

# Thermal Stability of Polyacrylonitrile in the Melt Formed by Hydration

BYUNG GHYL MIN,<sup>1\*</sup> TAE WON SON,<sup>1</sup> WON HO JO,<sup>2</sup> and SOO GHIL CHOI<sup>2</sup>

<sup>1</sup>Advanced Fiber Science Laboratory, Division of Polymer Science, Korea Institute of Science and Technology, P.O. Box 131 Cheongryang, Seoul, Korea, and <sup>2</sup>Department of Textile Engineering, Seoul National University, San 56-1, Shinlim, Kwanak, Seoul, Korea

## SYNOPSIS

Differential scanning calorimetry (DSC) and intrinsic viscosity measurement have been used to investigate the thermal stability of PAN-based copolymer in the melt formed by hydration. Samples containing various water contents were annealed at temperatures between 160 and 180°C for periods up to 60 min. The melting point ( $T_m$ ) and crystallization temperature ( $T_c$ ) increased with annealing time, irrespective of annealing temperature and water content. The increase in  $T_m$  with annealing time was interpreted in terms of thermodynamic parameters. The decrease in the heat of fusion ( $\Delta H_f$ ) with the increase of annealing time implies that the number of nitrile groups is reduced during annealing in the melt. The decrease in the entropy of fusion ( $\Delta S_f$ ) calculated from  $T_m$  and  $\Delta H_f$  suggests that the polymer chain becomes more rigid as the annealing time (or temperature) increases; however, the intrinsic viscosity does not increase during annealing. From both thermodynamic analysis and intrinsic viscosity, it is concluded that the increase in  $T_m$  is caused by chain rigidity mainly due to the intramolecular cyclization of nitrile groups. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

An important characteristic of polyacrylonitrile (PAN) is its particularly high melting point (320°C),<sup>1,2</sup> which is attributed to chain stiffness and couplings between nitrile groups due to dipole-dipole interaction.<sup>3</sup> Hence, pure PAN and fiber-forming acrylonitrile copolymers (abbreviated to PAN-based polymers hereinafter) are not stable because exothermic reactions, such as the oligomerization of nitrile groups, crosslinking, and decomposition, occur at temperatures lower than the melting point.<sup>4,5</sup> As is well known, this thermal instability is indispensable in preparing stabilized acrylic fiber that can be further heat-treated in an inert atmosphere to form carbon fiber. On the other hand, it makes it almost impossible to prepare an acrylic fiber through melt spinning alone. Accordingly, it is essential to depress

melting points ( $T_m$ ) of PAN-based polymers by reducing dipole-dipole interactions between nitrile groups in order to prepare acrylic fibers through melt spinning. Coxe<sup>6</sup> first reported that the addition of small amounts of water to PAN-based polymer sufficiently lowers  $T_m$  to permit melt spinning. His invention is very significant because it offered a possibility of replacing the wet and dry solution spinning process with a less expensive and nonpolluting melt spinning process.<sup>7-10</sup> However, the melt may be still susceptible to thermal degradation even though the hydrated melt is formed at a lower temperature. Because physical properties of the final product can be considerably influenced by the thermal degradation during melt processing, it is important to understand the effects of melt processing conditions on the thermal behavior of PAN-based polymers. Nevertheless, the thermal stability of PAN-based polymers in the hydrated melt has not been reported yet. In this study we wish to report the effects of annealing temperature, time, and water content on the thermal stability of PAN-based polymer in the hydrated melt.

\* To whom all correspondences should be addressed.

## EXPERIMENTAL

### Material

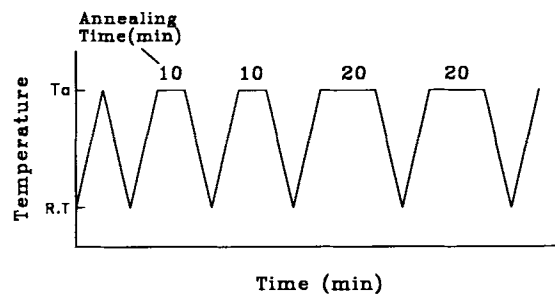
The PAN-based polymer was obtained from Tae Kwang Industrial Co. (Korea) in the form of fine powder. It was reported that the copolymer is composed of 88 wt % of acrylonitrile (AN) and 12 wt % vinyl acetate. Intrinsic viscosity was measured at 25°C from a dilute dimethylformamide (DMF) solution. Average molecular weight ( $M_v$ ) was then estimated to be 82,000 g/mol according to the Mark-Houwink-Sakurada equation.<sup>11</sup>

$$[\eta] = 2.43 \times 10^{-4} M_v^{0.75} \quad (1)$$

These parameters are corrected strictly for PAN at 25°C. Therefore, the parameters for the sample in this study are expected to differ slightly from the parameters cited above, but no corrections were made. The polymer was dried in a vacuum oven at 50°C prior to use.

### DSC Measurements

The differential scanning calorimetry (DSC) measurements were carried out using a DuPont 910 DSC programmed with a 1090 thermal analyzer. All experiments were performed using a Perkin-Elmer large-volume stainless steel capsule (Part 319-0218), which is capable of withstanding the vapor pressure of water up to 220°C. Frushour<sup>12</sup> measured the melting point depression of PAN-based polymers with water using these capsules for the first time. Polymer and water were uniformly mixed at a given ratio using a high-speed home mixer, and then ca. 50 mg of the mixture was transferred to the capsule. In order to investigate thermal stability of the polymer in the hydrated melt state, the DSC measurements are performed according to the thermal program shown in Figure 1. The samples were heated at 10°C/min from room temperature to the final test temperature (160, 170, or 180°C) and held for a given annealing time, and then cooled to room temperature at 10°C/min. This cycle was repeated until the total annealing time reached 60 min. The change of melting point and crystallization temperature ( $T_c$ ) with annealing time in the melt was investigated from the endothermic and exothermic peaks obtained in every heating and cooling procedure, respectively.  $T_m$  and  $T_c$  were taken as the maxima in the endothermic and exothermic peaks, respectively, and the annealing time was taken as the cumulative annealing time. The heat of fusion ( $\Delta H_f$ )



**Figure 1** DSC program for the preparation of annealed samples.

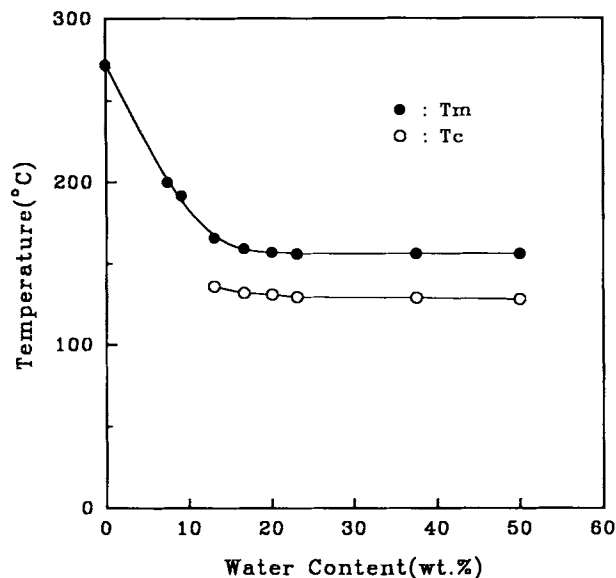
was calculated from the peak area using an indium standard.

### Measurements of Intrinsic Viscosities

A stainless-steel container, equipped with a Teflon gasket to prevent water evaporation during annealing, was used to prepare samples for the measurement of intrinsic viscosity. This container packed with a polymer-water mixture was put into a silicone oil bath controlled to a test temperature and annealed for a different time. The annealed polymer was ground and dried before dissolving in DMF. Intrinsic viscosity was determined by extrapolation to an infinite dilution of specific viscosity at 25°C.

## RESULTS AND DISCUSSION

The melting point depression of pure PAN polymer, by hydration thermally induced side reactions, makes it impossible to observe the melting point using DSC directly. However, the polymer used in the present study is a copolymer having 12 wt % of vinyl acetate, which lowers  $T_m$  considerably by reducing the regularity and strength of the intermolecular dipolar bonding networks.<sup>12</sup> Thus, it was possible to observe a melting endotherm at a rapid heating rate (80°C/min). The melting point of the copolymer was 270°C, which is much lower than the 320°C of PAN. The  $T_m$  of the dry polymer is further depressed when water is added. It is known that the plasticization of PAN-based polymer by water is mainly due to decoupling of the coupled nitriles and the replacement with hydration.<sup>13</sup> The melting point depression of PAN-based polymer by hydration is dependent on water content, as shown in Figure 2. The  $T_m$  decreases very rapidly as water is added until a plateau region of constant  $T_m$  is reached. This tendency agrees with the report of Frushour.<sup>13</sup> In the

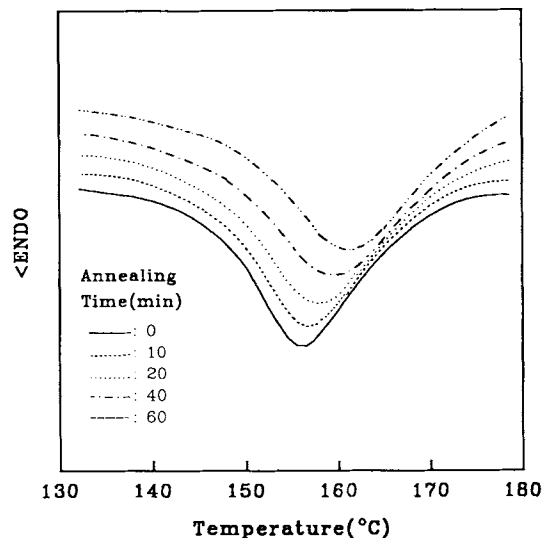


**Figure 2** Melting point ( $T_m$ ) and crystallization temperature ( $T_c$ ) of the PAN-based polymer versus water content.

present system the critical water content above which the  $T_m$  remains constant was found to be ca. 23 wt %. This is consistent with the content at which all the nitrile groups in the polymer associate with water in the equivalent mole ratio. From the results it is concluded that a nitrile group hydrates with only one water molecule, and the excess water does not participate in hydration but exists in a separate phase from the hydrated melt.

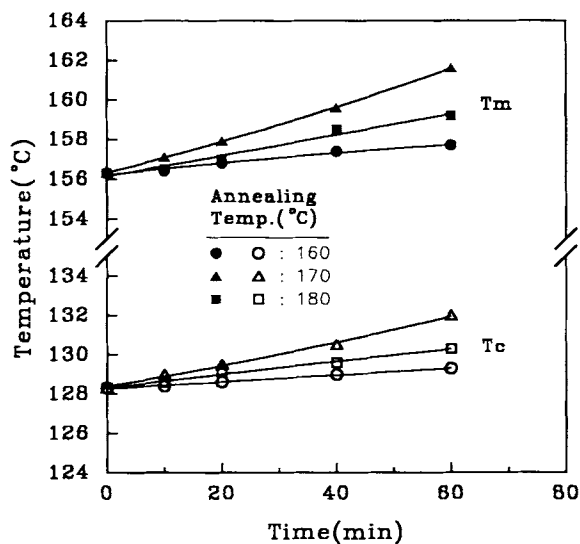
#### Thermal Stability of the Melt Formed by Hydration

Figure 3 shows the DSC traces for a sample containing 23 wt % of water after the sample is annealed at 180°C. The melting point increases with the annealing time. This indicates that physical and/or chemical changes have taken place during annealing. It is well known that the high dipole moment of the nitrile group causes strong attraction or repulsion between nitriles, which compels the individual macromolecules into a somewhat irregular helical conformation.<sup>1</sup> Accordingly, it is considered that the potential energy surrounding each nitrile group in the molecules has a distribution. The energy needed to form hydration would be different corresponding to the potential energy state of the nitrile group. In other words, relatively free nitrile groups will hydrate at lower temperature, while coupled nitrile groups hydrate at a higher temperature. Since there is no mechanical operation to induce physical change



**Figure 3** Typical DSC traces of the samples containing 23 wt % water after annealing at 180°C.

of the polymer chain in the sealed capsule for DSC measurement, the change of endotherms in peak position due to annealing in the melt is attributed to the change in chemical structure. The effects of annealing temperature and water content on  $T_m$  and  $T_c$  of the samples are demonstrated in Figures 4 and 5, respectively. To understand the effect of free water, water contents are all above the critical point. Irrespective of the annealing temperature and water content,  $T_m$  and  $T_c$  increased with the annealing time. The increasing tendency of these to increase



**Figure 4** Changes in  $T_m$  and  $T_c$  of hydrated polymers containing 23 wt % water as a function of the annealing temperature and annealing time.

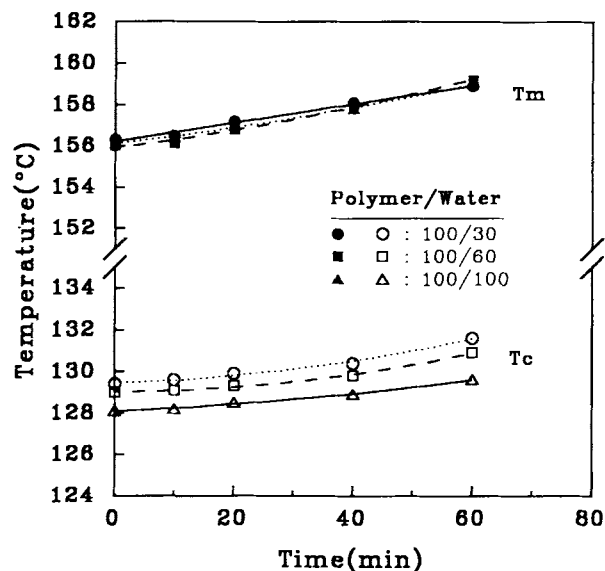


Figure 5 Changes in  $T_m$  and  $T_c$  as a function of the water content and annealing time.

with time is accelerated as the annealing temperature increases. However, where the annealing temperature is constant at 170°C, the dependence of  $T_m$  on water content is not notable, but a lower  $T_c$  is observed as water content increases. Therefore, it is concluded that the free water influences the kinetics of crystallization rather than the hydration strength. In order to analyze the reason why  $T_m$  increases with the annealing treatment, DSC results were analyzed using a thermodynamic relation among  $T_m$ , heat of fusion ( $\Delta H_f$ ), and entropy of fusion ( $\Delta S_f$ ):

$$T_m = \frac{\Delta H_f}{\Delta S_f} \quad (2)$$

Generally, a high  $T_m$  can be caused by a high  $\Delta H_f$  and/or by a low  $\Delta S_f$ . As presented in Table I and plotted in Figure 6, the heat of fusion of the polymer, which is estimated from the area of endothermic peak and normalized to the same polymer weight, shows a decreasing tendency as the annealing time increases, though not to a large extent; however, the tendency becomes distinct as the annealing temperature increased. Since it is obvious that the heat of fusion for the mixture of PAN-based polymer and water reflects the total absorbed energy for hydration between nitriles and water, the decrease of  $\Delta H_f$  with the annealing time is concluded to result mainly from the reduction of hydration amounts. Consequently, it will be understood that part of the nitrile is degraded to other chemical structures during the annealing process. This speculation has validity

Table I Thermodynamic Parameters Derived from Melting Point Measurement (Water Content, 23 wt %)

Annealing Temp. (°C)	Annealing Time (min)	$T_m$ (K)	$\Delta H_f^a$ (J/g)	$\Delta S_f^a \times 10^2$ (J/K g)	
—	0	429.3	21.2	4.94	
160	10	429.4	21.2	4.94	
	20	429.8	20.7	4.82	
	40	430.4	20.4	4.74	
	60	430.7	20.0	4.64	
	170	10	429.5	20.9	4.89
170	20	430.0	20.6	4.70	
	40	431.5	19.7	4.64	
	60	432.2	19.3	4.47	
	180	10	430.1	20.7	4.81
	180	20	430.9	19.8	4.64
40		432.6	19.2	4.49	
60		434.6	17.9	4.19	

\* Normalized to the polymer.

considering the well-known fact that nitrile groups in PAN are easily oligomerized, crosslinked, or oxidized by thermal treatment. At any rate, the increase of  $T_m$  is not interpreted by the change of  $\Delta H_f$  alone:  $\Delta S_f$  is calculated from  $T_m$  and  $\Delta H_f$  and normalized to the same polymer weight.  $\Delta S_f$  decreased with the increase of the annealing time and annealing temperature, as shown in Figure 7. Since

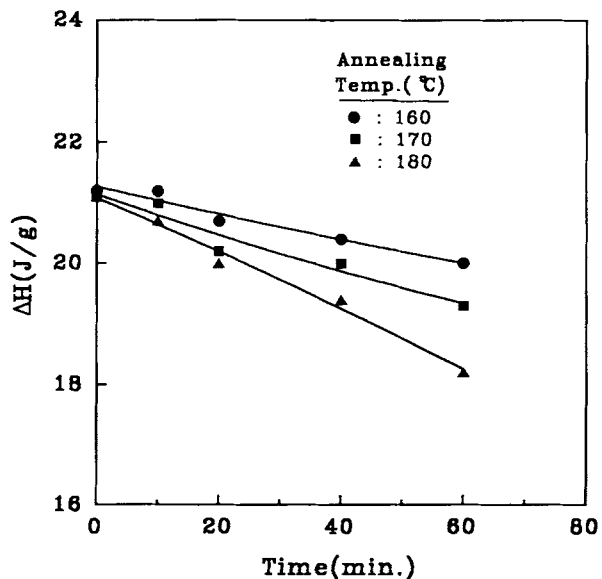
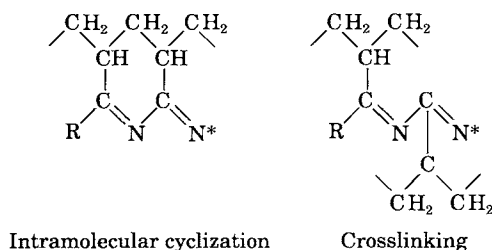


Figure 6 Changes in the heat of fusion of hydrated polymers containing 23 wt % water as a function of the annealing temperature and annealing time.

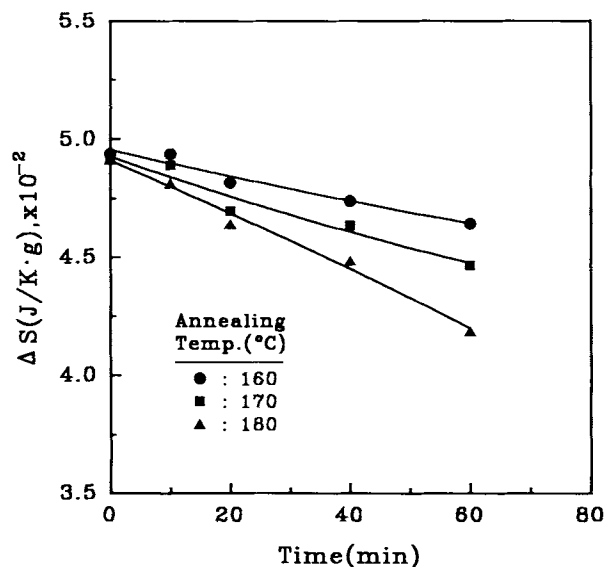
$\Delta S_f$  is a parameter related to chain flexibility, the decrease of  $\Delta S_f$  indicates that the polymer chain became more rigid as the annealing progresses. It is believed that the main reason for the increase of  $T_m$  is the increase of chain rigidity with annealing due to annealing.

### Change in Intrinsic Viscosity

There are two possible chemical transformations responsible for chain rigidity, namely, intramolecular cyclization of nitriles and crosslinking:



Intrinsic viscosities were measured to determine which reaction is dominant during annealing. Intrinsic viscosity data, presented in Table II show that crosslinking is not a primary reaction for the hydrated melt at least in the range of temperature and water of the present experiment. Of course, it is also certainly feasible for nitrile groups of neighboring molecules to be thermally crosslinked due to the presence of a strong dipole-dipole attraction.<sup>3</sup> However in the melt, as the attractive force has al-



**Figure 7** Changes in the entropy of fusion of hydrated polymers containing 23 wt % water as a function of the annealing temperature and annealing time.

**Table II** Intrinsic Viscosities ( $[\eta]$ ) of Dry Polymer and Annealed Polymers

Water Content (wt %)	Annealing Temp. (°C)	Annealing Time (min)	$[\eta]$
0	—	0	1.18
	160	20	1.13
		40	1.10
23	170	60	1.11
		20	1.12
		40	1.08
	180	60	1.00
		20	1.12
		40	1.05
37.5	170	60	0.98
		20	1.13
		40	1.04
50	170	60	1.05
		20	1.14
		40	1.07
		60	1.06

ready been shielded or removed by hydration, the crosslinking reaction would be less probable in the melt than in the solid state. Other observable differences were moderate coloration and the decrease of solubility when the samples were annealed. It has been widely accepted that thermal coloration in PAN is caused by the imine structure formed by cyclization of nitrile groups rather than intermolecular crosslinking.<sup>2,14</sup> Around the concentration of 0.5 g polymer in DMF at which intrinsic viscosity is determined, a clear solution is easily prepared within an hour at room temperature for the unannealed polymer. After annealing for 1 h in the melt at 170°C the polymer scarcely dissolved even after stirring for 3 days at room temperature. Increasing the temperature to 50°C is required to make a clear solution within an hour. Grassie<sup>14</sup> reported that pure polyacrylonitrile heated at 170°C for 1 h leaves about 80% of residual gel (when heated at 100°C for 1 h in DMF), and that the gel density in DMF is a measure of the development of crosslinking. Consequently, it is reasonable to say that crosslinking is not extensively developed in our annealed samples because a clear solution is obtained around 50°C.

### CONCLUSIONS

In summary, it is concluded that the increase in  $T_m$  of the hydrated melt after annealing is caused by chain rigidity mainly due to intramolecular cycli-

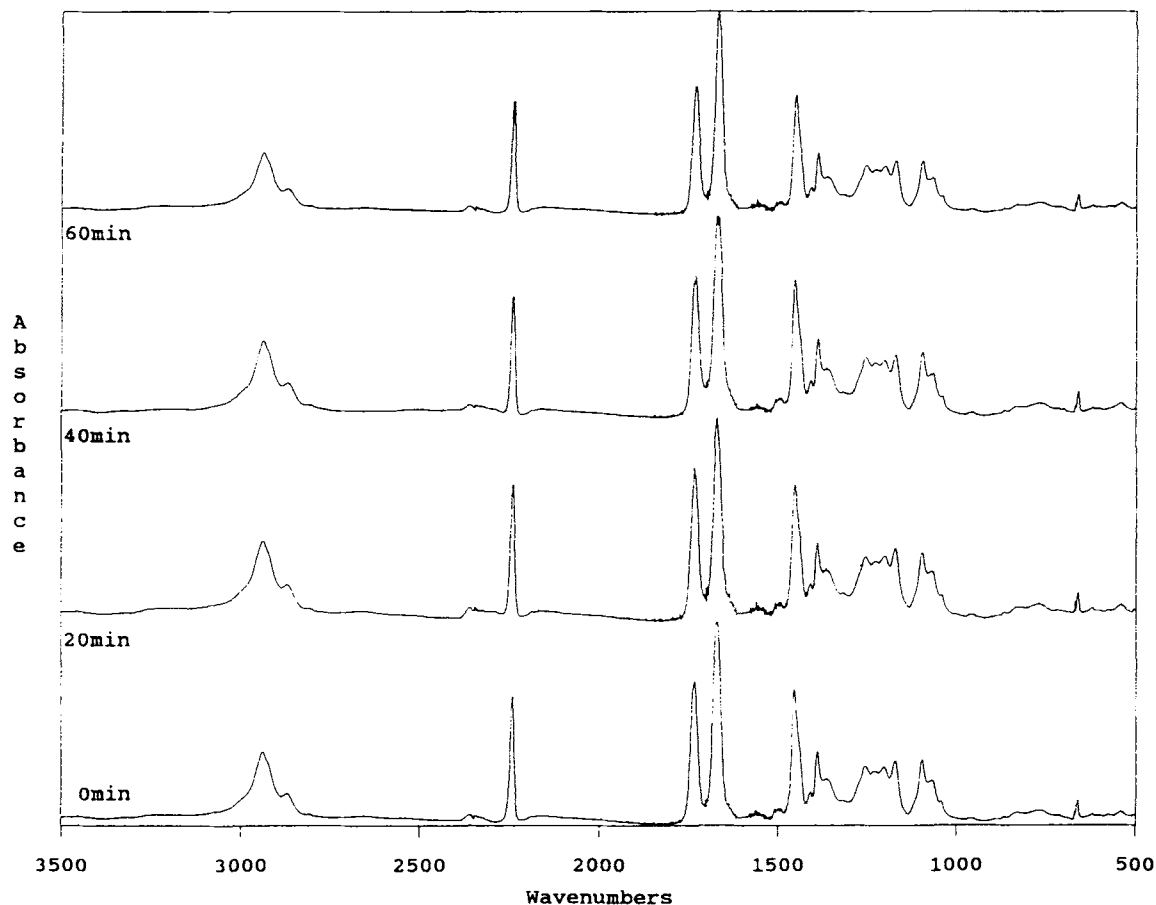


Figure 8 FTIR spectra taken from films cast before and after annealing at 180°C.

zation of nitrile groups to form the random imine structure rather than intermolecular crosslinking. Thermodynamic analysis provides a useful method for the present study to understand a particular phenomenon of the  $T_m$  increase after annealing in the melt. The proposed chemical degradation of the nitrile group could not be directly proved by spectroscopy due to experimental difficulty. Moreover, the changes in FTIR spectra, even when they are taken from films cast after annealing, were hardly notable because the degree of degradation in this experimental condition is too low to be analyzed by infrared spectra, as shown in Figure 8. Investigation on the effect of annealing on the rheological properties, crystallization kinetics, and structure of the final product is in progress.

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