340- and 1350-cm^{-1} absorption.

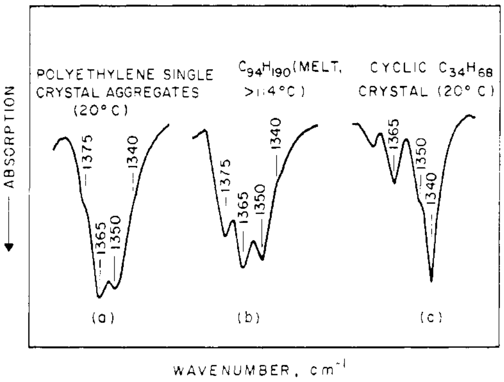

Figure 6. Spectra in 1400–1300-cm^{-1} region of polyethylene single crystal aggregates (20°), n-$C_{94}H_{190}$ melt (>114°), and crystalline cyclic hydrocarbon ($C_{34}H_{68}$) at 20°.

Folding in Polyethylene Single Crystals

The extended chain portion of the n-hydrocarbon crystal appears to make no contribution to absorptions at 1340 and 1350 cm^{-1} as evidenced by the lack of any absorption occurring at these frequencies in C_6 to C_{94}. Apparently the crystal structure is not too relevant. We can speculate that if any absorption does occur it is due to the presence of fold structure or bending associated with the amorphous content of the specimen.

Figure 6 shows the 1300–1400-cm^{-1} region for a mat of polyethylene single crystal aggregates, C_{94} n-hydrocarbon melt and the cyclic hydrocarbon crystal. For predominantly adjacent reentry to occur, the ratio of the 1340/1350 for the polyethylene single crystal aggregate (Figure 6a) should be similar to the cyclic hydrocarbon crystal (Figure 6c) but in fact appears to be similar to the n-hydrocarbon melt ratio (Figure 6b). We conclude that in the polyethylene single crystals as normally prepared we do not have appreciable adjacent reentry (tight fold). Based on the ratio of the 1340/1350 absorptions the surface structure of the monolayer single crystal is somewhat between the amorphous state and that of a tightly folded surface structure (adjacent reentry).

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