Infrared Spectra of Polymers. I. Effect of Crystallinity on the Infrared Spectrum of Polyethylene and on the Infrared Spectra of Nylon 6 and Nylon 11

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The melt and polarization spectra of dotriacontane and polyethylene in the 750–1500 cm⁻¹ region and of nylon 6 and nylon 11 in the 450–4000 cm⁻¹ region are presented. In addition, the melt and crystal spectra of stearone are presented in the 650–3500 cm⁻¹ region. The effect of crystallinity on the spectrum of polyethylene is discussed. With the aid of published Raman spectra of crystalline hydrocarbons, an assignment of frequencies for polyethylene is made. The effect of crystallization on the spectrum of stearone is discussed and unusual features pointed out.

Orientations in films of nylon 6 and nylon 11 are shown to be in the extrusion direction. The effect of melting on the hydrogen bonding and on the CO and NH frequencies is discussed. A partial assignment and classification of frequencies is made. When the films are melted, certain peaks vanish. These are ascribed to splitting arising from crystal forces.

INTRODUCTION

IN order fully to exploit the spectra of polymers, it is necessary, as with any substance, to carry out a detailed analysis and assignment of frequencies.

The authors had occasion to make a careful examination of polyethylene and two polyamides, nylon 6 (polycaprolactam, $((-(CH_2)_5CONH-)_n)$ and nylon 11 $((-(CH_2)_{10}CONH-)_n)$, the polymer of ω-amino-undecanoic acid. Although these or similar materials have been studied before, most of the published studies were made at low resolution, over a limited spectral range, or in one phase only. It was therefore thought worthwhile to carry out a careful study of these substances, with a view to making the most complete analysis possible of the spectra.

It may be noted that these three substances have some superficial similarity. Nylon 11 has a normal hydrocarbon chain of ten carbon atoms in its repeating unit so that its spectrum might be expected to resemble that of a hydrocarbon to some extent.

Experimental

Two infrared spectrophotometers were used in this work. A Perkin-Elmer model 21 (CaF_2 and NaCl optics) was used for the 2–15 micron range and a Beckman IR 2-T (KBr optics) was used for the 15–25μ range.

Polarization spectra in the 2–15μ range were obtained with a standard Perkin-Elmer silver chloride polarizer. A slotted cardboard mask was put into the reference beam to compensate for light lost in the polarizer. Sample orientation was changed by rotating the sample with the polarizer fixed.

Spectra of melts were obtained in a vertical high temperature cell built around the heating element and thermocouple from a Perkin-Elmer horizontal cell with heated sample stage. The heated stage was mounted vertically in the sample beam on a yoke. The sample was held sandwiched between circular rocksalt windows, in a tubular cell. The windows were clamped in place by

a sleeve which screwed into the tube. This assembly was fitted into the well of the vertical heated stage.

Two polyethylenes were used, one of moderate (I) and one of high (II) crystallinity and low methyl concentration.[1] Measurements on these samples were augmented by measurements on n-dotriacontane and on stearone. The n-dotriacontane, obtained from the Eastman Kodak Company, was recrystallized from ethanol. The stearone, obtained from the Armour Company, was twice recrystallized from toluene.

The polyamide samples were in the form of films from the corresponding polymers. For obtaining melt spectra, the polyamide films were heated until the 3077 cm⁻¹ peak vanished (195°–200°C). The melt spectra of the polyamides were run over short regions of the spectrum on a given try, allowed to solidify, and then rerun. It was hoped in this way to minimize thermal decomposition or oxidation. That this was achieved was shown by the lack of discoloration in the resolidified samples and the similarity of the spectra of the original and resolidified samples.

In some samples of polyethylene melt, where scattering was serious, the scale was magnified by putting the polarizer mask in the reference beam. This clarified detail which would otherwise have been obscured (Fig. 3).

Theory

The group theoretical treatment of chain molecules[2] shows that the symmetry of a chain molecule may be described by a one-dimensional space group, a "line" group. Analysis of the character tables for line groups shows that only those normal modes which are totally symmetric under translation may appear as active fundamentals. Of these, only those modes which belong to the same irreducible representation as a component of

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[1] The crystallinities by an x-ray diffraction method [J. Polymer Sci. **18**, 17 (1955)] were found to be 75 and 90 weight percent for polyethylene samples I and II.

[2] M. C. Tobin, J. Chem. Phys. **23**, 819 (1955).

the dipole moment or polarizability may appear. However, some combinations between the vibrational branches and rotational or translational branches may be spectrally active. This could activate the entire branch associated with a forbidden fundamental, or broaden a permitted fundamental.

In crystalline polymers, bands which are singlets in the amorphous material may split in the crystal. This will happen if more than one chain passes through the unit cell. In crystals, some modes which are translations or rotations in the free molecule may appear as active lattice vibrations or librations. These modes and their overtones may appear as combinations with internal motions of the chain.

In crystals such as those of the polyamides, where hydrogen bonding is strong, appearance of such combinations is quite likely. Likewise, whole vibrational branches may be activated through combinations with lattice modes. This would give rise to a broad band.

While it is not possible to obtain polymers in the form of the aligned, isolated chain, it is to be expected that frequencies observed in either the crystalline or amorphous material should not lie too far from those expected for such a chain. One may thus, by proper analysis of the experimental data, deduce fundamental frequencies for the hypothetical chain. The crystalline material, which is subject to strict selection rules, gives the most useful information, but valuable comfirmatory data may be drawn from the spectrum of amorphous material.

I. POLYETHYLENE

The infrared spectrum of polyethylene has been studied at high resolution by Rugg, Smith and Wartman.[3] Polarization spectra are given for stretched films over the entire 2–15μ range. Melt and solid spectra are given in the 7–15μ range.

The most thoroughly studied band is the 720–730 cm^{-1} doublet.[4–6] The motion giving rise to this doublet has been shown to be the CH$_2$ rocking motion across the chain. When the films are melted, the 730 cm^{-1} band disappears, leaving only a broad band at 720 cm^{-1}. The doublet has been shown to arise from splitting of the rocking motion by crystal forces.[2–6] The 730 cm^{-1} band absorbs along the crystal a axis and the 720 cm^{-1} band absorbs along the crystal b axis.[4]

Similar behavior has been reported for the CH$_2$ bending bands in the 1450–1475 cm^{-1} region,[5] but no spectra have been published. The weak bands in the 1300–1375 cm^{-1} regions have been studied experimentally,[3] but their behavior has not been analyzed.

It was therefore thought worthwhile to make a careful scan of the spectrum with a view to extending
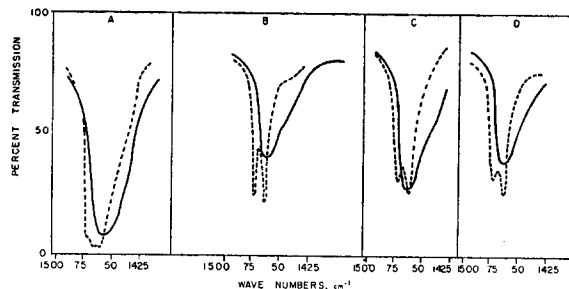

FIG. 1. Infrared spectra of solid and molten polyethylene, dotriacontane, and stearone in the 1400–1500 cm^{-1} region. (A) Polyethylene I, (B) polyethylene II, (C) dotriacontane, (D) stearone. Melt ——. Solid - - - -.

the results of Rugg, Smith, and Wartman, and making as detailed an assignment of frequencies as possible.

Selection Rules

Polyethylene has a line group with factor group isomorphous to $V_h{}^2$. The mutual exclusion rule holds between the infrared and Raman spectrum. The isolated chain has five infrared active frequencies. Four of these (two CH stretchings, one CH$_2$ bending, and one CH$_2$ rocking) are perpendicular and one (a CH$_2$ wagging) parallel.

In the crystal, each of the perpendicular bands splits into two components, one absorbing along the a axis and one along the b axis. The parallel band splits into two components, one absorbing along the c axis and one inactive. In addition to these bands, an active band absorbing along the c axis is predicted as the active component of a doublet arising from the forbidden A$_u$ CH$_2$ twisting motion of the chain.

Eight Raman-active frequencies are predicted.[7] These, too are expected to split in the crystal.

RESULTS

In Figs. 1 and 2 are shown spectra of the samples as melt and solid in the CH$_2$ bending region. In dotriacontane, stearone, and polyethylene II, there are two sharp peaks at 1463 and 1470 cm^{-1}. Polyethylene I has, in addition, a peak at 1465 cm^{-1}. When the samples are melted, the 1463–1470 cm^{-1} doublet is replaced by a single broad band at about 1464 cm^{-1}. The 1465 cm^{-1} band in I vanishes.

In Fig. 2 are shown polarization spectra of films of I and II as extruded and as stretched about 200% in the extrusion direction. It is seen that in the extruded films (unstretched) the 1470 cm^{-1} band is parallel and the 1463 cm^{-1} band is perpendicular. In the stretched films, both bands are perpendicular. This behavior is identical with that of the 720–730 cm^{-1} doublet, where the dichroism of the 730 cm^{-1} band is reversed by stretching.

[3] Rugg, Smith, and Wartman, J. Polymer Sci. 11, 1 (1953). This paper gives references to earlier literature.
[4] S. Krimm, J. Chem. Phys. 22, 567 (1954).
[5] R. Stein and G. B. B. M. Sutherland, J. Chem. Phys. 22, 1993 (1954).
[6] R. Stein, J. Chem. Phys. 22, 734 (1955).

[7] An incomplete Raman spectrum of polyethylene in CCl$_4$ solution has been obtained by Mr. E. F. LaPointe and Dr. E. Slowinski at the University of Connecticut. The present authors tried without success to obtain a Raman spectrum of polyethylene resin.
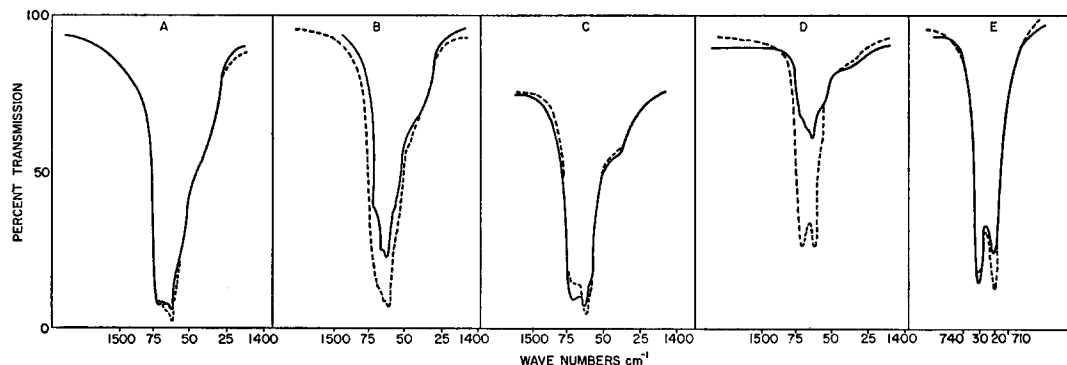
FIG. 2. Polarized infrared spectra of polyethylene I and polyethylene II in the 1400–1500 cm⁻¹ region. (A) Poly-ethylene I unstretched, (B) polyethylene I stretched 300% in extrusion direction, (C) polyethylene II unstretched, (D) polyethylene II stretched 200% in extrusion direction, (E) polyethylene I unstretched, 700–750 cm⁻¹ region. Parallel ——. Perpendicular - - - -.

The relative intensities of the 1463–1470 cm⁻¹ peaks vary in different film samples. This is probably an orientation effect.

The corresponding spectra for the 1300–1375 cm⁻¹ region are shown in Figs. 3 and 4. Polyethylene I and molten dotriacontane have bands at 1300, 1340, 1350, 1372, and 1375 cm⁻¹. The band at 1340 cm⁻¹ appears as a weak shoulder to 1350 cm⁻¹. The 1300–1372 cm⁻¹ bands are very weak in II and the 1375 cm⁻¹ methyl peak is almost absent. In crystalline dotriacontane, the bands at 1300, 1340, and 1350 cm⁻¹ are absent and 1372 cm⁻¹ appears as a weak shoulder to 1375 cm⁻¹. When the polyethylenes are melted, the band at 1372 cm⁻¹ loses intensity relative to that at 1350 cm⁻¹. These bands all have parallel dichroism.

In addition to these relatively prominent bands, there are a number of very weak bands in the spectrum of polyethylene.[8] These bands are tabulated in Table I, for polyethylene I and II, along with the data of Rossman. In Fig. 5, it is seen that the parallel peaks at 1052 and 1173 cm⁻¹ in II are crystalline. The perpendicular complex at 1050–1080 cm⁻¹ is amorphous, since it gains intensity when the films are melted. The band at 1130 cm⁻¹ must consist of both crystalline and amorphous

components, since it weakens, but does not vanish, on melting. The bands at 910, 992, and 1640 cm⁻¹ in II arise from vinyl unsaturation. The very weak band at 966 cm⁻¹ may arise from internal trans-unsaturation.

The spectrum of stearone is sufficiently unlike that of the hydrocarbons to merit a separate description. The most prominent feature (Fig. 6, Table II) of the spectrum is the CO stretching band at 1720 cm⁻¹ in the melt. This band shifts to 1700 cm⁻¹ in the crystal. There is also a band at 1412 cm⁻¹ in the melt which splits into a doublet at 1412–1420 cm⁻¹ in the crystal. This may be a CO bending band, since it was also observed in a sample of oxidized polyethylene wax. In the melt, the band contours in the 1300–1375 cm⁻¹ region resemble those in the hydrocarbons, except that there are no sharply defined peaks at 1340–1372 cm⁻¹. In the crystal, there is an irregular fine structure extending at least from 758 to 1320 cm⁻¹. The origin of this fine structure is unknown.

DISCUSSION

Infrared-Active Fundamentals

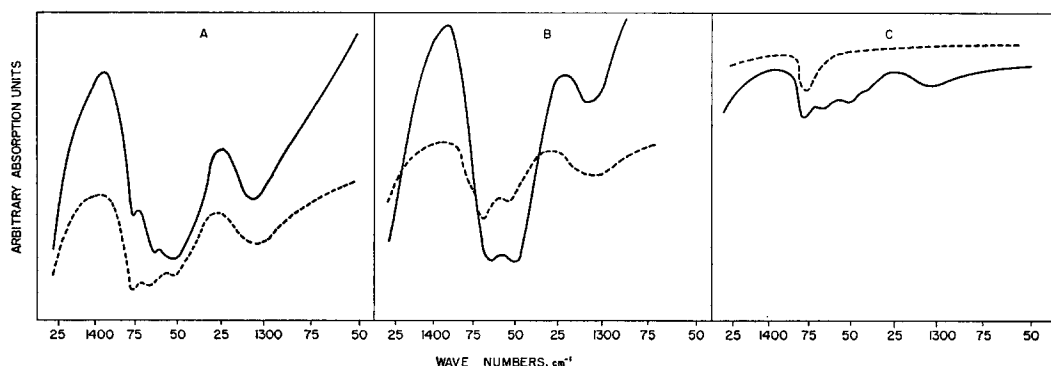The selection rules for the hypothetical, isolated chain of polyethylene predict, as infrared active modes, two

FIG. 3. Infrared spectra of solid and molten polyethylenes and dotriacontane in the 1250–1400 cm⁻¹ region. (A) Polyethylene I, (B) polyethylene II, (C) dotriacontane. Melt ——. Solid - - - -.

⁸ K. Rossman, J. Chem. Phys. 23, 1355 (1955).

CH_2 stretchings (B_{2u} and B_{3u}) one CH_2 bending (B_{3u}), one CH_2 rocking (B_{2u}) and one CH_2 wagging (B_{1u}). The former four modes should appear as doublets in the crystal, the last mode as a singlet. In addition, a B_{1u} twisting mode, arising from the forbidden A_u twisting mode of the chain, should appear in the crystal.

We were unable to resolve any structure in the polyethylene bands at 2920 and 2848 cm^{-1} with our calcium fluoride prism.

The 1463 and 1470 cm^{-1} crystalline bands are readily identified with the B_{2u} and B_{3u} crystalline CH_2 bending modes. The polarization spectra of Fig. 2 show that the 1470 cm^{-1} band is of the same species as the 730 cm^{-1} band. The assignment of these to B_{2u} or B_{3u} is arbitrary, depending on the way the x and y axes are oriented in the crystal. The B_{2u} CH_2 bending in polyethylene lies at

Fig. 4. Polarized infrared spectrum of polyethylene I in the 1250–1400 cm^{-1} region. (A) Unstretched (B) stretched 300% in the extrusion direction. Parallel ——. Perpendicular - - - -.

wagging mode and a B_{1u} twisting mode in the infrared spectrum of the crystal. We assign the B_{1u} wagging mode at 1372 cm^{-1}. The B_{1u} twisting mode should be very weak, since it arises from a forbidden mode of the chain.

Weak Infrared Bands of Polyethylene

The question now arises as to the origin of the amorphous bands at 1300–1372 cm^{-1} and the bands from 888 to 1173 cm^{-1}. The amorphous bands would be expected to arise (1) as characteristic bands of nonplanar chains or (2) from Raman bands activated in the infrared spectrum due to chain disorder. While no Raman spectra have been reported for polyethylene, Raman spectra have been reported for molten and crystalline normal hydrocarbons, including n-cetane.[9,10]

The Raman lines of crystalline polyethylene and of the hypothetical aligned chain may be inferred from these. The Raman bands for crystalline n-cetane are reported as 2963 (2), 2934 (1), 2878 (5), 2846 (3), 1471 (2b), 1442 (2b), 1295 (2), 1135 (2), 1058 (2), 888 (1), and 150 (2) cm^{-1}.

One may reasonably presume that when a Raman band becomes infrared active due to chain disorder, it will retain its parallel or perpendicular character. On

TABLE I. Weak infrared bands of polyethylene, cm^{-1}.

	Polyethylene I		Polyethylene II	
Rossman	Solid	Melt	Solid	Melt
4546				
4464				
4292				
3953				
3597			3500	
3367				
	2720		2720	
	2600		2600	
2421	2440		2440	
2347	2320		2320	
2174	2145		2145	
2037	2020		2020	
1909	1896		1896	
1822	1817		1817	
1715	1737		1737	
1640			1640	
1600				
1176	1173 weak	absent	1173e,d	absent
	1120–46a	1120 weak	1130a,e	1120 weak
1082	1080}	1080 sloping	1080}b,e	1080 sloping
	1064}b	to 1020	1064}	to 1020
	1052}	absent	1052e,d	absent
			992	992
969	966	966	966	?
			910	910
888	888	888	888 very weak	?

a More intense in solid than in melt.
b More intense in melt than in solid.
e Sharp peak.
d Parallel band.
e Perpendicular band.

1463 cm^{-1} in the melt and at 1465 cm^{-1} at room temperature.

We now consider the parallel bands at 1300, 1340, 1350, and 1372 cm^{-1} in polyethylene and in molten dotriacontane. These bands are weaker in polyethylene II than in polyethylene I. In crystalline dotriacontane, only the 1372 cm^{-1} band appears, as a shoulder to 1375 cm^{-1}. We may therefore assign the 1300, 1340, and 1350 cm^{-1} bands to the amorphous regions of the polymer. When polyethylene II (which is free of the methyl band at 1375 cm^{-1}) is melted, the 1372 cm^{-1} band loses intensity relative to the 1350 cm^{-1} band. We interpret this to mean that in polyethylene there are both crystalline and amorphous bands at 1372 cm^{-1}. The crystalline component absorbs more strongly than the amorphous component, since the band loses intensity on melting. The selection rules predict an active B_{1u}
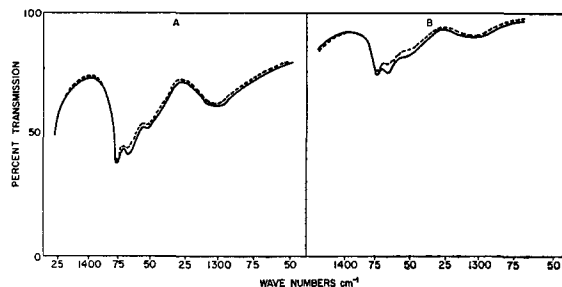

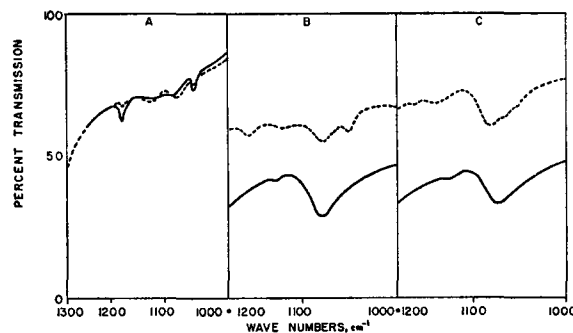Fig. 5. Polarized and melt spectra of polyethylene I and polyethylene II in the 1000–1200 cm^{-1} region. (A) Polarization spectrum of polyethylene II, 0.010 in. film. Parallel ——. Perpendicular - - - - (B) polyethylene II (C) polyethylene I, 0.020 in. films. Melt ——. Solid - - - -.

9 S. Mizushima and T. Simanouti, J. Am. Chem. Soc. 71, 1320 (1949).
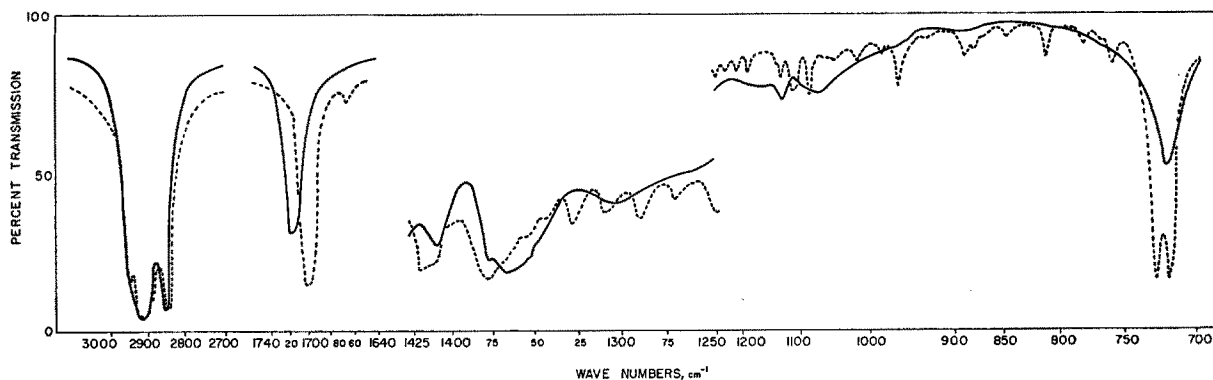10 E. Rosenbaum, J. Chem. Phys. 9, 295 (1941).

FIG. 6. Infrared spectra of solid and molten stearone. Melt ———. Solid ⋯⋯.

this basis, we assign the 1295 cm^{-1} crystalline Raman band and the 1300 cm^{-1} amorphous infrared band to the parallel B_{2g} CH$_2$ twisting or B_{3g} CH$_2$ wagging. The amorphous bands at 1340, 1350, and 1372 cm^{-1} have counterparts in the Raman spectra of molten hydrocarbons.[9] On the basis of their parallel dichroism, they

TABLE II. Infrared bands of stearone, cm^{-1}.

Solid	Melt
2950	2950
2920	2910
2848	2848
2700	2700
1700	1720
1668	
1472⎫	
1463⎬	1463
1420⎱	
1412⎰	1412
1380	1380
1365	1365
1350	1350
1340	1340
1328	1300
1310	
1290	
1270	
1245	
1225	
1205	
1185	
1135⎫	
1128⎬	1128
1108⎱	
1102⎰	1098
1082	
1060	1070
1045	
1012	
980	970
960	
921	920
888⎫	
878⎬	
870⎭	
848	
810	
779	
758	
730⎫	
719⎬	719
680⎭	

are ascribed to wagging or twisting modes characteristic of disordered chains.

The infrared band at 888 cm^{-1} is very weak in polyethylene II, and the Raman band at 888 cm^{-1} weakens with increasing chain length.[10] On this basis, we ascribe these bands to a methyl vibration.

The very weak crystalline and amorphous bands at 1130 cm^{-1} correspond to the Raman band at 1135 cm^{-1}. In view of their position in the spectrum and the perpendicular dichroism of the infrared bands, we assign these bands to the A_g C—C stretching mode. The appearance of the crystalline component, like the appearance of the band at 1052 , is ascribed to the effect of small crystallite size weakening the selection rules.[2]

In the region of the parallel crystalline band at 1052 cm^{-1} and the perpendicular amorphous bands at 1052, 1064, and 1080 cm^{-1}, there is only one Raman band. This lies at 1058 cm^{-1}. The types of normal mode which might be expected to lie in this spectral region are a skeletal mode (parallel), a CH$_2$ rocking (perpendicular) and CH$_2$ twisting or waggings (parallel). In the Raman spectrum of molten n-cetane, there is a series of Raman bands at 1050–1080 cm^{-1} corresponding to the infrared bands. These facts may be explained by supposing that two Raman-active normal modes lie at 1058 cm^{-1}. One of these, the perpendicular CH$_2$ rocking, is spread out into a progression by chain disorder. The remaining band appears at 1058 cm^{-1} in the crystalline infrared spectrum for the reason mentioned above.

The crystalline band at 1058 cm^{-1} may be assigned either as the B_{2g} skeletal motion, or the B_{3g} twisting or B_{2g} wagging motion. It seems preferable to assign it to one of the latter for the following reason. The normal hydrocarbons all have a low-lying Raman line, dropping from 425 cm^{-1} in n-butane to 150 cm^{-1} in n-cetane.[9] This does not arise from a crystalline lattice mode, since it appears in the spectrum of the melt. It seems too strong to be a chain torsion, since these are forbidden (nonfactor group) modes in a long chain.[2] It seems most likely that this is the B_{2g} skeletal motion, which is a C$_3$ bending motion. The band at 1058 cm^{-1}, then, arises from a methylene motion.
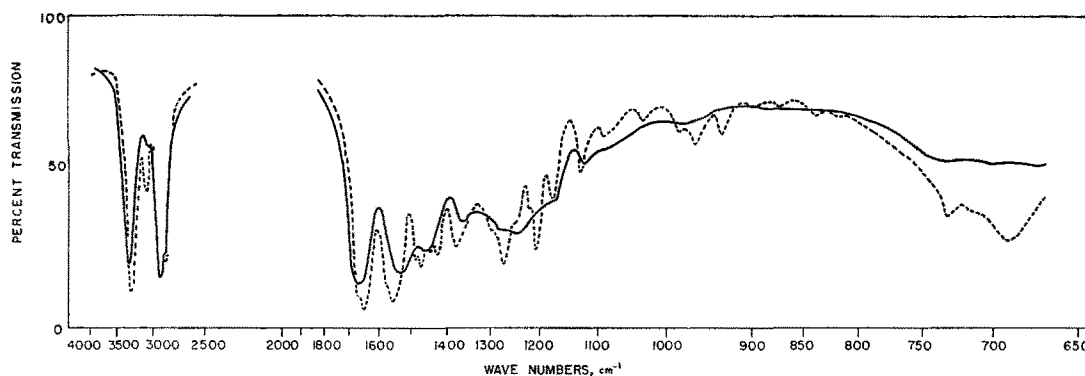
FIG. 7. Infrared spectra of solid and molten nylon 6. Melt ——. Resolidified ----.

The only remaining unassigned infrared band is the crystalline band at 1173 cm^{-1}. This may be the B_{1u} twisting motion of the crystal, arising from the forbidden A_u twisting mode of the isolated chain.

Overtones and Combination Tones

Besides the fundamental bands discussed, a number of weak infrared bands appear in the overtone region. In order to discuss these, it is necessary to locate the CH$_2$ stretching and bending fundamentals. The infrared active bands are seen from Figs. 3 and 6 to lie at 1465 (B_{3u}), 2848, and 2920 (B_{2u} and B_{3u}) cm^{-1}.

There are two Raman bands reported for n-cetane, at 1442 and 1471 cm^{-1}.[9,10] The doublet does not arise from crystal splitting, since both bands are present in the melt. Neither is a methyl mode, since the only methyl band in this region[3] lies at 1456 cm^{-1}. We therefore ascribe the splitting to Fermi resonance with 2×730 and assign the Ag CH$_2$ bending at 1456 cm^{-1}.

There are four Raman bands, at 2963, 2934, 2878, and 2846 cm^{-1}. Methyl bands are reported at 2959 and 2874 cm^{-1} in the infrared spectrum, so that the corresponding Raman bands may be due to these. However, assuming the usual symmetric-below-asymmetric rule, the lower Raman band should be an A_g frequency. This could be

split by Fermi resonance with 2×1456 or 2×1465. We assume that this happens and assign the fundamental at 2862 cm^{-1}. There does not seem to be any reasonable way that the B_{1g} CH$_2$ stretching could be split by Fermi resonance, so that this mode is assigned at 2934 cm^{-1}.

The assignment resulting from the discussion of this and the two preceding subsections is summed in Table III, for the hypothetical aligned, isolated chain. Some of the infrared bands split in the crystal. None of the Raman bands of the crystal were reported as split, even though theory predicts such splitting. This splitting must be quite small.

As is seen from Table IV, this assignment may be used to account for the overtone bands observed in the infrared spectrum, in a plausible manner.

II. NYLON 6 ((−CH$_2$)$_5$CONH−)$_n$ AND NYLON 11 ((−(CH$_2$)$_{10}$CONH−)$_n$

Several studies have been made of specific regions of the spectra of polyamides. Bellamy[11] has given a review of the literature on polypeptides and polyamides. Thompson and Torkington[12] and Elliott, Ambrose, and Temple[13] have given low dispersion spectra of several polyamides. Ambrose, Elliott, and Temple[14] have given

TABLE III. Assignment of normal modes for the hypothetical polyethylene chain.

	Bands cm^{-1}	Factor group symmetry	Classification
ν_5	2934	B_{1g}	CH$_2$ stretching
ν_{13}	2920	B_{3u}	CH$_2$ stretching
ν_1	2862	A_g	CH$_2$ stretching
ν_{10}	2848	B_{2u}	CH$_2$ stretching
ν_{14}	1465	B_{3u}	CH$_2$ bending
ν_2	1456	A_g	CH$_2$ bending
ν_7	1372	B_{1u}	CH$_2$ wagging
ν_{12}	1300	B_{3g}	CH$_2$ twisting
ν_4	1173	A_u	CH$_2$ twisting
ν_3	1135	A_g	CC stretching
ν_8	1058	B_{2g}	CH$_2$ wagging
ν_6	1058	B_{1g}	CH$_2$ rocking
ν_{11}	719	B_{2u}	CH$_2$ rocking
ν_9	150	B_{2g}	C$_3$ bending

TABLE IV. Assignment of overtone and combination bands in the infrared spectrum of polyethylene.

4546	2934+1058+719
4464	2934+1372
4292	2848+1372
3953	2848+1058
2720	2×1372
2600	2×1300
2440	1300+1173
2320	2×1173 or 1300+1058
2145	1135+1058
2020	2×1058
1896	1173+719
1817	2963−1082 (?)

[11] L. Bellamy, *The Infrared Spectra of Complex Molecules* (John Wiley and Sons, Inc., New York, New York, 1940).
[12] H. Thompson and P. Torkington, Trans. Faraday Soc. **41**, 246 (1945).
[13] Elliott, Ambrose, and Temple, J. Chem. Phys. **16**, 877 (1948).
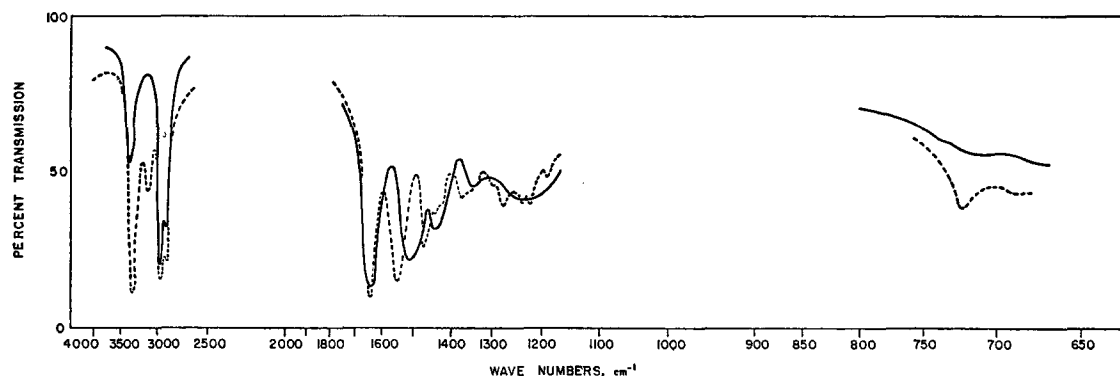[14] Ambrose, Elliott, and Temple, Proc. Roy. Soc. (London) **A199**, 183 (1949).

FIG. 8. Infrared spectra of solid and molten nylon 11. Melt ———. Resolidified - - - -.

spectra of 6,6 nylon under high resolution in the 2800–3600 cm^{-1} region. Kessler and Sutherland[15] have studied the 700–750 cm^{-1} region in deuterated and ordinary polyamides. They ascribe the absorption in this region to an NH deformation mode.

The crystal structures of several polyamides have been given by Bunn and co-workers.[16,17] They find 6,6 and 6,10 nylon to form triclinic crystals with one chain passing through each unit cell. Nylon 6, on the other hand, has a monoclinic unit cell (space group $P2_1$) with four chains passing through it. Each unit cell contains eight monomer units. This requires that in the crystal, the bands be parallel or perpendicular. Each band of the melt should split into four components in the crystal, although the splitting need not always be resolved. The split components should have the same dichroisms as the normal mode of the isolated chain from which they arise. The crystal structure of nylon 11 has not yet been determined, but will be assumed to resemble that of nylon 6.

The spectra of nylons 6 and 11 are shown in Figs. 7–10. The bands of the solid and molten films are tabulated in Table V.

Figure 7 shows the infrared spectrum of nylon 6 as obtained with a sodium chloride prism. Another spec-trum (not shown) was taken with a calcium fluoride prism. This provided the values given in Table V. The spectra in the KBr region are not shown, since only a few weak bands appeared.

Before discussing the spectra in detail, it is interesting to discuss the gross features. The bands are highly dichroic, indicating good orientation of the films in the extrusion direction. The spectrum of nylon 6 in film as extruded is shown. The spectrum of nylon 11 is of film stretched 100% in the extrusion direction. On melting, the sharp peaks below 1500 cm^{-1} vanish, leaving only broad background bands. Several of the bands shift and change in intensity. There are two possible explanations for the peaks. One is that they are individual normal modes which broaden when the films are melted. The other is that they are the components arising from the crystalline splitting of normal modes. This will be discussed below. The dichroisms of the 1550 and 1650 cm^{-1} bands are opposed, showing that the chains are in the β extended configuration.[11]

The spectra in the 2800–3500 cm^{-1} region are typical of polyamides. They are identical in our two films except for a weak shoulder at 3420 cm^{-1} in nylon 6. This indicates some unbonded NH. There has been con-siderable controversy over the nature of the bands at
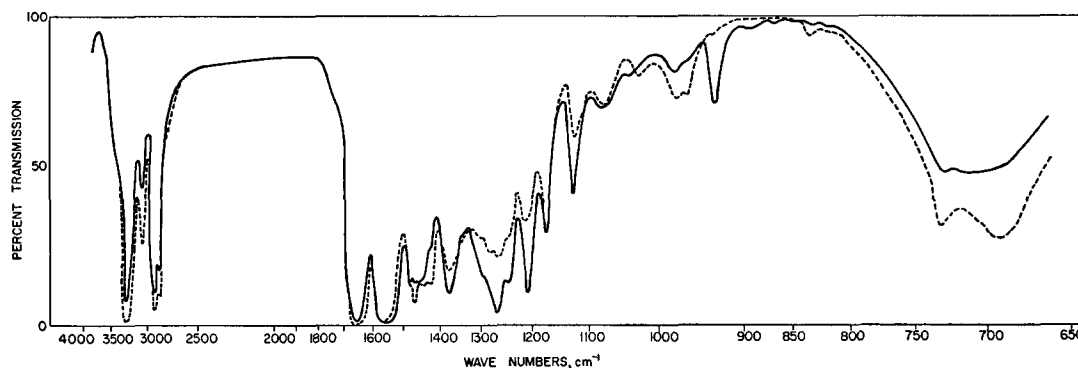

FIG. 9. Polarized infrared spectrum of nylon 6. Parallel ———. Perpendicular - - - -.

[15] H. Kessler and G. B. B. M. Sutherland, J. Chem. Phys. 21, 571 (1953).
[16] C. Bunn and E. Garner, Proc. Roy. Soc. (London) A206, 192 (1951).
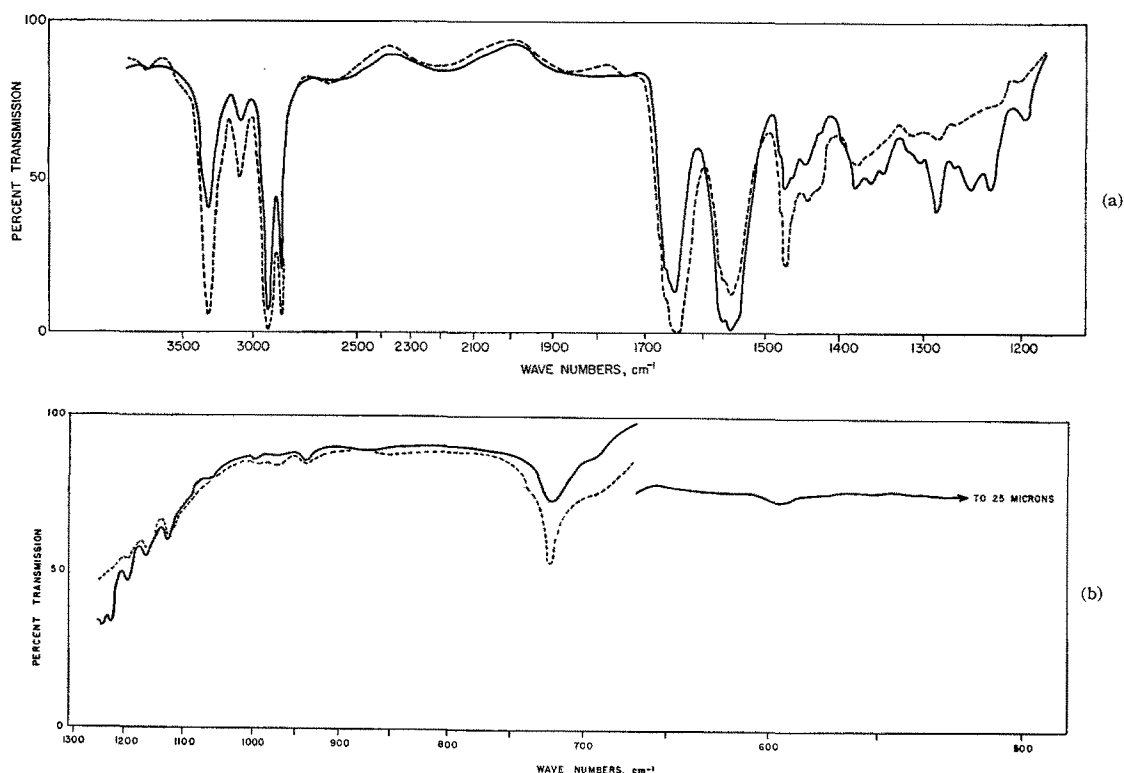[17] Holmes, Bunn, and Smith, J. Polymer Sci. 17, 159 (1955).

FIG. 10. Polarized infrared spectrum of nylon 11. Parallel ———. Perpendicular - - - -.

3077, 3210, and 3300 cm^{-1}.[11,18] Those bands are known to be NH frequencies since they disappear when the amido hydrogen is removed. When the films are melted, the band at 3077 cm^{-1} vanishes and the band at 3300 cm^{-1} loses intensity and shifts its position slightly. This makes it likely that the absorption at 3077 cm^{-1} arises from hydrogen-bonded NH in the crystal. Badger and Pullin[19] have suggested that the band at 3080 cm^{-1} may be the first overtone of 1553 cm^{-1}. It is not clear to us why the first overtone should be perpendicular when the fundamental is parallel. In any event, the crystalline nature of this band seems clear. The band at 3300 cm^{-1} must arise at least in part from amorphous portions of the polymer, since it shifts position only slightly when the films are melted. The smallness of this shift demonstrates that hydrogen bonding persists into the melt. The origin of the shoulder at 3210 cm^{-1} is uncertain.

Of greater interest are the perpendicular band at 1650 cm^{-1} and the parallel band at 1550 cm^{-1}. When the films are melted, the latter broadens, loses intensity, and shifts to about 1520 cm^{-1}. In nylon 11, the 1650 cm^{-1} band shifts little, but in nylon 6 it shifts to 1680 cm^{-1}.

There has been considerable debate[11] as to whether the 1550 cm^{-1} band is a parallel NH bending frequency or a vibration characteristic of the amido group as a whole. The present results indicate that it is to some extent localized in the NH bond, since this vibration is

[18] Disc. Faraday Soc. No. 9 (1950), p. 324 et. seq.
[19] R. Badger and A. Pullin, J. Chem. Phys. **22**, 1142 (1954).

TABLE V. Infrared bands of nylon 6 and nylon 11, cm^{-1}.

Nylon 11		Nylon 6	
Solid[a]	Melt	Solid[a]	Melt
3300⊥	3300	3420⊥	
3210⊥	3210	3280⊥	3310
3077⊥		3200⊥	
2924⊥	2924	3080⊥	
2849⊥	2849	2910⊥	2910
1658⊥	1658	2860⊥	2860
1553‖	1520	1650⊥	1680
1475⊥		1560‖	1520
1468⊥	1460 broad	1480⊥	
1459?		1465⊥	1450
1438⊥		1440⊥	
1422⊥		1420⊥	
1376‖		1370‖	1370
1357‖	1350 broad	1305‖	
1341‖		1280‖	1230–80
1312‖		1265‖	
1300‖		1240‖	
1282‖		1215‖	1220
1263‖		1205‖	1205
1247‖		1170 unpolarized	
1227‖	1220 broad	1115‖	1110
1195‖		1075‖	1080
1160‖		1040‖, 1030⊥	
1130‖		977⊥	
940‖		962⊥	
732⎱	690–730	926‖	
720⎰⊥	broad with	832‖	
690⎰	no peak	730⎱distinct	
592		690⎰peaks, ⊥	660–760
		580	broad with
		522	no peaks

[a] The notation ⊥ means that absorption is strongest when the electric vector is perpendicular to the extrusion (or stretch) direction. The notation ‖ means that the absorption is strongest when the electric vector is parallel to the extrusion (or stretch) direction.

clearly more sensitive to hydrogen bonding than the CO vibration. It should be noted that when the hydrogen bonding is relaxed, the NH and CO stretching frequencies go to shorter wavelengths, whereas the bending frequency goes to longer wavelengths. This is understandable, since the hydrogen bonding will introduce a considerable stretching component into the bending motion. This band is probably the best at which to study hydrogen bonding, due to its great sensitivity.

The spectra of both polyamides show a strong, broad absorption in the 650–800 cm^{-1} region. The bands are perpendicular and seem to consist of peaks on a broad background. When the films are melted, the peaks seem to fuse into a broad background absorption. The expected absorptions in this region are the CH$_2$ rocking and NH perpendicular bending. Kessler and Sutherland[15] have shown that the latter absorption falls in this region in polyamides. There is an indication of two maxima in both nylon 6 and 11, so that both absorptions may be present here. The unusual breadth of these bands must arise from the activation of a lattice wing as a combination. The CH$_2$ rocking in polyethylene is much sharper than these bands.

There remain to be discussed the absorptions in the 1000–1500 cm^{-1} range. These strongly dichroic bands are probably modes of the hydrocarbon residue. By analogy with polyethylene, we may assign the perpendicular bands at 1420–1480 cm^{-1} to CH$_2$ bendings and the parallel bands at 1200–1370 cm^{-1} to CH$_2$ twistings and waggings. The bands at 800–1100 cm^{-1} are probably C—C motions.

These bands are strongly dichroic. Furthermore, the peaks associated with any broad background band in the melt have the same dichroism.

This makes it likely that the sharp peaks represent the components of chain normal modes split by the crystalline field. There are about four peaks per background band in nylon 6, corresponding to the four chains per unit cell. The splitting seems to be 20 cm^{-1} in nylon 6 and 30 cm^{-1} in nylon 11. There could, of course, be some contribution to the structure from lattice-internal mode combinations.

A similar appearance of peaks on going from an amorphous to a crystalline state has been noted in cellulose.[20]

Note added in proof.—Dr. J. R. Nielsen and Dr. A. H. Woollet have, since acceptance of this paper for publication, presented Raman spectra of crystalline paraffins and polyethylene (Symposium on Molecular Structure and Spectroscopy (1956), Paper N8). They find new lines at 1168 and 1415 cm^{-1}. The line at 888 cm^{-1} is missing in Marlex-50 polyethylene, which is known to have a low methyl content. The infrared band at 1173 cm^{-1} must, then, arise from an activated Raman mode, probably the B$_{2g}$ CH$_2$ wagging. The B$_{1g}$ CH$_2$ rocking may be assigned at 1415 cm^{-1}. This leaves either the crystalline Raman band at 150 cm^{-1} (not observed by them) or 1058 cm^{-1}, and the amorphous infrared complex at 1050–80 cm^{-1} to be accounted for. The A$_u$ CH$_2$ twisting is apparently not observed.

[20] F. Forziati and J. Rowen, J. Research Natl. Bur. Standards 46, 38 (1951).