angle must be calculated from eq 10, and this variation may be small even though considerable distortion occurs. Insufficient data are available to perform this calculation with sufficient accuracy; in particular, directly measured values of τ_1 would be helpful.

In summary, the observed deviations are qualitatively consistent with the predictions of theory for the effect of intramolecular motion on the spectrum, although the data are not yet accurate enough nor extensive enough to establish definitely this as the cause. It seems unlikely, however, that these deviations are due to polydispersity, critical scattering phenomena, or concentration effects. Whatever their origin, the appearance of non-Lorentzian spectra at moderate molecular weights points out the need for caution in routine application of Rayleigh line-broadening measurements to the determination of translational diffusion constants, particularly if data are of limited accuracy. It is desirable to determine the spectrum for a given sample as a function of angle, since deviations which seriously affect the results may not be apparent in results obtained at a single angle.

Acknowledgments. We would like to thank Professors H. Z. Cummins and D. McIntyre for very helpful advice concerning design of the apparatus and Professor L. J. Fetters for supplying the high molecular weight polystyrene sample.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported in part through National Science Foundation Grant GP-8328.

Infrared Spectroscopic Approaches to the Polymer Transitions.
I. The Multiple Transitions in Poly(acrylonitrile) (PAN)

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ABSTRACT: The multiple transitions in poly(acrylonitrile) (PAN) were investigated by means of infrared absorption spectrophotometry in the range from 80 to 145°. The temperature behavior of peak absorbance and infrared dichroism and the time-temperature dependence of peak absorbance at various temperatures were examined. From these data, four transition points (90, 110, 120, and 140°) were detected and the results suggest that the band for the CN group is the most sensitive one for the thermal transition in PAN. The nature of the temperature dependence of peak absorbance in the infrared spectrum of the polymer was also discussed.

Many authors have reported thermal transitions in polymers; however, their natures have not been clear. If it is considered that a polymer transition is associated with a change in the state of molecular motion in a polymer molecule (or a change of conformation), the behavior of the infrared spectrum in the transition regions may provide certain clues for understanding the nature of polymer transitions more clearly. In a polymer solution, such an attempt was first carried out by Takeda, Iimura, and Ochiai.[1]

In the solid state, recently, several authors[2–8] have demonstrated that infrared absorption spectrophotometry may be used to detect thermal transitions in polymers. Table I summarizes the thermal transition temperatures which were detected by infrared.

In the present paper, the multiple thermal transitions in poly(acrylonitrile) (PAN) in the range from 80 to 145° are reported using measurements of the temperature dependences of infrared absorbance and infrared dichroism, and time–temperature dependence of infrared absorbance at various temperatures.

Experimental Section

(1) Polymer. PAN was prepared according to the redox recipe of Beaman,[9] details of which are given in Table II.

(2) Molecular Weight. Intrinsic viscosities were measured in dimethylformamide (DMF) solution at 25° and molecular weight (M_n = 689,000) calculated from the relation of Onyon[10] ($[\eta] = 1.97 \times 10^{-3} M_n^{0.625}$).

(3) Preparation of Sample. The PAN homopolymer films used in this work were cast from 2% solutions of the polymer in DMF. The residual DMF in the films was extracted with methanol and they were then dried under vacuum at low temperature. The well-dried films (50–60 μ) were stretched 300% at room temperature. None of the films used in this work was annealed.

(4) Infrared Measurements. A Nihon Bunko DS-402G type of infrared spectrophotometer and heated cell apparatus were used. This instrument has a frequency accuracy of ± 2 cm^{-1} and a transmission accuracy of $\pm 0.5\%$ under the conditions used. The temperature was raised at a rate of about 0.3°/min. The temperature of the sample was controlled with a thermoregulator and temperatures were

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TABLE I
DETECTION OF POLYMER TRANSITION TEMPERATURES BY IR ABSORPTION SPECTROPHOTOMETRY

Polymer	Bands, cm^{-1}	Temperature, °C	Ref
Polyamide			
Nylon 610	940	32–42	2
66	940	35–50	
6	930	37–46	
PVC	690	71	5
	640		
	615		
Polystyrene	1450	85	5
	940	70	2
	750	105, 92	3
PVA	3340	70, 79	3
PTFE	627	30, 50, 90, 130	6
	639		
PET			
Amorphous	896	161 ± 15 (°K)	4
Mylar A	973	244 ± 8 (°K)	
	843	217 ± 4 (°K)	
	1380	149 ± 6 (°K)	
	970	56, 85	2
Polypropylene	973	30	8
	1164		

TABLE II
CONDITIONS FOR THE REDOX POLYMERIZATION OF ACRYLONITRILE

Potassium persulfate	0.1 g
Sodium bisulfite	0.033 g
Sodium salt dodecylbenzenesulfonic acid	2.0 g
Acrylonitrile	80.0 g
Distilled water	120.0 g
Time	3 hr
Temperature	35°

measured with a thermistor placed near the sample. A survey spectrum (4000–650 cm^{-1}) was measured at several temperatures to establish those absorption bands which change upon elevating the temperature in air. (In a preliminary experiment, it was confirmed that PAN was not decomposed by heating in these regions.) The temperature dependences of the infrared dichroism at 2950 and 2237 cm^{-1} were also examined. Polarization of the infrared radiation was accomplished with a AgCl plate polarizer. In the present work, the effects of machine polarization were neglected. The band intensities were determined by the "base line" method.

Results and Discussion

(1) The Nature of the Temperature Dependence of Peak Absorbance in the Infrared Spectrum of Polymers. Fukawa[5] has stated that the change in peak absorbance with temperature closely resembles the temperature dependence of the refractive index, which is related to the dielectric constant. Anton[2] has suggested that since the dielectric constant can also be related to the dipole moment, changes in dipole moment due to temperature, especially in polar polymers, will affect the intensity of certain peaks in the infrared region. Sibilia and Paterson,[7] on the other hand, have proposed that presumably at the glass transition point the change in chain geometry produces enough of a change in the dipole moment of the $-CH_2-$ group to cause a significant change in the intensity of the –CH– stretching vibration. Most recently, Hannon and Koenig[4] reported the following: (1) infrared spectrophotometry is sensitive to transition behavior in polymers through changes related to the thermal expansion coefficient at the transition temperature, (2) infrared spectrophotometry is uniquely sensitive to a particular portion of the molecule and the environmental changes in this particular structural entity. On the other hand, for low molecular weight compounds several authors[11-14] have observed a linear temperature dependence of the peak absorbance for liquids and solids. It is known[15] that the dipole moment is constant in the case of rigid molecules, but that in the case of molecules which have a rotation axis the dipole moment tends to change with temperature due to some intramolecular motions based upon intramolecular rotations or molecular flexibility. Thus, we would like to propose that at a transition temperature the freedom of polymer molecules may be increased to allow some intramolecular rotations, and that therefore the change in the intensity of the infrared region may be attributed to molecular motions (motion of the main chain or side groups). Consequently, we suppose that the polymer transitions which are detected by infrared are associated with a change in the dipole moment or with changes in the normal coordinate of the vibration with onset of molecular motion.

In the infrared study of PAN[16,17] the sensitive bands corresponding to those identified with conformational change in PVC[18,19] have not been assigned. Thus, it is difficult to interpretate the transition mechanism in terms of conformational change.

(2) Multiple Transitions in PAN. In a preliminary experiment, the spectra were measured at 10° intervals, and three transition points (85–90, 100–110, and 140–145°, respectively) were detected. In order to examine these transitions in more detail, the spectra were measured at 1° intervals. These results are shown in Figure 1a. They suggest that the band for the CN group (2237 cm^{-1}) is the most sensitive for observation of thermal transition in PAN. Hayakawa and his colleagues[20] have proposed that the transition in PAN differs from the ordinary glass transition in the amorphous phase. Our infrared results support their conclusions, based upon the following points: (1) the temperature behavior of peak absorbance in the spectrum of PAN is more complex than those of other polymers,[2-6] (2) the transition point is observed as a clear abrupt change. However, a physicochemical explanation for these different phenomena cannot be

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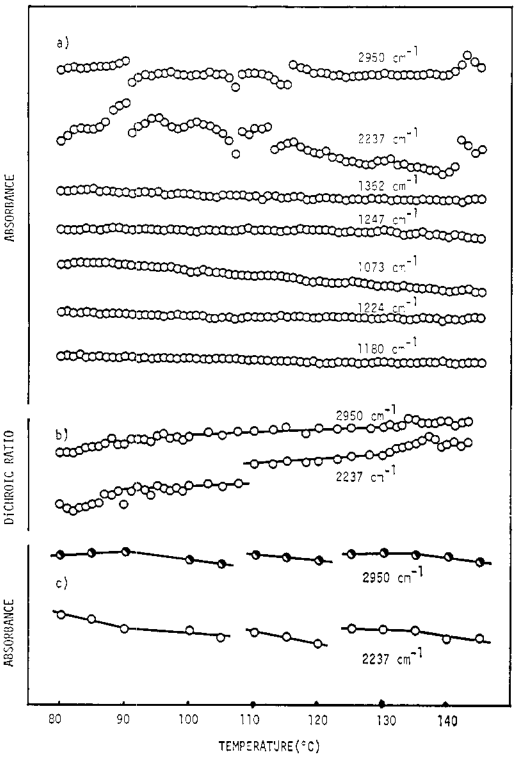

Figure 1. (a) Temperature dependence of absorbance of various bands for infrared spectrum of PAN; (b) temperature dependence of infrared dichroisms for 2950 and 2237 cm^{-1}; (c) temperature dependence of average absorbance of 2950 and 2237 cm^{-1}. Data are taken from Figure 2.

presented at this time. The temperature dependences of the infrared dichroism at 2950 and 2237 cm^{-1} are shown in Figure 1b. Although the data scatter, three transitions are observed; particularly sharp is the change of dichroism for the CN group near 110°. Although it is unknown why the dichroism of the CN group change abruptly at this point while that for CH group does not change, this result is very interesting for an understanding of the transition mechanism. It is generally known[21] that the temperature observed as a glass transition temperature depends upon the time-scale of the measurements. Thus, the rate of heating is most important for detecting the transition temperature. In order to study this problem and the possibility of changes in the peak absorbance by relaxation, the time–temperature dependence of the peak absorbance was examined. As indicated in Figure 2, the peak absorbance does not depend upon the heating time except at a few temperatures. The average peak absorbances at various temperatures are plotted against temperature in Figure 1c. Near 120°, a new inflection point is observed. It can be concluded that this transition proceeds in a more delayed fashion than the other three transitions.

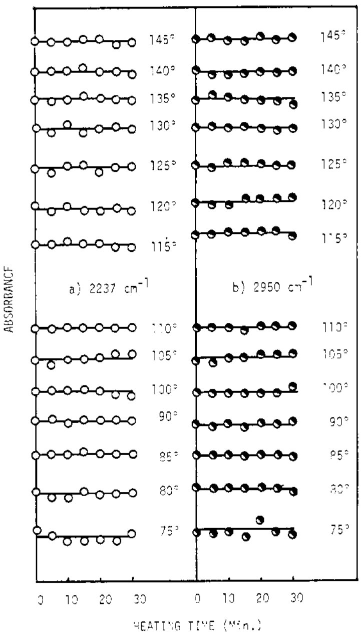

Figure 2. Time–temperature dependence of (a) 2237- and (b) 2950-cm^{-1} bands in the absorbance of infrared spectrum of PAN.

Acknowledgments. The authors acknowledge the kind discussions of Mr. Tetsuo Kanamoto, Tokyo College of Science, and they thank Mr. Akihiro Kawashima, Department of Electrical Engineering, Seikei University, for his helpful advice on thermal control.

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