Detection of Polymer Transition Temperatures by Infrared Absorption Spectrometry*

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Synopsis

Infrared bands in the 900–1100 cm^{-1} region are sensitive to thermal energy. These bands can result from intermolecular coupling, producing the crystal lattice, or from intramolecular coupling of the various atomic groups in a regular helix or coiled chain. In either case an increase in temperature will disrupt the coupling mode, resulting in a form of structural relaxation and a reduction in the integrated absorbance. It is proposed that the temperature at which the peak areas begin to decrease be assigned as the T_g. This is measured by continuously scanning a selected peak in the infrared spectrum of a polymer film while it is heated at a rate of about 1°C/min. Using this technique polyamides (nos. 6, 66, and 610) exhibited transitions in the 30–50°C range, and by studying the increase in the free NH region (3440 cm^{-1} of nylon 66 two other transitions were detected at 80 and 137°C; the latter represents a change in the nylon 66 crystal state. An amorphous film of poly(ethylene terephthalate) displayed a transition at 58–68°C (T_g) and at 85°C, which is the crystallization temperature. Films of poly(vinyl acetate) and polystyrene exhibited transitions at 25–37°C and at 70°C, respectively.

Introduction

The origin of a polymer transition cannot be deduced solely from such techniques as differential thermal analysis (DTA), modulus techniques, and dilatometry. However, with a combination of infrared spectrophotometry, x-ray, and NMR both the conformation and the nature of a thermal transition in a polymer can be determined. In actual practice there are relatively few cases recorded in the literature, especially cases dealing with thermoplastic polymers, in which infrared spectrophotometry is used as the prime tool for detecting thermal transitions. The technique involved is extremely simple and informative and is applicable to both macro and micro samples. By slowly heating a sample in a cell and continually scanning a selected peak the thermal response of the peak with temperature can be studied. The nature of any transition detected can then be correlated with the peak assignment.

Infrared bands in the 900–1100 cm^{-1} region are especially sensitive to thermal energy, and they have been associated with C—C or C—O stretch-

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ing vibrations in the zigzag chain portion of the polymer. These heat-sensitive bands can also be classified as either regularity or crystalline bands. The latter originate from intermolecular coupling, which results in the crystal lattice. The regularity bands originate from intramolecular coupling of atomic groups in the helix or coiled chain.[1] Other regions reported useful for detecting transitions include the CH_2 rocking or twisting modes (1350–1180 cm^{-1}) or the C—C stretching vibrations in the far infrared (≤ 700 cm^{-1}). Infrared peaks in the spectrum of a polymer that are sensitive to molecular strain resulting, for example, from crystal chain packing will decrease in intensity at the temperature where relaxation of the strain first occurs. This usually occurs in the vicinity of the T_g of the polymer. Actually, the T_g represents a type of structural relaxation. It is that temperature at which there is an onset of motion of chain segments in the amorphous region of a polymer, and the polymer goes from a hard, glassy state to a soft, rubbery one. Fukawa[2] in studying changes in the infrared spectrum of poly(vinyl chloride) with increasing temperature found that the discontinuity in a plot of the absorbance ratio of the 690–635 and 690–615 cm^{-1} peaks with temperature occurs at 71–$73°C$, which corresponds to the T_g as determined by the temperature dependence of the specific volume. He states that the change in peak absorbance with temperature closely resembles the temperature dependence of the refractive index, which is related to the dielectric constant. Since the dielectric constant can also be related to the dipole moment, changes in the dipole moment due to temperature, especially in polar polymers, will affect the intensity of certain peaks in the infrared region.

Other dynamic studies in which the infrared peak intensity was measured simultaneously as a function of temperature have been described. Martin et al.[3] for example, determined phase transitions of waxes by continuously monitoring the intensity at 728 cm^{-1} as a sample was cooled. Both infrared and x-ray techniques were used by Nichols[4] to study the effect of temperature on the orientation and crystallinity of nylon 66, poly(ethylene terephthalate) (PET), and polyethylene, and by Sutherland and Jones in
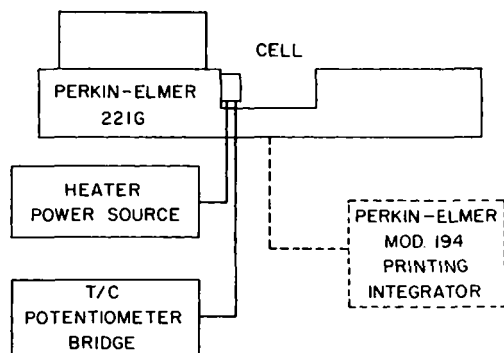

Fig. 1. Experimental set-up for detecting polymer transitions.

the structural definition of the polyisoprenes.[5]   Static techniques, in which the film was scanned at room temperature after an annealing treatment, have also been used to detect the T_g.

Nikitin and Volchek[6] found that the dichroism of the 1370 cm^{-1} peak for a prestretched poly(vinyl acetate) film measured at room temperature after annealing at various temperatures in the relaxed state decreases sharply at 30°C, which is the T_g.   Sibila and Paterson[7] have shown that the initial decrease in the intensity at 3000 cm^{-1} for monochlorotrifluoro-ethylene–vinylidene fluoride copolymer coincides with the T_g (52°C).

The objective of this paper is to demonstrate the utility, and expand the technique, of infrared spectrophotometry as a means of detecting and defining the nature of thermal transitions.

Experimental

Any of the heated infrared cell setups, described in the literature, that accommodate film samples can be used.[8,9]   Figure 1 shows the essential components used in our laboratory: A model 221G Perkin-Elmer infrared spectrophotometer, a Perkin-Elmer power supply for heating the cell, a potentiometric bridge for measuring thermocouple response and temperatures, and a peak integrator, which is optional.   The band intensity can be measured directly with increasing temperature by automatically recording the absorbance change of a fixed peak, but we found that peak areas give more accurate results, since in some cases the change in the shape of the peak is more dramatic.   An internal standard peak was used only when the
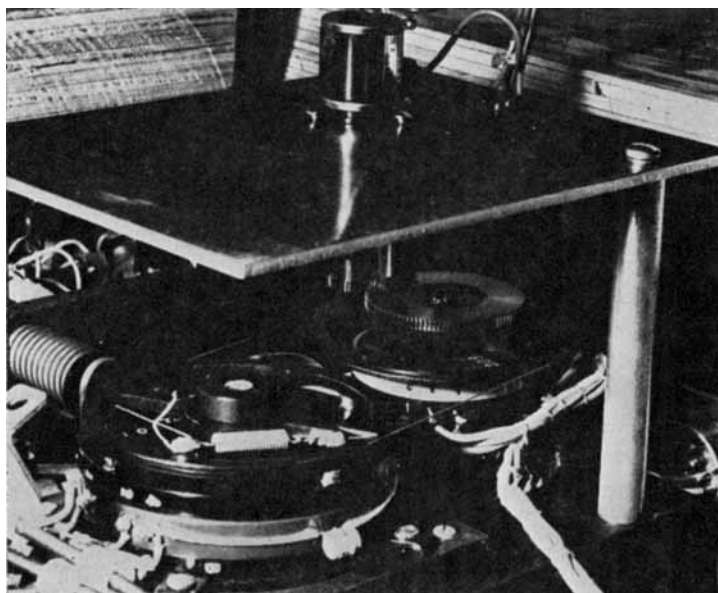

Fig. 2. Mechanical coupling of 10,000 ohm potentiometer to the wedge servomechanism of the Perkin-Elmer model 221G infrared spectrophotometer.
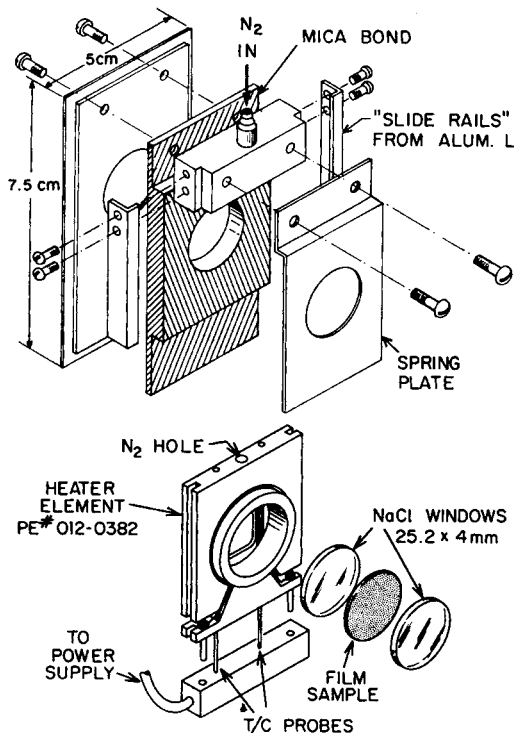
Fig. 3. Infrared heated cell.

solid film was near the softening point or in the melt. Unresolved peaks, particularly in the polyamide NH region, were resolved with the DuPont Curve Resolver prior to area measurements. Peak areas can be measured by any convenient method. The data presented in this paper were compiled both by planimeter and by cutting out and weighing the Xerox copy of the peak. Since many peak areas are needed for each run, the use of a semiautomatic integrating system was also evaluated. The Perkin-Elmer Model 194 print-out integrator was connected to a 10,000-ohm potentiometer, which was mechanically coupled to the wedge servomechanism of the spectrophotometer, as shown in Figure 2. Peak area reproducibility was good for the 940 cm^{-1} peak for nylon 610, but the system was not feasible when the pen did not return to a common baseline. However, the setup did demonstrate the ease by which this method can be automated. The heated cell was fabricated to accommodate a Perkin-Elmer heating jacket, as shown in Figure 3. Nitrogen, passing through the cooling coils, which were immersed in solid carbon dioxide, and entering through the top of the cell, was used to cool the cell to about 10°C. A slight N_2 bleed was allowed to flow through the cell while heat was applied in the 10–30°C range in order to counter the effect of the heat emanating from the infrared beam and to maintain a consistent heating rate.

The film sample, which was about 1 or 2 mils in thickness, was placed between two NaCl windows, which were then pressed against the thermocouple by the action of the spring plate. In order to check out the temperature between the NaCl windows and the thermocouple probe, a second thermocouple was pressed between two blank NaCl windows; the temperatures recorded agreed to within 1°C.

When the heated cell was being used, the rheostat of the power supply was set at a position that produced a heating rate of 1°C/min up to at least 100°C, and the peak was scanned at every 3 or 4°C increments. With the semiautomatic integrator the spectrophotometer was automatically cycled over the peak area.

Results and Discussion

A film of PET was prepared by melt-pressing a polymer having a number-average molecular weight of 12,000 at 17,000 lb at 285°C for 1 min and then using normal air-quenching. The peak at 970 cm^{-1}, which is associated with *trans*-ethylene configuration and is also known to be sensitive to crystallinity and orientation,[10] was scanned with the film in the relaxed state from 17 to 150°C. Peak area measurements in Figure 4 show that in the initial heat-up a major transition occurs in the 58–85°C region. This sudden rise in 970 cm^{-1} peak area coincides with an increase in x-ray crystallinity, a density change from 1.3380 to 1.3820, and, as shown in Figure 5, the film cross section contracts by about 10% and assumes a more grainy appearance in a dark field, owing to spherulite formation. The curve shown in Figure 4 also resembles the plot of density with temperature from 20 to 100°C produced by Mayhan et al.[11] When the same quenched film is rescanned, a very slight decrease in peak area (about 4% within a 5°C range) occurs at about 58–60°C. This rescan emphasizes the importance of knowing the thermal history of a polymer in detecting transitions.
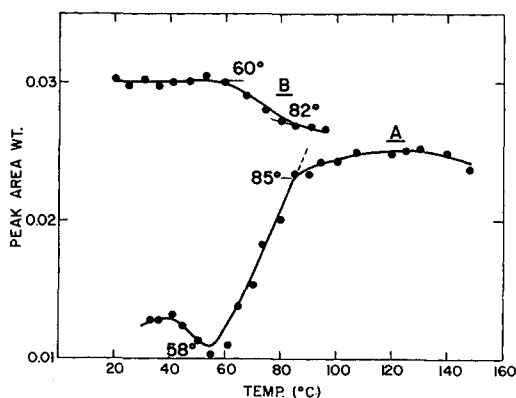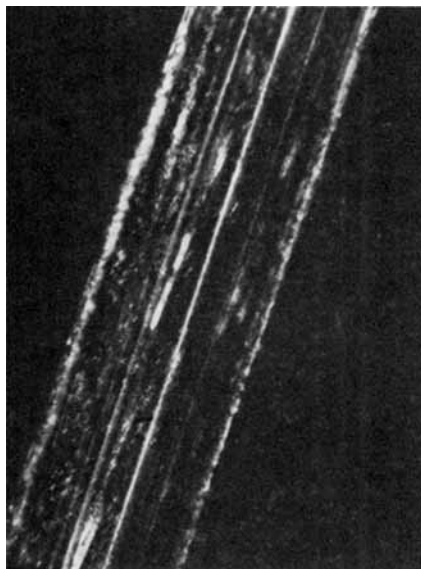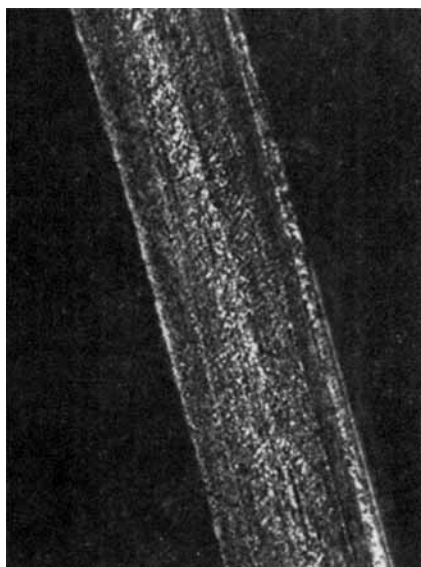

Fig. 4. Poly(ethylene terephthalate) transitions: area 970 cm^{-1} peak vs. temperature: 20–100°C range: (A) amorphous film (initial heat-up); (B) annealed film (reheat-up).

According to DTA, the T_g of PET was detected at about 56°C as a shift in the baseline of the thermogram, and a very small exothermic peak was observed at 82°C.   Mitsuishi and Ikeda, of the Fiber and Textile Research Institute, Teijin Limited of Japan, reported a T_g of 51°C by DTA and

(a)

(b)

Fig. 5. Poly(ethylene terephthalate) film cross sections: (a) amorphous film, 0.069 mm thick; (b) annealed film (85°C), 0.062 mm thick.

by specific volume–temperature measurements for highly oriented, amorphous PET monofilaments; the transition at 83°C was associated with the beginning of crystallization. According to their interpretation, the molecular chains in the highly oriented sample begin to relax without crystallization at the T_g.

Keavney and Eberlin,[12] in developing their DTA technique for detecting thermal transitions in polymers, found that the glass transition temperature was independent of heating rate at least within the 1–6°C/min range. However, because of the geometry of the heated cell shown in Figure 3
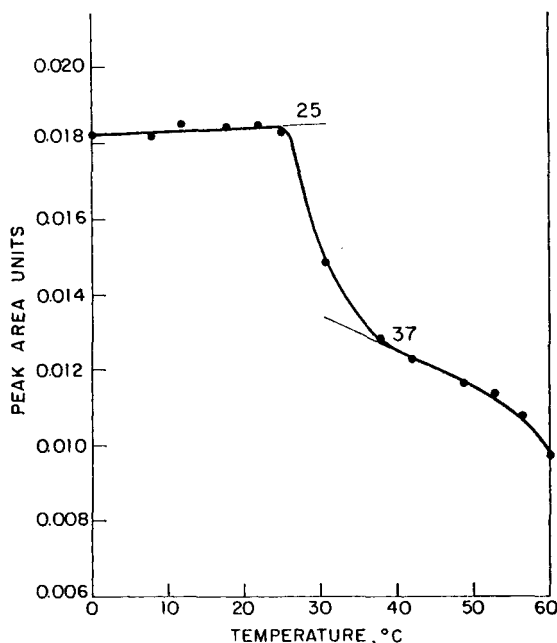

Fig. 6. Poly(vinyl acetate) transition area 920 cm⁻¹ peak vs. temperature 0–60°C range.

a temperature gradient exists across the film sample, and very slow heating rates are required to ensure a uniform distribution of heat across the sample. In studies of the transition in PET a heating rate of 1°C/min was found to be ideal for detecting transitions below 100°C with a relatively high degree of precision and accuracy. When the heating rate was increased to, for example, 8.5°C/min, the maximum peak area change for the 970 cm⁻¹ peak in PET occurred at 90°C rather than at 85°C.

The T_g of a commercial poly(vinyl acetate) film occurs at 30°C according to the temperature response of the moderately intense peak at 920 cm⁻¹, as shown in Figure 6. A transition in a 5-mil polystyrene film was detected at 70°C by monitoring the peak at 940 cm⁻¹ with 5× scale expansion. The T_g for polystyrene was reported to be at 85°C.[2]
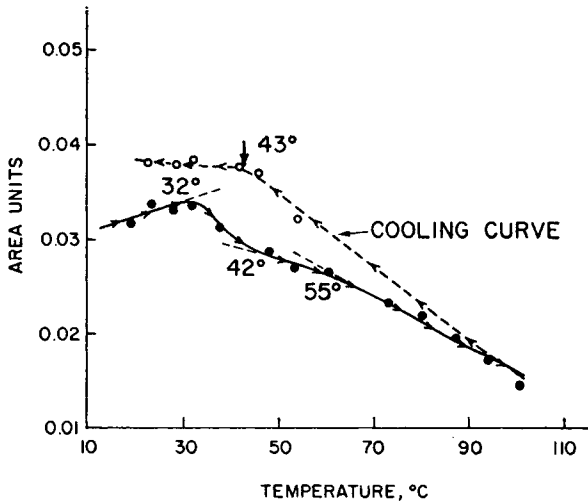
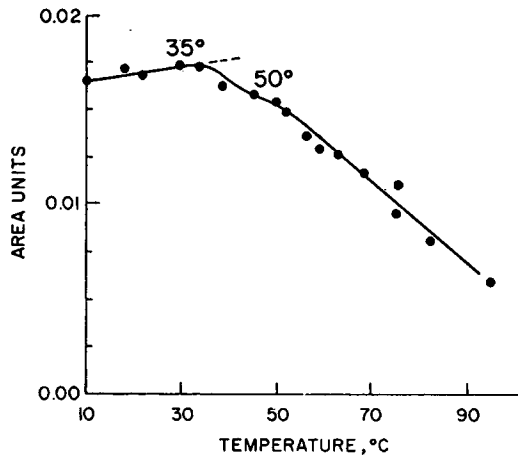Fig. 7. Nylon 610 transition area 940 cm^{-1} peak vs. temperature 10–100°C range 2 mil film.

Fig. 8. Nylon 66 transition area 940 cm^{-1} peak vs. temperature 10–90°C range 1 mil film.

Polyamide T_g's usually lie within a broad temperature range. Melt-pressed films of the three common polyamides, nylons 6, 66, and 610, all within a number-average molecular weight range of 14,000–17,000, show infrared peak area discontinuities in the 35–60°C range. The curve for nylon 610 (Fig. 7) shows breaks at 32, 42, and 60°C. This figure also illustrates the fact that the T_g can be detected by the cooling curve, which implies that a permanent deformation of the film (e.g., reduced thickness) at temperatures less than 100°C is not responsible for the transition. Scans taken on a Perkin-Elmer scanning calorimeter indicated that the T_g of

nylon 610 lies in the 25–42°C range, with the midpoint at about 34°C; the specific heat C_p was found to be 0.078 cal/g-deg.

The C_p for nylon 66 was 0.067 cal/g-deg and the T_g midpoint in a 40–53°C range fell at about 48°C according to calorimetric traces; the cold crystallization temperature occurred at 68°C. Polyamides, particularly nylon 66, have been reported to have a few transition temperatures other
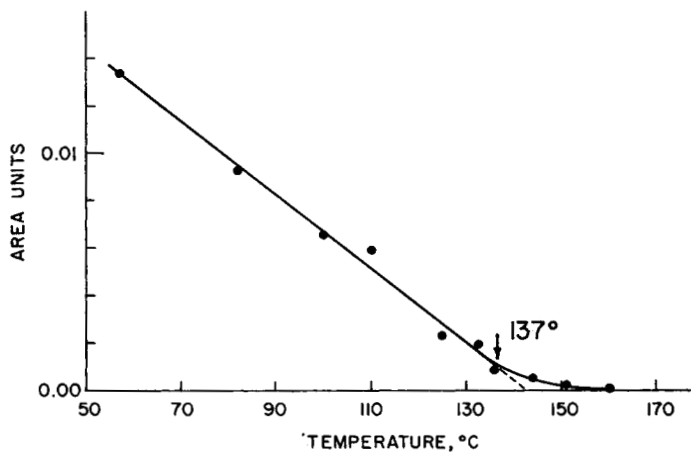

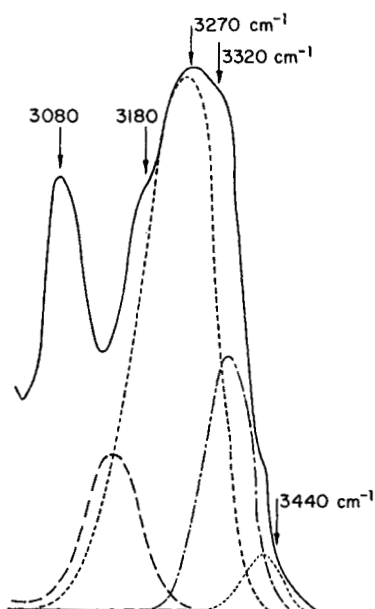Fig. 9. Nylon 66 transition area 940 cm^{-1} peak vs. temperature 50–170°C range 1 mil film.

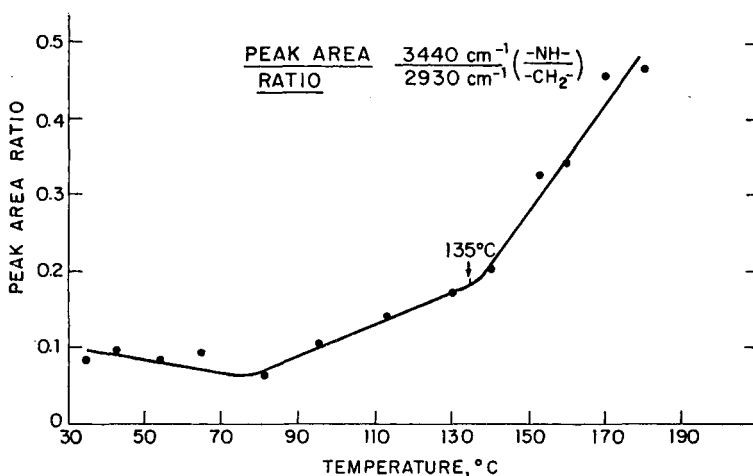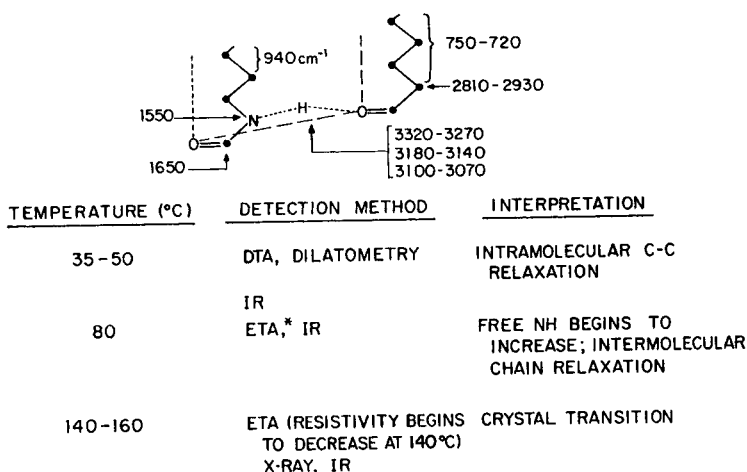Fig. 10. Nylon 66 NH region 130°C; peaks drawn with DuPont Curve Resolver.

Fig. 11. Nylon 66 free NH vs. temperature.

than the T_g (e.g., 80 and 140–160°C) prior to melting. A more complete study was made of nylon 66 to determine whether the nature of these transitions can be defined by infrared absorption spectrometry. The 940 cm^{-1} peak undergoes two changes in slope. First, we have the change corresponding to the T_g (35–50°C range) shown in Figure 8. As the temperature increases, this peak changes its rate of area loss at 137–140°C and almost completely disappears at 160°C, as shown in Figure 9. If we examine the overall x-ray diffraction pattern of nylon 66 with a hot camera, we find a similar effect occurring at about 140°C. According to Brill,[13] nylon 66 goes from the monoclinic to the hexagonal crystal. If this transition is truly due to a change in crystal form, we should also see a sudden change in the temperature response of the free NH measured at 3440 cm^{-1}. Peak area measurements of the free NH peak poses a problem. The peak is very weak, and it appears as a shoulder on the bonded NH peak. Trifan and Terenzi,[14] in measuring the free NH, use a baseline technique. The free NH peak can also be resolved with the DuPont Curve Resolver; Figure 10 shows the resolution of the NH region at 130°C. The peaks at 3270 and 3180 cm^{-1} have been assigned to trans- and cis-amide configurations, respectively. The 3080 cm^{-1} peak has been assigned to cis and trans intramolecular hydrogen-bonding, and it has been reported that this peak decreases in intensity with increasing temperature.[15] The peak at 3320 cm^{-1} may be due to a resonance form of the amide. Area measurements made on the free NH peak within the 30–100°C range were not very precise. A plot of the area ratio of the free NH over the methylene peak at 2930 cm^{-1} with temperature resulted in two breaks in the curve; the first break occurs at 80°C and the second at about 135°C (Fig. 11). Moisture must be eliminated from the sample prior to any measurements. This was accomplished by first heating the sample to 140°C for several minutes and then

TEMPERATURE (°C)	DETECTION METHOD	INTERPRETATION
35-50	DTA, DILATOMETRY	INTRAMOLECULAR C-C RELAXATION
80	IR ETA,* IR	FREE NH BEGINS TO INCREASE; INTERMOLECULAR CHAIN RELAXATION
140-160	ETA (RESISTIVITY BEGINS TO DECREASE AT 140°C) X-RAY, IR	CRYSTAL TRANSITION

* ELECTROTHERMAL ANALYSIS

Fig. 12. Transitions in nylon 66.

cooling to room temperature. Nitrogen is passed slowly into the cell to prevent oxidation at the elevated temperatures.

Let us now combine this information with observations made by other T_g-detecting techniques and speculate on the nature of the transitional modes for nylon 66. See Figure 12.

TABLE I
Detection of Polymer Transition Temperatures by
Infrared Absorption Spectrophotometry

Polymer	Band, cm^{-1}	Temp., °C	Method	Ref. no.
Monochlorotrifluoroethylene–vinylidene fluoride copolymer	3000	52[a]	stat.	7
Poly(vinyl acetate)	1370	30[a]	stat. dichr.	6
	920	25–37[a]	dyn.	—
Polystyrene		85[a]	dyn.	2
	940	70[a]	dyn.	
Poly(vinyl chloride)	690, 635 615	71[a]	dyn.	2
Poly(ethylene terephthalate)	970	56[a] 85 (cryst.)	dyn.	—
Polyamides:				
Nylon 6	930	37–46	dyn.	
Nylon 610	940	32–42	dyn.	
Nylon 66	940	35–50	dyn.	
	3440	80	dyn.	
	3440	137	dyn.	

[a] Glass transition (T_g) temperature.

In conclusion, it appears that infrared spectrophotometry can, with the proper cell design, temperature programming, peak selection, and careful peak area measurements, provide another means of detecting polymer transition, which can be identified once the proper peak assignments are made. As long as a polymer film does not change thickness or become tacky with increasing temperature, a single peak can be scanned to detect a transition. Otherwise, a second peak, one that is insensitive to temperature but sensitive to film thickness, must be used as an internal standard. Table I summarizes the application of infrared spectrophotometry for detecting the T_g of various polymers.

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