

Study of Structure and Thermal Properties of Polypropylene and Chlorinated Polypropylene by Infrared Spectroscopy and Differential Scanning Calorimetry

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Synopsis

The infrared spectra of chlorinated polypropylene (CPP) are interpreted and tentative assignments of C-Cl stretching vibration of CPP are proposed. Recently, infrared spectrophotometry has been applied as a useful tool for the investigation of polymer transitions. The solid-state transition in isotactic polypropylene (IPP) was studied by infrared method in the range of -50° to 30°C ; and from the temperature dependence of the peak absorbance, transition at -10°C was detected. This temperature of -10°C agrees well with the T_{g2} detected by other methods. From these results, it is presumed that T_{g2} is attributed to a motion (thermal expansion) of IPP segments in either crystalline and amorphous region. The thermal transition of chlorinated isotactic polypropylene (CIPP) was also examined with differential scanning calorimetry and infrared method, and two thermal transitions were observed. A higher transition (T_H) has a minimum at a degree of chlorination of about 39 wt-%; and a lower transition (T_L) changes linearly with increasing degree of chlorination. Infrared results indicate that T_H may be associated with a motion (thermal expansion) in chlorinated segments, and T_L may be associated with a motion in unchlorinated segments. These results of infrared studies also suggest that CIPP may have a block structure.

INTRODUCTION

The structure of chlorinated polypropylene has been investigated by infrared spectrophotometry,¹⁻³ but a critical interpretation for the spectrum of this polymer has not been offered. Characteristic infrared frequencies of rotational isomers of alkyl chlorides have been studied by Shipman et al.⁴ and Shimanouchi et al.⁵ According to Shipman et al., the frequency of the so-called C-Cl stretching mode is a function of the detailed structure in the vicinity of the C-Cl bond. In primary chlorides the frequency region depends on whether a hydrogen atom or carbon is trans to the chlorine atom across the common C-C bond. In secondary chlorides it is found that the trans substituents on both C-C bonds adjacent to the C-Cl bond are important in determining the frequency region, and a similar result is observed for tertiary chlorides. Frequency ranges for the various

rotationally isomeric structures of primary, secondary, and tertiary chlorides were given.⁴ If another chlorine atom is trans to the chlorine atom, the frequency ranges are similar to that given for a trans carbon atom.^{5,21}

In the present paper, the author deals with changes of the peak position and the shape of the absorption bands and with some new absorptions which appear with chlorination. From assumptions of Shipman and Shimanouchi, the tentative assignments of a C-Cl stretching vibration of chlorinated polypropylene (CPP) will be proposed.

The thermal properties (especially thermal transitions) of polypropylene have been extensively investigated by thermal analysis,⁶ mechanical testing,⁶ broad-line NMR,⁷ etc., but the relation between structure and transition temperature has not been cleared. In isotactic polypropylene (IPP), three transitions (T_{g1} , T_{g2} , and T_{g3}) have been observed. On the other hand, in chlorinated polypropylene (CIPP), Minsker et al.⁸ have reported anomalous transition behavior of CIPP, but the origin of this transition has not been elucidated.

Recently, several authors have demonstrated that infrared absorption spectrophotometry may be used to detect thermal transitions in solid-state polymers.⁹⁻¹⁷ Infrared spectrophotometry is sensitive to transition behavior in polymers through changes related to the thermal expansion coefficient at the transition temperature and offers a unique possibility for measuring these transitions, since it is uniquely sensitive to a particular structural entity.¹² More recently, Tsuge et al.¹⁶ have reported that T_{g3} in IPP can be detected by infrared, but infrared study for T_{g1} and T_{g2} has been limited in temperature range.

In the present work, the thermal transitions (T_{g1} and T_{g2}) in IPP were estimated by using a cryogenic cell, and the thermal transition of CIPP was also examined with differential scanning calorimetry (DSC) and infrared method, and consequently two thermal transitions were observed. From the infrared results, a molecular mechanism of the anomalous transition in CIPP was proposed.

The results of this study may be useful for understanding the mechanism of the chlorination of polypropylene and offer interesting possibilities for the structure and the thermal properties of CIPP and IPP.

EXPERIMENTAL

Materials

Isotactic Polypropylene (IPP). A commercial polypropylene was extracted with methyl ethyl ketone at 80°C for 50 hr and the insoluble fraction was used.

Atactic Polypropylene (APP). A commercial APP was extracted with ethyl ether at 35°C for 12 hr and the soluble fraction was used. The crystallinity of the former was estimated about 50% and that of the latter, almost 0% by x-ray method.

Chlorination

These polypropylenes were dissolved in $\text{Cl}_2\text{C}=\text{CCl}_2$ and chlorinated with gaseous chlorine at 130°C for 20, 40, 60, 120, and 180 min under irradiation with the mercury lamp. The chlorinated products were precipitated by pouring into methanol, and were collected and dried under vacuum at room temperature. The degree of chlorination was determined by Erdy's method.¹⁸ The results are shown in Table I.

TABLE I
Degree of Chlorination^a

	CA-1	CA-2	CA-3	CA-4	CI-1	CI-2	CI-3	CI-5
Degree of chlorination, wt-%	31.5	53.8	63.7	65.5	32.5	39.4	45.9	56.5

^a CA: Chlorinated atactic polypropylene; CI: chlorinated isotactic polypropylene; the numbers 1, 2, 3, 4, 5 indicate chlorination period (20, 40, 60, 120, 180 mins, respectively).

Infrared Measurements

Chlorinated isotactic polypropylene (CIPP) films were cast from solutions of the polymer in toluene and dried under vacuum at room temperature. IPP film was prepared by a hot-press method (190°C , 500 kg/cm^2 , and 5 min). Infrared spectra of APP and its chlorinates were measured on a CS_2 solution. Furthermore, CIPP films were placed between two KBr plates and the temperature was raised at a rate of $2^\circ\text{C}/\text{min}$ and cooled spontaneously. The heated cell and thermal programming controller system used in this work are shown in Figure 1. The temperature was varied in the range of $25^\circ\text{--}110^\circ\text{C}$. All the spectra were measured on a JASCO Model IR-G infrared spectrophotometer. The band intensities were determined by the "baseline" method. The baselines used in this work are indicated in Figure 3.

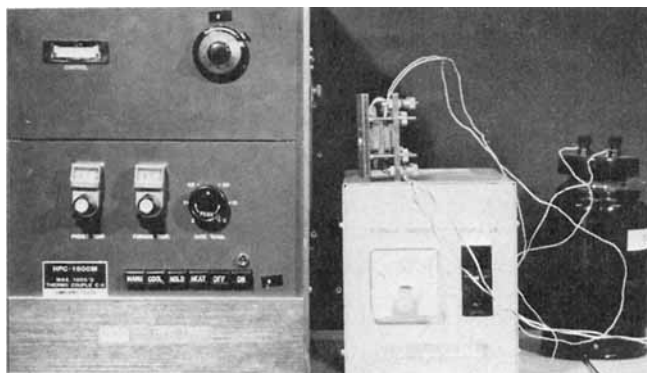


Fig. 1. Heated cell and thermal programming controller system.

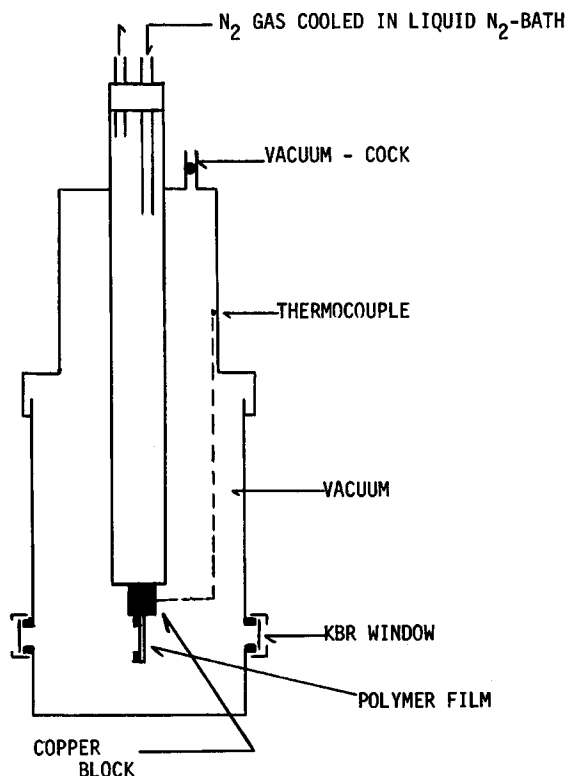


Fig. 2. Schematic drawing of cryogenic cell used for IR studies.

Cryogenic Cell

A simplified schematic drawing of the cryogenic cell used in this work is shown in Figure 2. A copper-Constantan thermocouple was used to measure temperature. Experiments were run between -50°C and 25°C .

Calorimetry

The thermal behavior (-50°C to 140°C) of these samples was examined on a Rigaku differential scanning calorimeter (DSC). The temperature was raised at a rate of $10^{\circ}\text{C}/\text{min}$.

Gel Permeation Chromatography

The mean molecular weight of CIPP was determined on a Waters gel permeation chromatograph (GPC-200). The solvent used was THF.

RESULTS AND DISCUSSION

Infrared Spectra of IPP, CIPP, APP, and CAPP

The infrared spectra of IPP and CIPP are shown in Figure 3. Figure 3 indicates the following interesting points:

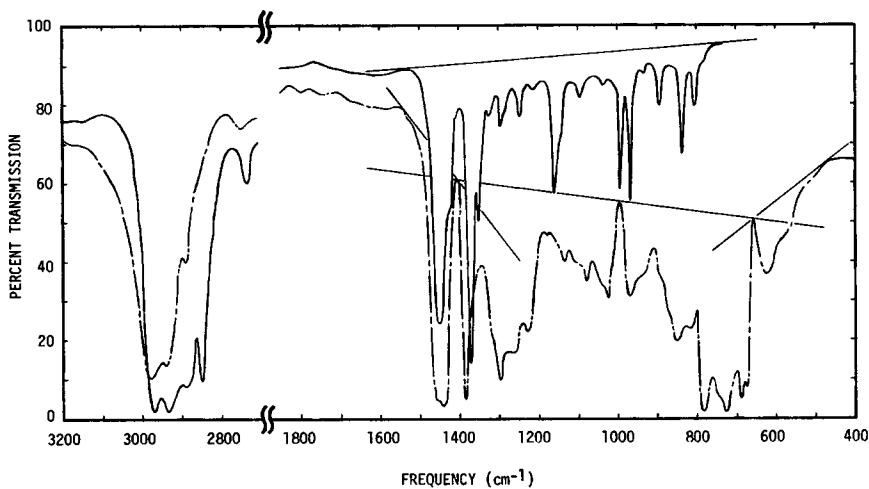


Fig. 3. Infrared spectra of IPP and CIPP (-5).

1. In the 2960–2840 cm^{-1} range, five absorptions (2950, 2924, 2878, 2868, and 2838 cm^{-1}), which have been assigned to carbon–hydrogen stretching vibration,^{19*} were present in the spectra of IPP and CIPP. The absorption frequencies for these bands in CIPP are higher than those in IPP with increasing degree of chlorination. (Fig. 4) The peak intensities of these absorptions decrease with increasing degree of chlorination. In CAPP, similar results were obtained. If chlorine influenced only frequency shifts in this region, distribution of chlorine on the primary, secondary, and tertiary carbon in the PP chain can be determined by infrared data. However, at the present time, it is impossible to confirm that the above assumption is reasonable, and therefore distribution of chlorine in the PP chain will not be discussed in this paper.

2. In the spectra of CIPP, the helix band of IPP¹⁹ at 998 cm^{-1} and the band at 890 cm^{-1} in IPP disappeared. The band at 970 cm^{-1} in IPP was broadened and the band at 1168 cm^{-1} in IPP shifted to 1135 cm^{-1} with increasing degree of chlorination. It has been reported that the band at 1168 cm^{-1} in solid IPP shifts to 1151 cm^{-1} in liquid IPP¹⁹ and asymmetry of the 970 cm^{-1} band is sensitive to helical structure.²⁰ Therefore, in CIPP, the crystal structure may be broken. This is confirmed from the past that crystallinity estimated by the x-ray method was almost 0%.

3. The absorptions in the range of 1460–800 cm^{-1} were broadened, and the relative absorbance to the band at 970 cm^{-1} (internal thickness band) increased with increasing degree of chlorination. The stereochemical difference due to the presence of configurational isomers may be reflected in

* 2950 cm^{-1} : CH_3 asym. stretch (overlapped antisym. and sym. with respect to the H–C– CH_3 plane); 2924 cm^{-1} : CH stretch; 2878 cm^{-1} : CH_2 antisym. stretch; 2868 cm^{-1} : CH_3 sym. stretch; 2838 cm^{-1} : CH_2 sym. stretch.

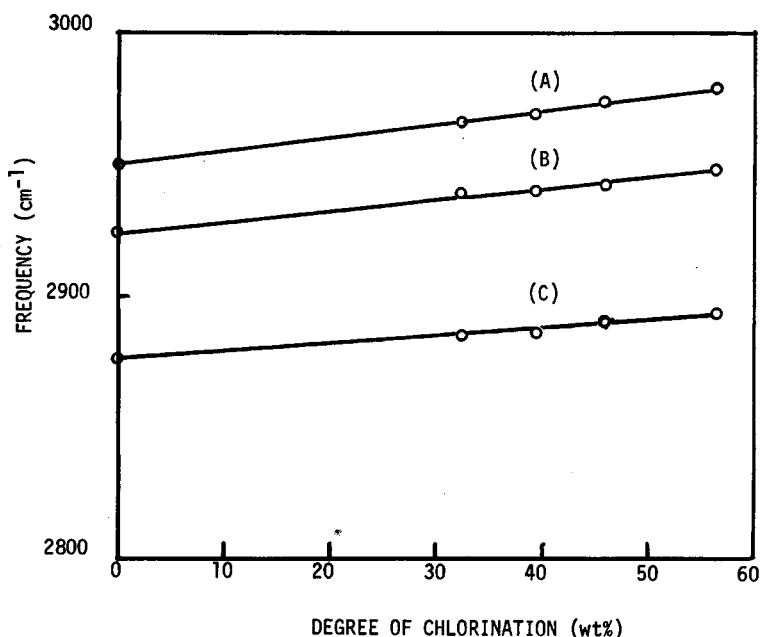


Fig. 4. Frequency shifts of the bands at 2950 (A), 2924 (B), and 2878 (C) cm^{-1} vs. degree of chlorination.

broadening of the infrared bands, and the increasing relative absorbance may be caused by the increase in dipole moment change.

4. In the spectra of CIPP and CAPP, the new absorptions in the range of 800–570 cm^{-1} (far-infrared region), which are probably assigned to C–Cl stretching vibration, appeared. The notation of Mizushima et al.²¹ is convenient for these assignments. According to this system, P, S, and T specify the chemical type of chloride: primary, secondary, and tertiary, respectively. The subscript of H, C, and Cl specifies that the chlorine atom is trans to a hydrogen atom, a carbon atom, and another chlorine atom, respectively.

On the other hand, characteristic infrared frequencies of rotational isomers of alkyl chlorides were studied by Shipman et al.⁴ and Shimanouchi et al.⁵ The results of these investigations were applied for the assignments of C–Cl stretching vibration of CIPP and CAPP. The following tentative assignment will be proposed. The band at 780 cm^{-1} can be assigned to P_{Cl} , S_{CC} , S_{CCl} , or S_{ClCl} . But this band increased suddenly in intensity with 57 wt-% of chlorination, and S_{CC} , S_{CCl} , and S_{ClCl} conformations are not expected to exist in appreciable concentration; so this band is probably associated with P_{Cl} , the chlorine atom attached adjacent to tertiary carbon. The band at 725 cm^{-1} can probably be assigned to P_C . As the peak intensity of the band at 705 cm^{-1} decreased with increasing degree of chlorination (more than 33 wt-%), this band may be assigned to P'_H . The frequency of this band is about 20 cm^{-1} higher than that of Shipman's

results.⁴ (The notation $P_{H'}$ means that the CH_2Cl group is attached to a carbon atom to which the other carbon atoms and a hydrogen atom are also attached.) The band at 685 cm^{-1} can probably be assigned to $P'_{H'}$, but this band overlaps with the band at 675 cm^{-1} , so the change in peak intensity cannot be examined. The band at 685 cm^{-1} may be assigned to S_{ClH} . The band at 675 cm^{-1} can probably be assigned to S_{CH} . The band at 620 cm^{-1} can be assigned to S'_{HH} (bent), S_{HH} (planar), T_{CHH} , or T_{ClHH} . The bands at 620 cm^{-1} and 570 cm^{-1} are wider than other bands of C-Cl stretching vibrations. According to Shipman et al.,⁴ the absorptions of tertiary chlorides are somewhat wider than those of primary and secondary chlorides, so the band at 620 cm^{-1} can probably be assigned to T_{CHH} and T_{ClHH} corresponding to P_{Cl} . The band at 570 cm^{-1} can probably be assigned to T_{HHH} . Due to steric hindrance effects, the occurrence of the other considerable conformations appears improbable. The assignments of the above bands are summarized in Table II.

TABLE II
Assignment of C-Cl Stretching Vibration

Frequencies of C-Cl stretching vibration, cm^{-1}	Chemical-geometrical combination	Applicable range of Shipman's study, ⁴ cm^{-1}
780	P_{Cl}	700-760 (Shimanouchi's general law ⁵)
725	P_C	723-730
705	$P_{H'}$	679-686
685	$P_{H'}$ or S_{ClH}	
675	S_{CH}	655-674
620	T_{CHH} and T_{ClHH}	611-632
570	T_{HHH}	560-581

Thermal Transitions of IPP and CIPP

Isotactic Polypropylene (IPP). Three thermal transitions ($T_{\rho 1}$ at about -30°C , $T_{\rho 2}$ at about 0°C , and $T_{\rho 3}$ at about 25°C) of IPP were detected, but thermal transition mechanism have not been fully interpreted.^{6,7,16} According to Kamide et al.,⁶ $T_{\rho 1}$ has been attributed to motions of PP main-chain segments in the amorphous region, and $T_{\rho 2}$ and $T_{\rho 3}$ have been associated with motions reflecting stereo regularity. The results of the temperature-dependent infrared studies in the range of $0-70^\circ\text{C}$ indicated an abrupt change on the curves of the bands at 1164 , 996 , 973 , and 840 cm^{-1} at 25°C , and this temperature agrees well with $T_{\rho 3}$ detected by other methods.⁸

In this work, the temperature dependence of the infrared spectrum of IPP was examined; and from these results, the transition phenomena of IPP were considered. In Figures 5 and 6, the results of the temperature-dependent infrared studies on IPP are shown. Figures 5 and 6 illustrate

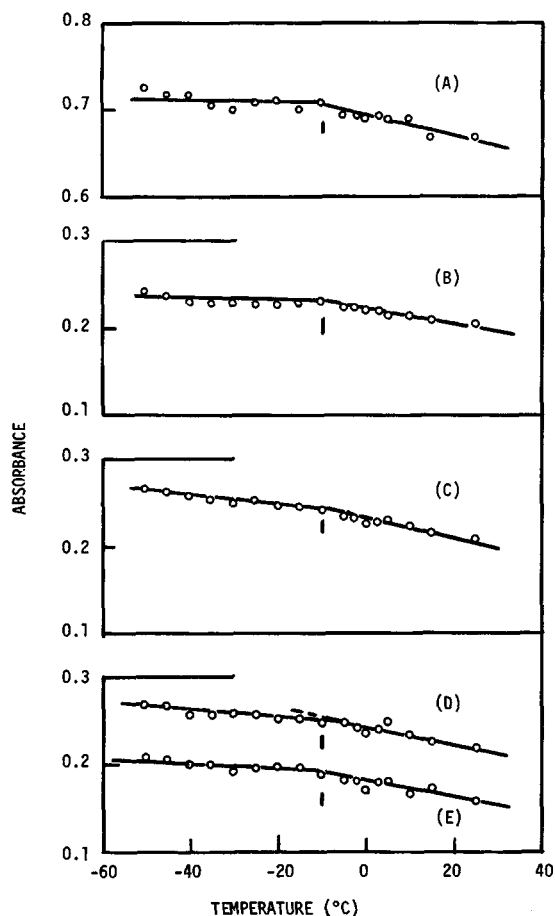


Fig. 5. Peak absorbance for 1450 (A), 1160 (B), 998 (C), 970 (D), and 838 (E) cm^{-1} bands in IPP as a function of temperature (rising temperature).

the peak absorbances for 1450, 1168, 998, 970, and 838 cm^{-1} bands as a function of temperature. The band at 1450 cm^{-1} is assigned to CH_2 asymmetric deformation vibration.¹⁹ The parallel bands at 1168 and 970 cm^{-1} arise from the coupled vibrations of the antisymmetric stretching mode of the axial and equatorial C-C bonds and the methyl rocking mode in the amorphous region.^{19,22} The band at 998 cm^{-1} (crystalline or helix band)¹⁹ arises from the C-methyl stretching mode and the methyl rocking mode in the H-C- CH_3 . The band at 838 cm^{-1} (crystalline band)²² arises from the coupled CH_2 rocking mode and CH bending mode of the axial band. From these results, it is evident that an abrupt change (near -10°C) is observed on the curves of these bands. This temperature of -10°C agrees well with T_{g2} detected by other methods. No abrupt change was observed on the curves of other bands, but not all other bands are associated with thermal transition. Because absorbance of these bands is more weak than

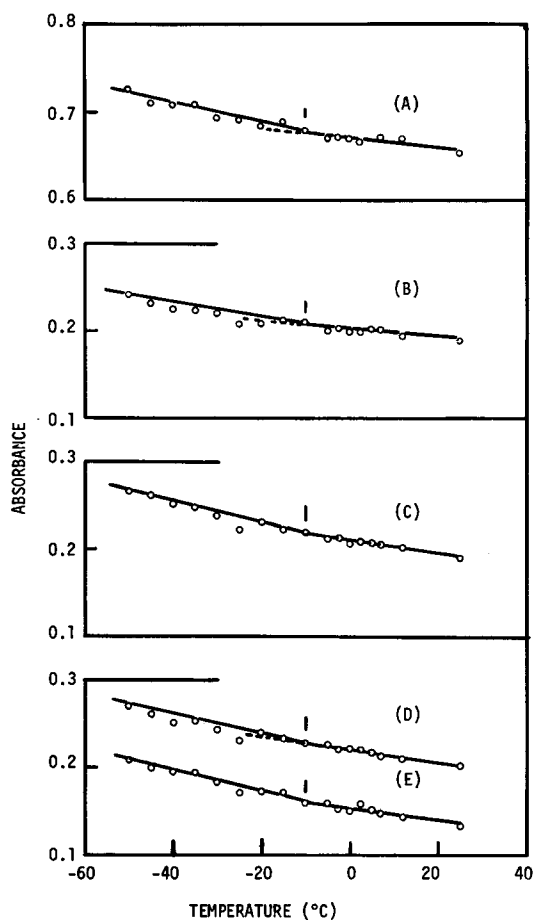


Fig. 6. Peak absorbance for 1450 (A), 1160 (B), 998 (C), 970 (D), and 838 (E) cm^{-1} bands in IPP as a function of temperature (falling temperature)

that of the illustrated bands, abrupt change is not necessarily observed on curves of these bands. These results indicate that T_{g2} occurs in either the crystalline or the amorphous region. The absorbances of these bands decreased with increasing temperature. This phenomenon can be explained by the theory that the increase in the average distance between molecules during thermal expansion of the solid (or liquid) diminishes the induced dipole moment of the interaction and consequently the magnitude of the absorption, as reported by Lisitsa.²³ After all, T_{g2} is attributed to a motion (thermal expansion) of IPP segments in either the crystalline or the amorphous region. The different shapes of these temperature-dependent curves at increasing or decreasing temperature may be caused by heat hysteresis. T_{g1} cannot be detected by the infrared method in this work.

Chlorinated Isotactic Polypropylene (CIPP). In general, when hydrogen atoms on the polymer chain are replaced by chlorine atoms, the ther-

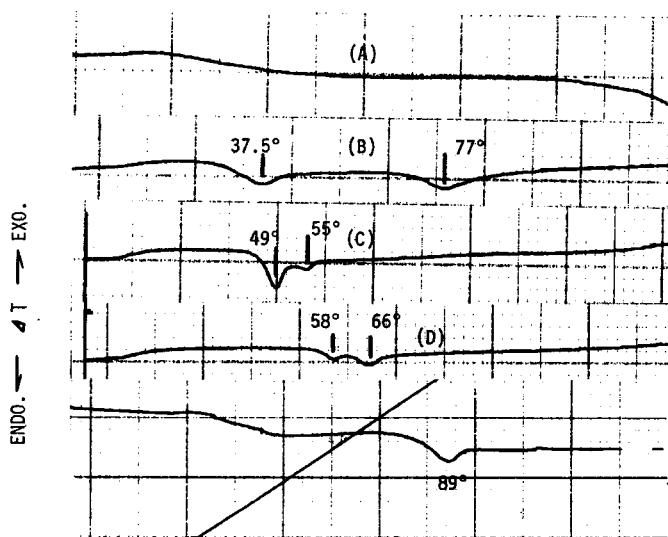


Figure 7. DSC thermograms for isotactic PP and various chlorinated PP's. Effects of degree of chlorination on transitions: (A) PP; (B) 32.5 wt-%; (C) 39.4 wt-%; (D) 45.9 wt-%; (E) 56.5 wt-%.

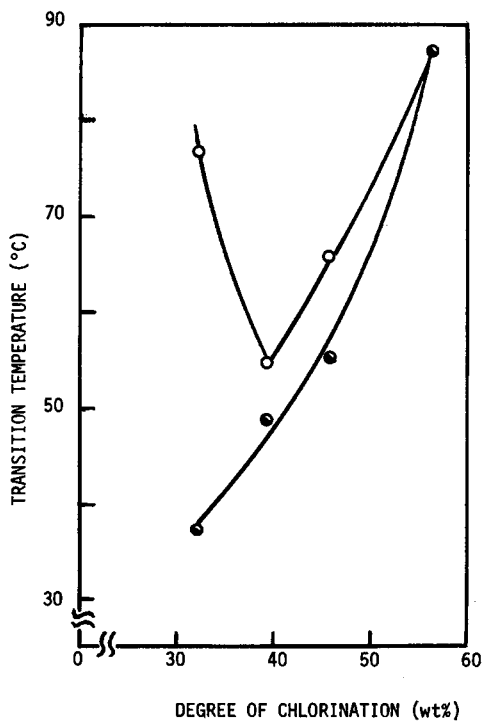


Fig. 8. Transition temperatures of various chlorinated polypropylenes.

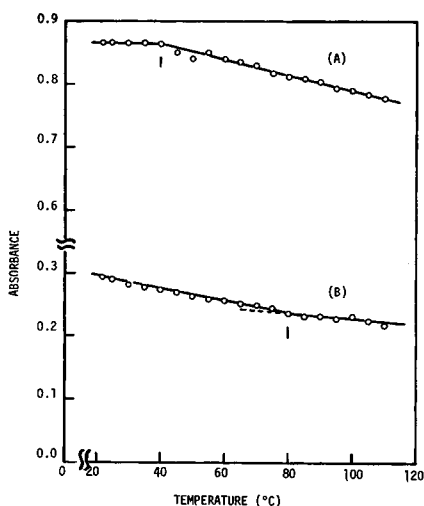


Fig. 9. Peak absorbance for 1450 (A) and 680 (B) cm^{-1} bands in (see Table I) CI-1 as a function of temperature.

mal transition temperature of the polymer is expected to rise with decreasing chain flexibility. In Figure 7, calorimetric results of IPP and CIPP which have different degrees of chlorination in the range of 0–140°C are shown. These thermograms are reproducible; no exothermic peak is observed, and therefore the degradation of these samples can be neglected. Figure 7 indicates that two transition points exist in CIPP and that these transitions have anomalous behavior; namely, a higher transition (T_H) has a minimum at a degree of chlorination of about 39 wt-%, and a lower transition (T_L) changes linearly with increasing degree of chlorination (Fig. 8).

This clearly different behavior is associated with a difference in molecular mechanism between T_H and T_L . Infrared results are useful for interpretation of each mechanism. In Figures 9–12, temperature-dependent infrared studies of CIPP are shown. The band at 1450 cm^{-1} is assigned to the CH_3 asymmetric deformation vibration.¹⁹ The band at 1370 cm^{-1} is assigned to the CH_3 symmetric deformation vibration.¹⁹ The band at 970 cm^{-1} arises from the coupled vibrations of the antisymmetric stretching mode of the axial and equatorial C–C bonds and of the methyl rocking modes. In this paper, the band at 725 cm^{-1} is assigned to P_C ; the band at 680 cm^{-1} is overlapping with the band at 685 cm^{-1} and that at 675 cm^{-1} ; the band at 685 cm^{-1} is assigned to $P_{H'}$ or S_{CH} ; and the band at 675 cm^{-1} is assigned to S_{CH} .

These results of the infrared studies indicate that T_H may be associated with a motion (thermal expansion) in chlorinated segments and T_L may be associated with that in unchlorinated segments. The behavior of T_H agrees, with the results that the softening point of CIPP has a minimum at 15–20%.⁹ According to Minsker et al.,⁹ the molecular weight of CIPP

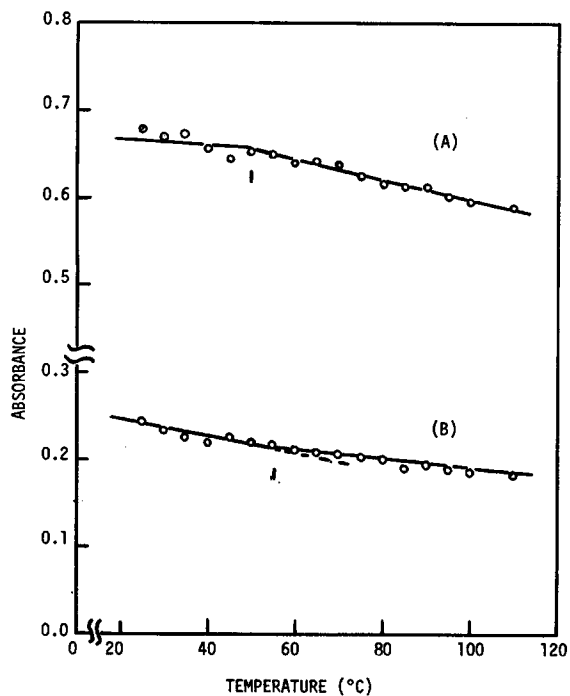


Fig. 10. The peak absorbance for 1450 (A) and 680 (B) cm^{-1} bands in CI-2 (see Table I) as a function of temperature.

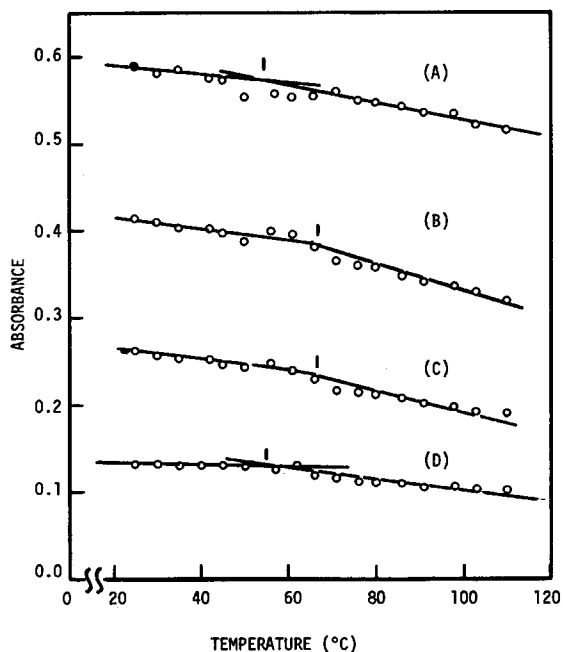


Fig. 11. Peak absorbance for 1450 (A), 970 (D), 725 (B), and 680 (C) cm^{-1} bands in CI-3 (see Table I) as a function of temperature.

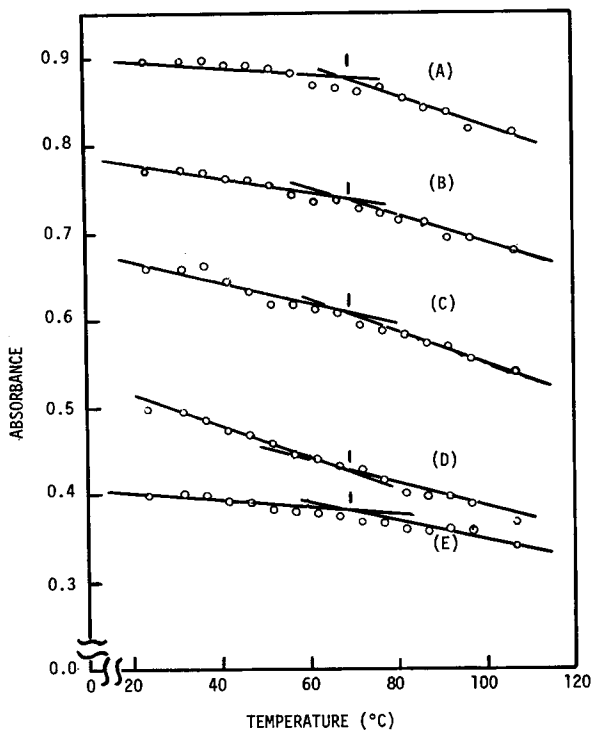


Fig. 12. Peak absorbance for 1450 (A), 1370 (B), 725 (C), 685 (E), and 675 (D) cm^{-1} bands in CI-5 (see Table I) as a function of temperature.

decreases with increasing degree of chlorination, so the softening point of CIPP has a minimum value. However, in this work, the mean molecular weight determined by GPC was constant in the range of 33–57 wt-% chlorination. Accordingly, the behavior of T_H is due to the structure of CIPP, but a critical interpretation of this behavior will not be discussed. The thermal physical properties of CIPP may be governed by T_H . The temperature of T_H is equal to that of T_L at about 57 wt-% of chlorination, because the number of unchlorinated segments of CIPP decreases with increasing degree of chlorination. Consequently, the results of these infrared studies also indicate that CIPP may have a block structure in analogy with chlorinated polyethylene as reported by Oshima et al.²⁴

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