Fourier Transform Infrared Study of Plasticized and Unplasticized Poly(vinyl chloride)

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ABSTRACT: The molecular structure of plasticized and unplasticized poly(vinyl chloride) (PVC) has been examined. The crystalline vibrational spectrum, obtained for normal commercial PVC, is in agreement with that of extended syndiotactic PVC, prepared from urea complex. The plasticized PVC spectra indicate that the crystalline regions are not solvated by the plasticizer. The plasticizer does solvate amorphous chain segments, and this possibly results in complex formation of the type C═O···Cl–C between the carbonyl of the plasticizer and the chloride atom of PVC.

Infrared spectroscopy has been utilized extensively to study the molecular structure of poly(vinyl chloride) (PVC). The spectroscopic results have not been able to be applied to plasticized PVC, in spite of its commercial importance, because of the spectral interference caused by the absorbance bands of the plasticizer. This paper reports the results of a Fourier transform infrared spectroscopic (FTS) study on both PVC and plasticized PVC. The data processing capabilities of FTS[1,2] have been used not only to separate the crystalline spectrum from the total spectrum for commercial PVC but also to separate spectra for polymer and plasticizer components in plasticized PVC.

For PVC much infrared work has been directed toward the detailed assignment of its spectral bands, especially the crystalline vibrational modes[3] and the conformationally sensitive carbon–chlorine stretching modes.[4–6] X-ray diffraction results[7] have indicated that the crystalline component in PVC is an extended syndiotactic structure. Normal, commercially prepared PVC (polymerized at about 50°C) has a very low degree of crystallinity and, as a result, cannot be exclusively used for the determination of crystalline bands in PVC. For the assignment of crystalline modes, infrared spectra have been obtained for stereoregular syndiotactic polymers,[8,9] especially prepared in urea complex[10] and at low temperatures (−78°C).[3] These spectra together with the spectrum for normal PVC and the spectra of deuterated analogs of PVC have been used to determine the bands that are of crystalline or noncrystalline origin and to make detailed vibrational assignments for these bands.[3] These infrared results[3] and the complementary Raman results[11] strongly support the extended syndiotactic conformation for the crystalline regions in PVC. The results from normal coordinate analysis[12,13] of the extended syndiotactic PVC chain are in agreement with the experimental vibrational assignments.

As mentioned previously, the crystalline bands are not resolved in the infrared spectrum of normal, commercial PVC because of the interference from the overlapping amorphous bands. Witenhafer[14] has detected and measured crystallinity in normal PVC by a compensation technique on a high quality grating spectrophotometer. The compensated crystalline spectrum shows only the more intense bands that are also present in the crystalline spectrum of urea complex PVC. A much improved method is included in this paper.

Experimental Section

1. Sample Preparation. The commercial and laboratory samples of unplasticized PVC, used in this study, were obtained from Dr. D. E. Witenhafer of the B.F. Goodrich Chemical Co. The commercial polymer was Geon vinyl 103EPF7 (B.F. Goodrich Chemical Company) with 0.5% Thermolite 73 (M & T Chemical Company) stabilizer added. The laboratory polymer was synthesized by means of ^{60}Co irradiation at −37°C. Samples of the commercial polymer were obtained as films, that had been cast from tetrahydrofuran (THF) solutions in the previously reported infrared compensation procedure.[14] Cast films were also prepared for the irradiated polymer in similar fashion. Briefly, the cast films, after drying in air for 1 day, were heated at 100–110°C for 1 hr to remove residual THF, which was indicated by the loss of the THF band at 1065 cm^{-1}. The films that were to be quenched to the glassy state were then heated to 220–230°C for about 15 sec and quenched into ice–water. The heat treatments were performed in silicone oil.

The plasticized PVC samples were obtained as cast films from the Diamond Shamrock Co. The commercial PVC resin (PVC-40) and the plasticizer, dioctyl phthalate (DOP), were dissolved in THF, and films were cast from this solution. These plasticized films were dried to remove residual THF by the same procedure used for the unplasticized films. Plasticized films were prepared in the following proportions: 5, 20, and 50 parts DOP per 100 parts PVC which correspond to 4.8, 16.7, and 33.3% DOP by weight.

2. Infrared Spectroscopy. The infrared spectra were obtained on a Digilab Model FTS-14 Fourier Transform Spectrophotometer. Each spectrum was recorded in double precision at a resolution of 2 cm^{-1} with a total of 200 scans. The frequency scale is calibrated internally with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. The precision in the reported frequencies is 1 cm^{-1}. The spectra were stored in the system's memory for further data manipulations.

Results

1. Unplasticized Poly(vinyl chloride). (a) Crystalline Vibrational Bands of PVC. Before the crystalline spectrum was obtained for the normal commercial PVC, the PVC sample polymerized at −37°C was investigated. This low-temperature polymer has a higher degree of stereoregularity and therefore crystallinity.[9] Thus, its crystalline spectrum will be more representative of the extended syndiotactic conformation of the PVC chain. Infrared spectra for this PVC polymer are shown in Figure 1. The bottom and middle spectra are for a cast film and a quench film, respectively. The spectrum of the quenched film is still partially crystalline. However, the important point is that the two spectra have different degrees of crystallinity. The top spectrum is a difference spectrum obtained by absorbance subtraction of the quenched film spectrum from the more crystalline cast film spectrum. The procedure employed for absorbance subtraction has been outlined previously.[2] Such a method is similar to the compensation technique used with a dispersive spectrophotometer (where a compensation wedge was used in the reference beam[14]). However, here the compensation is done by digital subtraction of varying amounts of two stored spectra. In this specific case, the ideal criterion for subtraction would be the elimination of the noncrystalline components of the cast film spectrum by subtraction of the desired amount of the more amorphous quenched film spectrum. The remaining

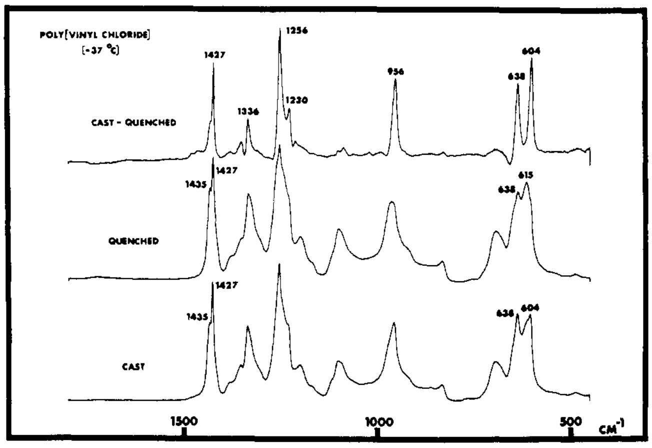

Figure 1. Infrared absorbance spectra of poly(vinyl chloride) prepared at −37°C by irradiation: bottom, cast film; middle, quenched film; top, crystalline regions (cast film–quenched film).

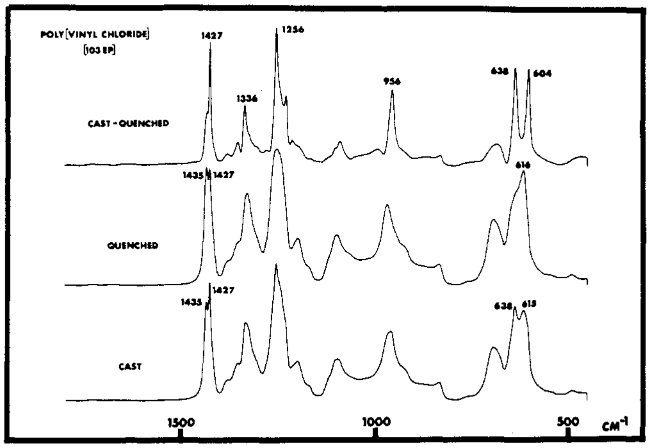

Figure 2. Infrared absorbance spectra of normal commercial poly(vinyl chloride): bottom, cast film; middle, quenched film; top, crystalline regions (cast film–quenched film).

spectrum can then be attributed to the crystalline regions of the PVC sample. The methylene deformations at 1435 and 1427 cm^{-1} have been assigned as amorphous and crystalline bands, respectively.[3] The actual criterion for subtraction was the desired elimination of the 1435 cm^{-1} amorphous band with the necessary requirement that the subtraction does not "distort" any region of the spectrum, such as CH stretching bands (2800–3000 cm^{-1} region) being made negative. The top spectrum in Figure 1 was obtained in this manner. While an exact quantitative subtraction was not performed, this difference spectrum is a qualitative spectrum representing the crystalline regions of the PVC, prepared at −37°C by irradiation.

The crystalline vibrational spectrum for the commercially prepared polymer was obtained in a similar manner. Spectra of the cast and quenched films are shown in Figure 2 together with the crystalline difference spectrum. In comparison with the PVC polymerized at −37°C (Figure 1), notice the expected lower degree of crystallinity in the normal PVC spectra as evidenced by the smaller difference in intensities between the 1427 and 1435 cm^{-1} methylene deformations. The two spectra are extremely similar, and the frequencies are identical within experimental error and are listed in Table I. The crystalline frequencies reported for syndiotactic PVC polymerized in urea complex[3] and those calculated for an isolated chain in the extended syndiotactic conformation[13] are also included in Table I for comparison. The close agreement between the three sets of frequencies indicates that the chains in the crystalline regions of normal PVC have the extended syndiotactic conformation. As a measure of comparison between the crystalline spectra obtained here by FTS and that previously obtained by dispersive spectroscopy,[14] the crystalline frequencies that were previously observed[14] are labeled by an asterisk in Table I. It is seen that a definite improvement has been obtained with the FTS method.

Table I
Frequencies of Crystalline Poly(vinyl chloride)[a]

Difference spectrum[b]	Urea complex spectrum[c]	Normal coordinate analysis[d]
1427*[e]	1428	1445
1381	1387	1404
1354	1355	1311
1336*	1338	1322
1256*	1258	1278
1230*	1230	1233
1214	1195	1169
1104	1105	1122
1089*	1090	1076
1024	~1030	1022
956*	960	1002
832	835, 840	835
638*	640	639
604*	604	619

[a] Frequencies in cm^{-1}. [b] Data for difference spectra in Figure 3. [c] Data from Krimm et al.[3] [d] Data from Tasumi and Shimanouchi[13]. [e] Frequencies labeled with an asterisk are those crystalline frequencies detected by Witenhafer.[14]

It can be noted that the carbon–chlorine stretching vibrations in the 670–710 cm^{-1} region have not been completely eliminated by the subtraction procedure. This point will be covered in a succeeding section.

(b) Crystalline Vibrational Bands as a Function of Crystallization Conditions. The quenched films, made from the commercial polymer, were recrystallized under different conditions. The crystalline vibrational spectra were obtained for the crystallized samples. The crystalline spectra were essentially identical with those shown in Figure 2 except for the methylene rocking vibration (956 cm^{-1}) and the carbon–chlorine stretching vibrations (638 and 604 cm^{-1}).

The various recrystallization conditions employed in this study are listed in Table II together with the specific frequencies for the methylene rocking and carbon–chlorine stretching modes. The crystalline spectra for the carbon–chlorine stretching modes are shown for selected samples in Figure 3. As can be seen, the modes decrease in frequency as the recrystallization temperature is increased to the range of 95–105°C after which the frequencies remain essentially constant.

The question arises as to whether the observed spectral changes are a result of the particular subtraction procedure. First, a quenched film was taken to be representative of the amorphous areas in all of the samples, regardless of the recrystallization conditions. Absorbance subtractions were also performed between films recrystallized at 85°C for 60 and 240 min and films recrystallized at 105°C for 10 sec and 5 min. Here, the spectra used for the more crystalline and more amorphous spectra were for samples crystallized at the same temperature. In each instance, the subtracted crystalline spectrum, including the frequencies of these three particular vibrational modes, were the same as the crystalline spectrum obtained by subtraction where the

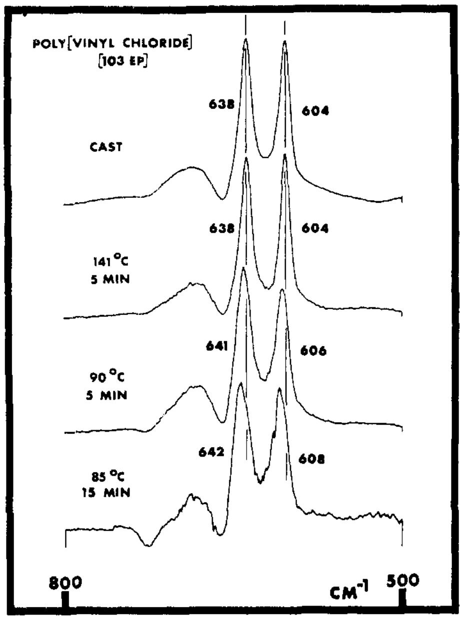

Figure 3. Carbon–chlorine stretching vibrations of crystalline regions for normal poly(vinyl chloride) sample: (1) recrystallized at 85°C for 15 min; (2) recrystallized at 90°C for 5 min; (3) recrystallized at 141°C for 5 min; (4) cast film.

quenched film spectrum was used for the more amorphous spectrum. Hence, it appears that the change in the amorphous spectrum as a function of crystallization conditions is negligible and that the use of the quenched film for the amorphous sample in the subtraction procedure is acceptable. There is also the possibility that the observed spectral changes result from an increase in crystallinity. For this point, the relative degree of crystallinity for the recrystallized samples has been estimated in Table II. As previously mentioned the methylene deformations at 1427 and 1435 cm^{-1} have been assigned to the crystalline and amorphous phases.[3] Even though the 1427 cm^{-1} band is still intense in the quenched spectrum, the ratio of intensities of the 1427 and 1435 bands will give a relative measure of crystallinity for samples made from the same polymer. The intensity ratio for the quenched film is 0.98. As can be seen from Table II, the observed frequency shifts in the methylene rocking modes and the carbon–chlorine stretching modes are not explained by the specific degree of crystallinity in the film.

Both the methylene deformation mode[15] and the carbon–chlorine stretching modes[4–6] are very sensitive to chain conformation. The glass transition temperature of this commercial PVC was reported as 82.5°C.[14] These spectral results indicate that annealing of PVC directly above T_g results in imperfect crystalline regions. At an annealing temperature higher than 13–23°C above T_g, the crystalline perfection has improved to the point where differences in perfection can no longer be detected by infrared spectroscopy.

(c) **Carbon–Chlorine Stretching Vibrations in the 670–710 cm^{-1} Region.** It will be recalled that the carbon–chlorine stretching vibrations in the 670–710 cm^{-1} region were not completely removed by the subtraction procedure (see Figure 2). The carbon–chlorine stretching region of the three spectra shown in Figure 2 for the commercial PVC are expanded in Figure 4 for closer examination. It can be seen from the difference spectrum that there has been a shift in frequency toward lower values in the 670–710 cm^{-1} region in going from the amorphous quenched sample to the more ordered cast film. This same trend is observed in going from the quenched film spectrum to the recrystallized film spectra.

Table II
Results for Recrystallized Films of Poly(vinyl chloride)

Recrystallization conditions		Frequency, cm^{-1}			
Temp, °C	Time, min	$\gamma_r(CH_2)$	$\nu(C-Cl)$ A_1	$\nu(C-Cl)$ B_2	I_{1427}/I_{1435}[b]
85	15	963	642	608	1.04
85	60	961	641	607	1.09
85	240	961	641	607	1.10
90	5	959	641	606	1.11
95	5	958	639	605	1.16
105	10[a]	958	638	604	1.15
105	5	958	638	604	1.18
141	5	957	638	604	1.12
179	5	958	638	604	1.06
Cast film		956	638	604	1.20

[a] Seconds. [b] Relative degree of crystallinity.

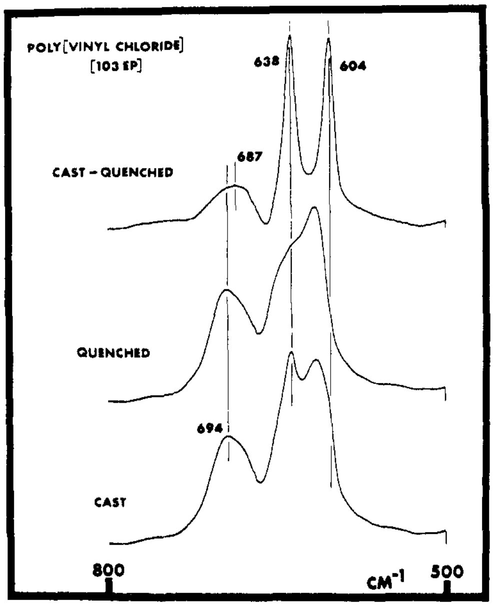

Figure 4. Carbon–chlorine stretching region for normal poly(vinyl chloride): bottom, cast film; middle, quenched film; top, crystalline regions (cast film–quenched film).

Infrared studies[4,5] of model compounds have shown that the carbon–chlorine stretching frequency is sensitive to the rotationally isomeric structure in the vicinity of this bond. These results have been applied to PVC where changes in conformational structure are related to changes in the physical state of the polymer.[6] Briefly, from a series of alkyl chlorides[5] the carbon–chlorine frequency has been shown to depend on the substituents that are trans to the chlorine atom across both adjacent carbon–carbon bonds. For substituents X and Y, this has been designated as S_{XY}. Krimm and coworkers[3] have attributed the 680–700 carbon–chlorine stretching band to noncrystalline structures in PVC. They[3] have shown that this band is actually separable into two bands, centered at 685 and 693 cm^{-1}, and that both are S_{HC} modes. Further, the 693 cm^{-1} band is attributed to the least stable of two permissible conformations for syndiotactic pairs of adjacent chlorine-containing units, while the 685 cm^{-1} band represents the more stable of two possible conformations for isotactic pairs.[3]

The observed decrease in frequency for this 680–700 cm^{-1} band from a quenched sample to a more ordered crys-

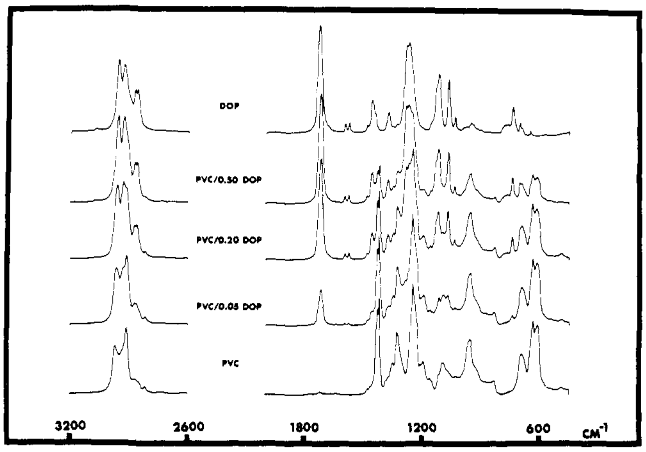

Figure 5. Infrared absorbance spectra of plasticized poly(vinyl chloride) films.

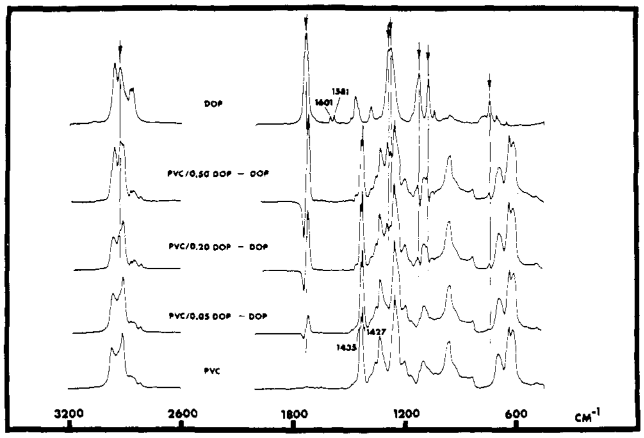

Figure 6. Difference spectra: plasticized poly(vinyl chloride) spectra–plasticizer Spectrum.

talline sample indicates that there is either a decrease in the 693 cm^{-1} band, an increase in the 685 cm^{-1} band, or both. Any of these results would correspond to an increase in a more stable conformation, whether it be for a synoiotactic or an isotactic pair. This observation is consistent with the concepts of annealing.

2. **Plasticized Poly(vinyl chloride).** The infrared absorbance spectra for the three PVC films plasticized with DOP are shown in Figure 5 along with spectra for unplasticized PVC and the DOP plasticizer. It is easy to see the difficulty involved in analyzing the plasticized PVC spectra because of the overlapping spectral bands of PVC and DOP. This task is simplified by appropriate processing of the spectral data for this two-component system.

Analysis of the plasticized PVC spectra, shown in Figure 5, can be approached by removal of the DOP contributions to the total spectra. The DOP spectrum was subtracted from each of the plasticized PVC spectra, and the results are shown in Figure 6. The criterion for subtraction was the elimination of the 1601 and 1581 cm^{-1} in-plane ring vibrations. As can be seen from the difference spectra in Figure 6, insufficient subtraction of the DOP spectral contribution occurred at several positions, each marked with an arrow, because of changes in DOP band intensities and positions which resulted from interactions between DOP and PVC in plasticized films. This point will be covered later. The subtraction has enabled the conformationally sensitive carbon–chlorine stretching region to be examined. This region is shown in Figure 7. There is a decrease in frequency for the S_{HC} modes from 695 to 692 cm^{-1} as the plasticizer content is increased. As with the unplasticized samples examined previously, this frequency decrease reflects an increase in a more stable conformation in the amorphous regions.

From the difference spectra shown in Figure 6, it is apparent that there is some crystallinity present in the plasticized films. From the ratio of band intensities of the two methylene deformations at 1435 and 1427 cm^{-1} the degree of crystallinity is approximately the same in the plasticized and unplasticized PVC films. The crystalline and amorphous spectral components were examined. A quenched glassy sample of the PVC used in the plasticized films was prepared. This spectrum was subtracted from each polymer spectrum in Figure 6. The crystalline frequencies were the same as reported for the unplasticized PVC of the previous sections. This can be seen for the carbon–chlorine stretching region in Figure 8. The crystalline spectrum obtained for this unplasticized PVC sample was likewise subtracted from the plasticized spectra of Figure 6. The resultant amorphous spectra were essentially identical with the quenched PVC sample with the exception of the S_{HC} region already mentioned.

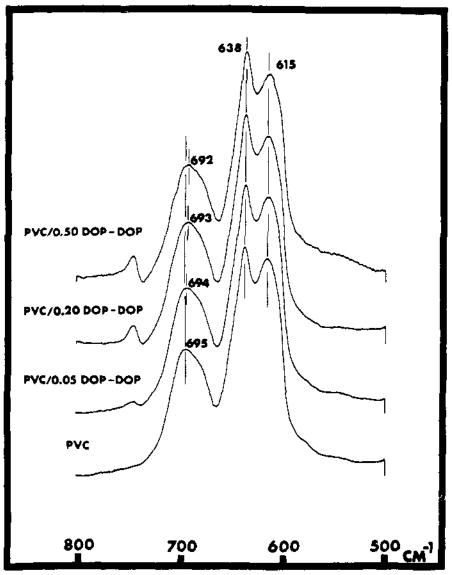

Figure 7. Carbon–chlorine stretching region for plasticized poly(vinyl chloride) difference spectra.

The spectral contribution from the PVC was also removed from the original plasticized spectra of Figure 5. These difference spectra, shown in Figure 9, were obtained by subtraction of the PVC spectrum of Figure 5 from the plasticized PVC spectra. The accurate subtractions of the PVC bands that are obtained demonstrate the essentially identical PVC crystalline and amorphous spectral components just mentioned. The frequencies and relative intensities for the DOP bands as a function of plasticizer content are listed in Table III. The DOP bands that change in position are shown in Table IV. The C=O and C—O modes, especially the C=O group, are affected by plasticization while the methylene and methyl modes are essentially unaffected.

Discussion

The mechanism of plasticization is not adequately understood. It has been proposed that plasticized PVC consists of a three-dimensional network with cross-links of crystallites. The amorphous regions are assumed to be sol-

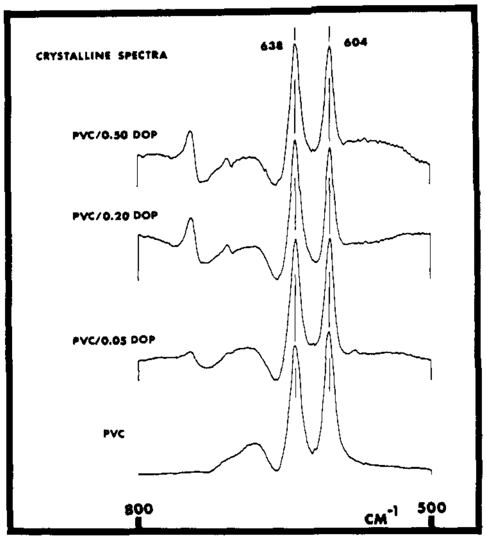

Figure 8. Carbon–chlorine stretching vibrations of crystalline regions for plasticized poly(vinyl chloride) difference spectra.

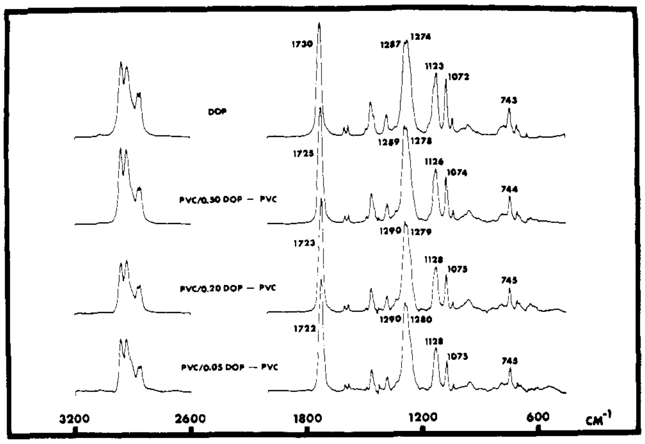

Figure 9. Difference spectra: plasticized poly(vinyl chloride) spectra–poly(vinyl chloride) spectrum.

vated by plasticizer while the crystalline domains are not affected.[16] A nodular structure has been observed in plasticized PVC by electron microscopy.[17,18] Tsou and Geil[18] proposed that possibly there is a crystalline core at the center of each nodule that is not affected by plasticization and that nodular surface material and internodular material can be plasticized. The vibrational results of this study indicate that the crystalline domains are not affected by the plasticization. The crystalline vibrational spectra for the plasticized films were essentially identical with that for unplasticized PVC, including the carbon–chlorine stretching modes. These conformationally sensitive modes would be expected to show the effect of solvation by plasticizer, especially since they were sensitive to crystalline perfection in the unplasticized PVC samples as a function of annealing temperatures. Hence, it can be concluded that the crystalline domains are not plasticized with DOP. Previous wide angle X-ray diffraction results[18] for cast films of plasticized PVC had poor resolution due to the diffuse nature of the diffraction. But, the findings did similarly suggest that the crystalline regions were not affected by the plasticizer.

The effect of plasticization was observed in the amorphous regions, as reflected by changes in the amorphous

Table III
DOP Frequencies and Relative Intensities for Plasticized Films

	Relative peak intensity[a]				
Frequency, cm^{-1}	DOP	PVC/ 0.50 DOP	PVC/ 0.20 DOP	PVC/ 0.05 DOP	Tentative assignment
1730	11.2	13.9	15.1	16.1	ν(C=O)
1601	0.82	0.84	0.81	0.85	In-plane ring
1581	1.0	1.0	1.0	1.0	In-plane ring
1464	3.2	3.3	3.0	2.9	$\delta(CH_2)$, $\delta_s(CH_3)$
1381	1.9	2.0	1.9	2.0	$\delta_a(CH_3)$
1287	8.9	11.4	11.8	12.5	γ(C—O)
1274	9.1	11.2	11.4	11.9	ν(C—O)
1123	6.0	6.3	5.8	6.1	ν(C—O)
1072	5.3	5.3	4.7	4.3	ν(C—O)
1040	1.4	1.2	0.9	0.8	
743	2.3	2.6	2.6	2.7	CH out-of-plane ring

[a] Intensities are normalized to intensity at 1581 cm^{-1}.

Table IV
DOP Frequencies that Change upon Plasticization

DOP	PVC/ 0.50 DOP	PVC/ 0.20 DOP	PVC/ 0.05 DOP	Tentative assignment
1730	1725	1723	1722	ν(C=O)
1287	1289	1290	1290	ν(C—O)
1274	1278	1279	1280	ν(C—O)
1123	1126	1128	1128	ν(C—O)
1072	1074	1075	1075	
743	744	745	745	CH out-of-plane, ring

S_{HC} modes. The vibrational changes that occurred in the DOP modes upon plasticization indicate interactions between the DOP and amorphous PVC. The C=O modes of DOP are mainly affected by plasticization. From interaction studies for low molecular weight liquids, Heald and Thompson[19] have suggested that aggregations of the type C=O- - -Cl–C can occur. The results in this study, the changes in amorphous S_{HC} modes and the C=O modes of DOP upon plasticization, suggest the formation of complexes between DOP and C–Cl groups in amorphous PVC chain segments.

Conclusions

Fourier transform spectra have been obtained for plasticized and unplasticized PVC. The crystalline vibrational spectra, obtained for normal, commercial PVC and more syndiotactic PVC, polymerized at −37°C, are in agreement with extended syndiotactic PVC prepared from urea complex. Spectral changes in the crystalline regions for samples recrystallized from the quenched glassy state indicate crystallite imperfection when the annealing temperature is less than 20°C over T_g. Above this temperature no spectral change in the crystalline domains is detected by infrared spectroscopy.

The crystalline spectra that were obtained from processing of the plasticized PVC spectra indicate that the plasticizer does not penetrate into the crystalline domains. The plasticizer does solvate the amorphous chain segments possibly by complex formation of the type C=O- - -Cl–C.

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Notes

1,2-Dibromotetrafluoroethane as an Initiator for the Photopolymerization of Tetrafluoroethylene

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Since the discovery of poly(tetrafluoroethylene) there has been considerable interest in the photopolymerization of tetrafluoroethylene (TFE). Polymer has been produced in the mercury sensitized photolysis of gaseous TFE. However, analysis showed perfluorocyclopropane to be the main product in this reaction,[2] and at pressures less than 60 Torr it is reported to be the only product.[3] Photopolymerization of gaseous TFE has also been reported in the presence of mercury bromide,[4] phosgene,[5] and nitrous oxide.[6] Low molecular weight polymers are reported to be produced when trifluoroiodomethane,[7] tribromofluoromethane,[8] or trichlorobromomethane[9] are used as initiators in the photopolymerization of TFE. Direct photolysis of TFE results in surface photopolymerization at low monomer pressures[10] and solid polymer floc at monomer pressures above 8 Torr.[11]

This note reports that 1,2-dibromotetrafluoroethane is an efficient and novel initiator for the photopolymerization of tetrafluoroethylene. The solid polymer floc, which is the only product produced in the photolysis reaction, is very similar in structure to linear poly(tetrafluoroethylene) by chemical and infrared analysis. The polymer floc is obtained under reaction conditions where little or no polymer is produced if 1,2-dibromotetrafluoroethane is not present, and where oily telomers are the product if other halocarbons are used as initiators.

Experimental Section

Tetrafluoroethylene was obtained from Matheson Gas Products and was purified by distillation. 1,2-Dibromotetrafluoroethane (Du Pont Chemical Co., Freon 114B2) was purified by fractional distillation. Pentafluoroiodoethane and bromotrifluoromethane were obtained from PCR, Inc. Carbon tetrachloride, iodomethane, bromoethane, iodoethane, and bromine were reagent grade chemicals. The reaction chamber was constructed from a 3 l. Pyrex reaction flask[12] by sealing an optical grade quartz window (3 × 45 mm diameter) over a 3.5 cm hole drilled in the side wall of the flask at the point of largest circumference.

In preparation for a reaction, a tared polystyrene weigh tray (8.0 × 8.0 cm) was placed inside at the bottom of the chamber. The chamber was assembled, tested for leaks under reduced pressure, flushed with dry nitrogen, and evacuated to a pressure equal to atmospheric pressure less the desired monomer pressure. Freshly distilled TFE and initiator were introduced into the reaction chamber. The ultraviolet lamp (Hanovia Lamp Division, 140 W quartz utility lamp), which had thoroughly warmed up, was positioned directly 3 cm in front of the quartz window of the reaction chamber. The reaction was stopped at the end of the desired time interval by turning off the uv lamp and left undisturbed for 10 min to allow all of the polymer floc to settle. The chamber was then flushed with nitrogen and disassembled. The weight of polymer deposited on the plastic tray was determined.

Infrared spectra (KBr pellet) were obtained on a Perkin-Elmer 621 spectrophotometer. Mass spectra were measured using a Finnigan Model 1015 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

It can be seen from the data presented in Figure 1 that over the range of 0–8 mol % there is a direct correlation between the concentration of 1,2-dibromotetrafluoroethane and the amount of polymer produced. Observation of the reaction gives dramatic evidence of the effectiveness of 1,2-dibromotetrafluoroethane as an initiator. With no initiator present, no evidence of polymer formation is visible under these conditions. With as little as 1 mol % of 1,2-dibromotetrafluoroethane present, formation of solid white polymer floc is easily observed. The polymer, which appears to condense from the gas phase, deposits on the top side of all surfaces in the reaction chamber. It was necessary to carefully clean the chamber window between reactions and to limit the percentage of conversion to less than 10%. Complete kinetic analysis of this system has not been completed, but the conversion/time curve for this reaction is that expected of a heterogeneous polymerization, including the marked acceleration at the commencement of the reaction.[13] At a constant concentration of initiator (1.6 mol %), the rate of polymer deposition exhibited first-order dependence on monomer concentration (200 to 400 mm pressure range). Increasing the diameter of the quartz window from 3.5 to 10.8 cm increased the rate of polymer production by over 20-fold. No polymer formation was detected when a Pyrex filter was used in place of the quartz window, indicating that radiation of less than 300 nm is required for initiation. 1,2-Dibromotetrafluoroethane absorbs strongly