

# Studies on Macromolecular Entanglement. II. Modification of Macromolecular Entanglements by Heat Treatment

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## SYNOPSIS

The modifications of macromolecular entanglements in polyacrylonitrile copolymer fibers by heat setting in different mediums such as steam, hot air, and inert liquid are reported. The effects of applied tension, frozen internal stress, temperature, time, medium, crystallization, etc., during heat setting on the modification of entanglements are investigated in detail. These experimental results elucidate clearly the mechanism of entanglement and disentanglement and confirm fully the DSC method of swelling polymers for studying entanglement in solid polymer, as was previously published in Part I of this paper. © 1993 John Wiley & Sons, Inc.

## I. INTRODUCTION

In Part I of this paper,<sup>1</sup> we proved, from the melting behavior of swelling polymers, that the protrusion peak on the tail portion of the differential scanning calorimetry thermogram of swelling polymers (abbreviated as SDSC) is attributed to the structural unit of macromolecular entanglements and the total entanglement energy can be characterized by the area of this protrusion peak. Here, the total entanglement energy indeed includes two parts: the coupling association energy between neighboring entangled chains and the energy of the entanglement loopings. This fact will be discussed later.

In this article, the modification of macromolecular entanglements in fibers under relaxed and tensioned conditions by heat setting in saturated steam, hot air, or inert liquid, as exhibited via the change of the corresponding protrusion peak in SDSC thermogram, will be reported, and the mechanism of these modifications will also be investigated. The outcome of this investigation will show that the method of DSC of a swelling polymer is a powerful tool for studying the modifications of macromolecular entanglements in a solid polymer.

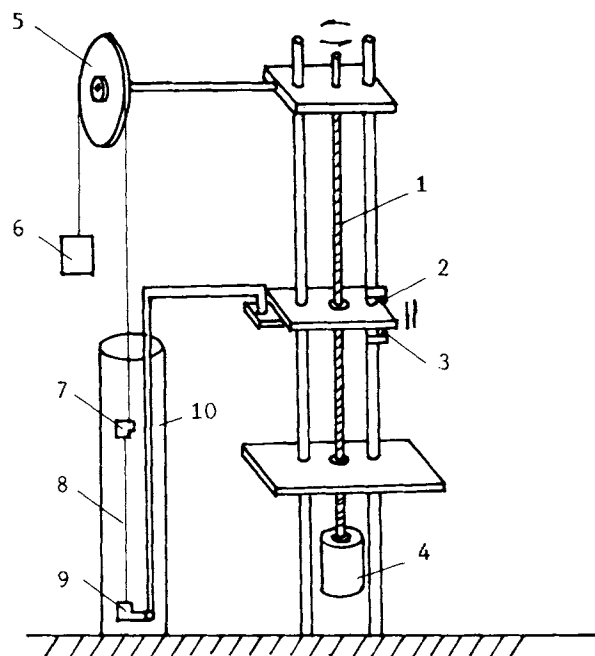
## II. EXPERIMENTAL METHODS AND RESULTS

### 1. Modification of Entanglements in a Fiber by Externally Applied Tension during Heat Treatment

The simple apparatus used here is shown in Figure 1. The apparatus was originally designed for stretching of fibers. When used here, the maintenance of a proper temperature, a proper tension (by applying an adjustable load), and a proper solvent, here 80% aqueous dimethyl formamide (DMF) solution for polyacrylonitrile copolymer (PAC) fibers, are required. A temperature of 75°C is selected for the PAC fiber. Alternate straining of the fiber at a frequency of about 1 Hz is chosen: The duration of straining may vary from a few minutes up to 30 min. The magnitude of entanglement is measured by the swelling DSC as described in Part I of this paper.<sup>1</sup>

The results obtained are shown in Figure 2. The amount of modification of entanglements is quite sensitive to the amount of applied tension, which, however, is altogether a matter of a few to 20 mg/den. The entanglement energy left in the PAC fiber sample after the stretching experiment shows a maximum at an applied tension of about 5 mg/den, which is nearly equal to the thermal shrinking stress of the PAC fiber sample at constant length.<sup>2</sup>

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**Figure 1** Simple apparatus for applying tension externally: (1) screw; (2) upper limit; (3) lower limit; (4) servomotor; (5) pulley; (6) weight; (7) upper clamp; (8) fiber; (9) lower clamp; (10) heating tube (filled with 80% DMF).

The direction of the applied tension and that of the shrinking stress are opposite to each other. When the two are equal in magnitude, the externally applied tension is just responsible for keeping a constant length of the fiber instead of shrinking or elongation. Since the disentanglement of macromolecular chains is, in general, accompanied by the length change of the fibers, around 5 mg/den applied tension, the entanglement energy left, whether coupling or looping, will be naturally at its maximum. Both applied tension and shrinking stress will tend to remove entanglements; the former tends to pull entangled chains out and the latter tends to withdraw entangled chains. Thus, the effective stress for modification of entanglements will depend on their algebraic sum. But for the external applied tension, at its best, some entanglements will always remain. The reason for this will be given below.

## 2. Heat Setting of PAC Fibers in Saturated Steam at Specified Temperatures

### a. Steam Heat-Setting Procedure

An autoclave that can be safely operated at a pressure of 4 atm with air previously removed by vacuum suction is required. The PAC fiber samples were

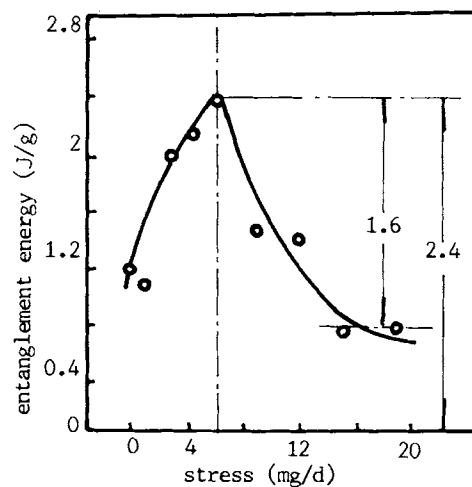
taken from Jinshan Jinglun fiber production plant at a stage just after steam drawing and washing, but prior to drum drying. They were air-dried in the laboratory.

Saturated steam heat setting was conducted in a laboratory autoclave at fixed temperatures of 100, 110, 120, and 130°C for different periods of time: 5, 10, 15, 20, and 30 min. The steam pressure was released at the right time and samples were taken out of the autoclave and preserved for swelling DSC analysis.

### b. DSC Analysis of Swelling PAC Samples Heat-set in Saturated Steam

This was carried out as usual, using 80% aqueous DMF solution and a polymer-solvent ratio of 2/10 (mg/ $\mu$ L). The thermograms so obtained are shown in Figure 3(a)-(d). Qualitative visual inspection of these thermograms at once leads to the following results:

1. In parallel with the rise of temperature and prolongation of heating time, crystallinity of the samples increases, as revealed by the increase of height of the paracrystalline peak (near 90°C) of the DSC thermogram (see Fig. 3). This result had been repeatedly observed in our early work.<sup>3</sup>
2. During the beginning period of steam heat setting, i.e., 5-10 min, especially in the case of relatively low temperature of 100 or 110°C, the area of the protrusion peak increases somewhat. In the succeeding 10 min, the area of the protrusion peak rapidly declines, and



**Figure 2** Effects of alternate stress on entanglements.

in the case of 120 and 130°C, the protrusion peak area even vanishes completely for the 20 min setting.

3. After 20 min of steam heat setting, the area of the protrusion peak increases again until at 30 min it may reach a value even greater than its original value of the fiber sample without steam heat setting.

### c. Evaluation of Protrusion Peak Area

To interpret quantitatively the modification of the protrusion peak by steam heat setting, the area of all the protrusion peaks was measured and are listed in Table I. This procedure of evaluating the protrusion peak area is illustrated in Figure 4. The zero-protrusion profile curve 4 in Figure 3(c) or (d) is used as the base line for cutting down the true protrusion area.

The precision of entanglement energy as estimated from two reproducible SDSC thermograms of one PAC fiber sample by the method described above is 2.7%. The same result for another PAC fiber sample is 14%. Thus, the precision of the prescribed method is varying and rather low. The sources of error are (1) the low reproducibility of the SDSC thermograms and (2) the difficulty of fitting the zero-profile to the experimental SDSC thermogram.

### d. Effects of Crystallization on Disentanglements

We suspected at first that such an irregular change of the protrusion peak area, as described above, might be related to the history of the original fiber samples and due to the presence of frozen internal stress in the partially drawn and air-dried fiber, as procured from the Jinshan Jinglun plant. Therefore, we supplemented the above results by another simple experiment: The original sample was heated for 1 min at 100°C to remove the frozen internal stress before steam heat setting. Swelling DSC tests of the so-treated samples were then done as usual. Nevertheless, the initial rise of the protrusion peak area in the case of steam heat setting at 100 and 110°C still persists. Therefore, the frozen internal stress has nothing to do with the rise of entanglements. Other causes must be sought. In the absence of the internal stress of one form or another (e.g., internal stress due to hot recrystallization or thermal shrinkage), or in their presence but being very weak, gentle heating of 100 and 110°C might be sufficient to induce a certain enhancement of entanglements

if the previous processing history of the sample has left only few entanglements in its texture.

At a higher temperature of 120 or 130°C, the relative crystallinity values of the heat-set samples are indicated by the height of the swelling DSC paracrystalline peak as well as measured by wide-angle X-ray analysis (WAXA). The crystallinity values are tabulated in Table II. A plot of the area of the protrusion peaks and crystallinity of the steam heat-set samples vs. the time of heat setting is shown in Figure 5. The innate relation among the three parameters seems quite evident. The stress generated by a process of hot recrystallization will induce macromolecular disentanglement.

Since a PAC fiber steam heat set under relaxed conditions generally will not show thermal shrinking stress, the induced stress must be due to hot recrystallization of the fiber that causes an increase of crystallinity and crystallite size. The direct measurements, using WAXS, on the original sample and the one that has been completely heat set at 100°C show an increase of crystallinity of about 9% (see Figure 5). All the above results indicate that the amount of entanglements can be modified in accordance with the change of temperature, time, and tension or internal stress to which the sample is subjected. A preliminary conclusion is that the existence of stress inside the macromolecular chains will be favorable to disentanglement and thermal Brownian motion of macromolecular chains will cause themselves to come into entanglements.

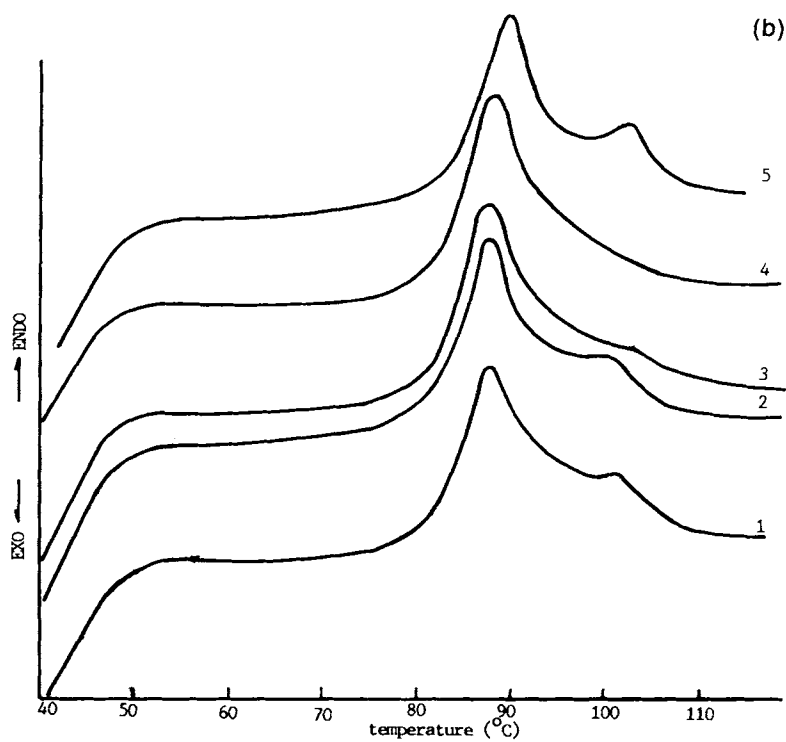
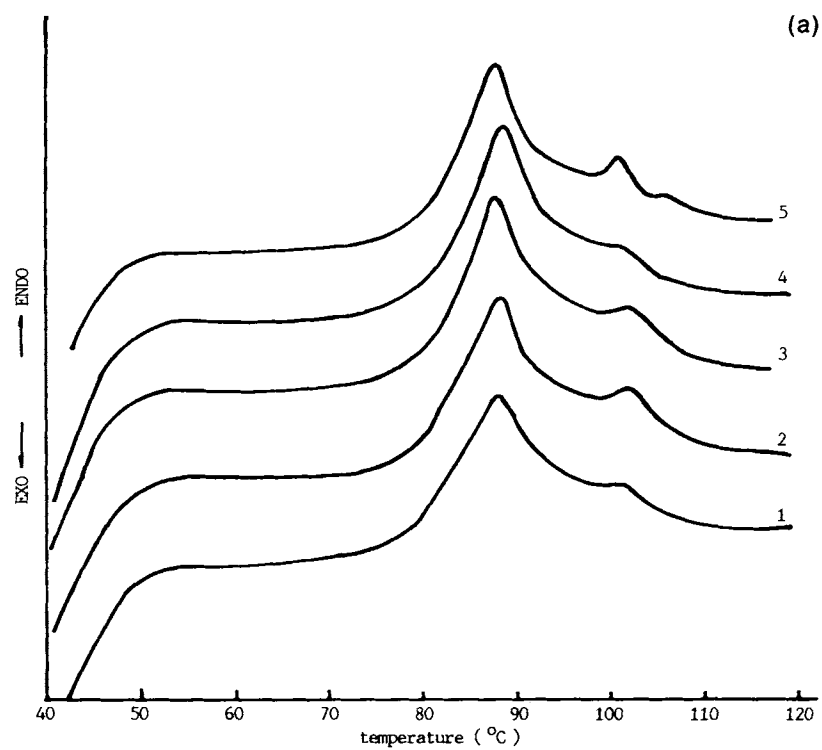
### e. Measurement of the Loop Strength of a Steam Heat-Set PAC Fiber

This was carried out on an Instron tester according to a routine procedure and the results are listed in Table III. The improvement of loop strength of PAC fiber by steam heat setting in the relaxed state is quite marked, but excessive heat setting will cause restoration of entanglements and worsening in loop strength. We shall return to this topic in the Discussion section.

## 3. Heat Setting of the PAC Fibers in Dry Air or Inert Liquid at Specified Temperatures

### a. Heating Apparatus and Procedure

A laboratory forced-convection drying oven was at first used as the heating apparatus. In the later stage of our experiments, it was found that during heating in a forced-circulation air-drying oven the temperature is far from uniform, as judged from the irreg-



**Figure 3** Swelling DSC thermograms of PAC fibers steam set at different temperatures. Setting time: (1) 5 min; (2) 10 min; (3) 15 min; (4) 20 min; (5) 30 min. Setting temperature: (a) 100°C; (b) 110°C; (c) 120°C; (d) 130°C.

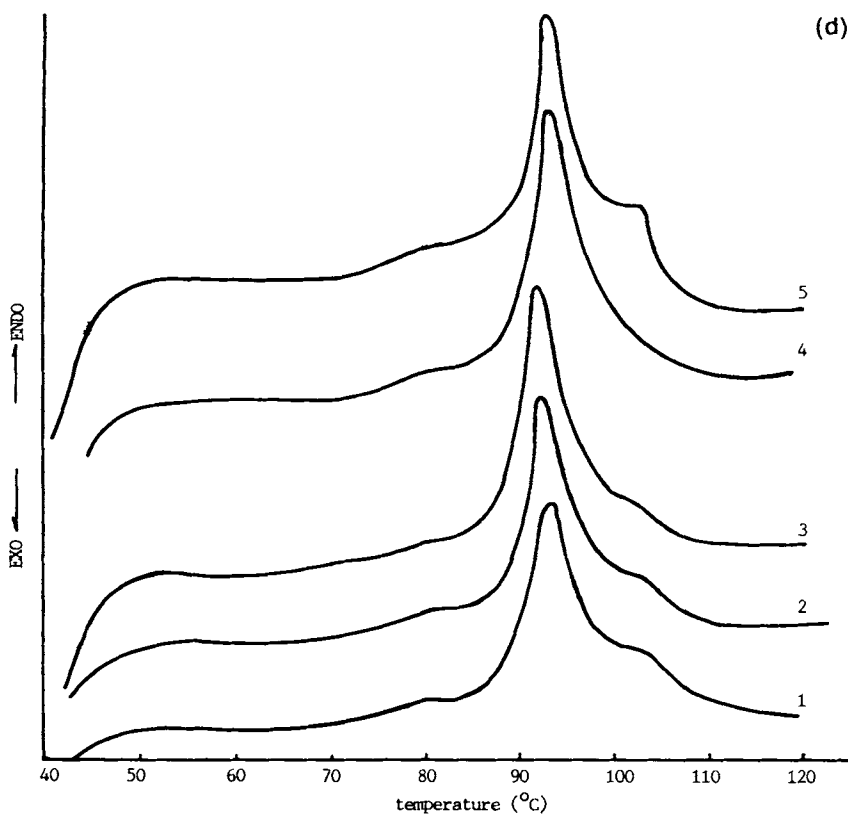
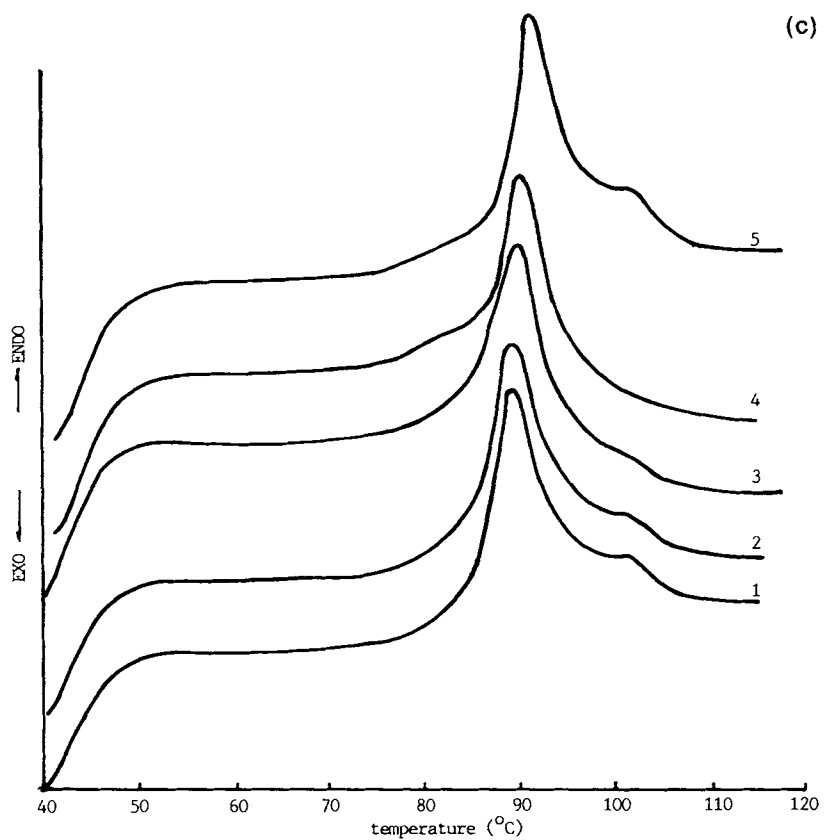


Figure 3 (continued from the previous page)

**Table I** Entanglement Energy (J/g) of Steam-Set PAC Fibers

Setting Temp (°C)	Setting Time (min)				
	5	10	15	20	30
100	4.8	6.7	6.0	3.0	8.6
110	5.0	6.3	4.2	3.0	7.2
120	3.5	2.2	1.1	0.0	4.5
130	2.8	1.9	1.2	0.0	5.3

ularity of variation of the paracrystalline peak. Furthermore, the yellowing of the heat-treated product indicated that the PAC fiber was overheated to a temperature above 180°C since a PAC fiber containing methylallylsulfonate (MAS) could not exhibit such a phenomenon at a temperature below 180°C. Therefore, the air-drying oven was replaced by a tube placed in a thermostatic liquid maintained at the required temperature and filled with an inert liquid (e.g., silicone oil), and a very fine thermoelement was used so that short-time heating can be measured with greater precision. Nevertheless, time of heating less than 1 min possesses only relative significance, rather than absolute meaning.

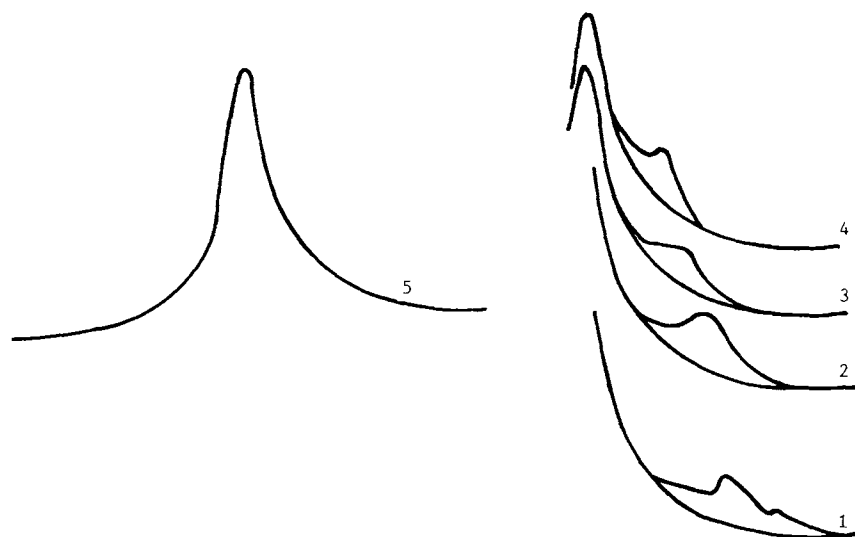
#### **b. DSC Analysis of Swelling PAC Samples Heat-Set in Hot Air**

This was done as usual. The obtained thermograms are shown in Figure 6(a)–(f). The distinction be-

**Table II** Crystallinity (% WAXA) of Steam-Set PAC Fibers

Setting Temp (°C)	Setting Time (min)				
	5	10	15	20	30
100	37.9	42.0	41.8	42.2	42.6
110	37.8	—	42.7	43.1	43.1
120	44.4	44.9	45.6	45.5	45.6
130	44.3	45.2	45.1	45.3	46.0

tween saturated steam and dry air heat-set samples is quite obvious. With hot air, the initial decrease of entanglements is very rapid; heating for 1 min or even less will remove the existing entanglements completely, but the recovery of the entanglements is rather slow. It requires a rather high temperature of 170–180°C, and even then the complete recovery of entanglements requires a time interval of more than 20 min. The rate of disentanglement at the beginning of hot-air heating is astonishingly rapid, probably due to the effects of frozen shrinking stress. One might even doubt the reality of the experimental facts as were shown in Figure 6(a)–(d). To clarify this point, we conducted the heating experiment in hot air in steps differing by seconds, e.g., 0, 10, 20, 30, and 40 s, so that the process of disentanglement can be continuously watched. This result is shown in Figure 6(e). From the result shown in Figure 6(e), the doubt about the reality of disentanglement can be completely cleared. The area A in relative



**Figure 4** Profile of the DSC thermogram for zero entanglement. (1)–(4) Area of different protrusion: (1) steam set at 100°C for 30 min; (2) steam set at 110°C for 30 min; (3) steam set at 120°C for 30 min; (4) steam set at 130°C for 30 min; (5) zero protrusion profile.

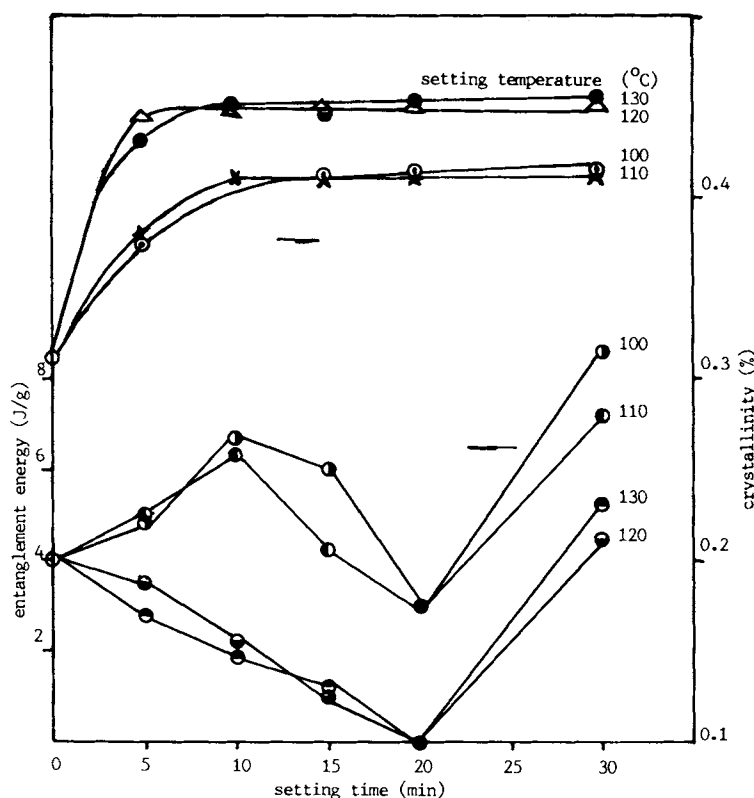


Figure 5 Duration of steam heat setting vs. entanglement energy and crystallinity.

units of the protrusion peak (which represents the total entanglement energy  $E$  in fibers) is plotted against the heat-setting time  $t$  in Figure 7 (a). The entanglement energy  $E$  will fall exponentially from its initial value  $E_0$  to  $E_t$  at the time  $t$  and finally reach  $E_\infty = 0$  as an asymptote. The curve can be expressed by using an Avrami type equation:

$$\theta = \frac{E_\infty - E_t}{E_\infty - E_0} = \text{Exp}(-Krt^n) \quad (1)$$

where  $\theta$  = fraction of entanglement energy still left at the time  $t$ ,  $Kr$  = a rate constant, and  $n$  = exponential order of the disentanglement reaction. Taking the logarithm on both sides twice, we have

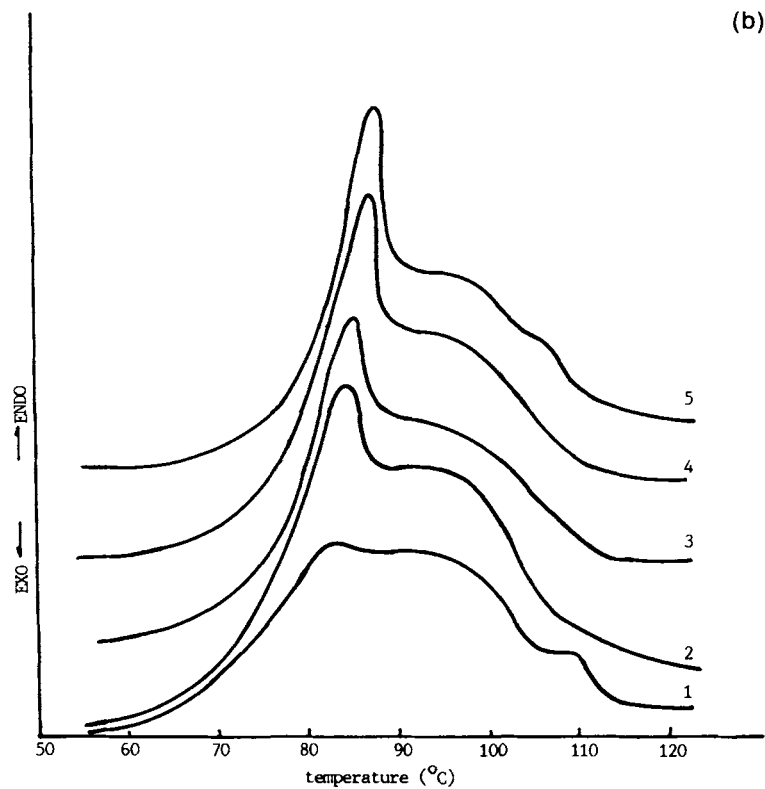
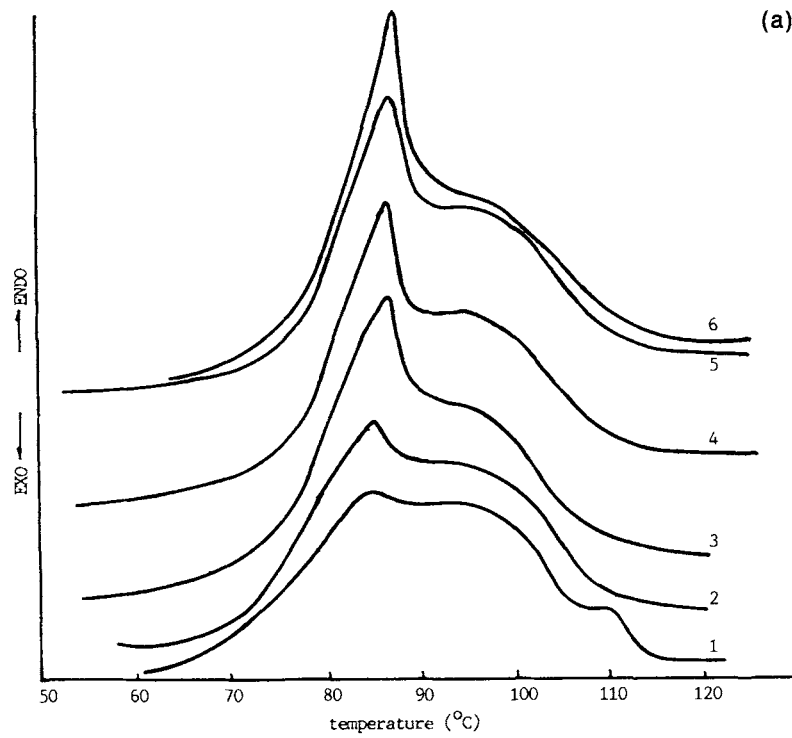
$$\ln(-\ln \theta) = \ln(Kr) + n \ln t \quad (2)$$

Plotting  $\ln \theta$  vs.  $t$  on an  $\ln - \ln$  scale is apparently a straight line with slope  $n$  and intercept  $Kr$ . From the data given in Figure 7(b), we have  $Kr = 0.0927$  and  $n = 0.963 \approx 1$  with a coefficient of variation 0.965. The time  $t$  at  $\theta = \frac{1}{2}$  is designated as  $t_{1/2}$  or half-life of the disentanglement reaction; it is, thus, 7.48 s in this case. This value shows that for the sample used here disentanglement in hot air at 120°C is a relatively rapid process if the frozen internal stress is not previously removed.

Alternatively, if the frozen internal stress is previously removed by heating for only 1 min at 100°C and then followed by heating in air at 120°C for a

Table III Loop Strength of Steam-Set PAC Fibers (Setting Temp 120°C)

Setting Time (min)	Entanglement Energy (J/g)	Breaking Strength (cN/dT)	Breaking Extension (%)	Loop Strength (cN/dT)	Loop Extension (%)
0	4.0	37.7	25.3	20.3	31.0
5	3.5	31.1	32.0	29.1	15.6
20	0.0	33.2	29.9	34.7	17.4
30	4.5	27.3	32.9	27.2	21.1



**Figure 6** Swelling DSC thermograms of PAC fibers heat set in hot air at different temperatures. (a) Heat-setting temperature 150°C. Setting time: (1) 0 min; (2) 1 min; (3) 10 min; (4) 30 min; (5) 40 min; (6) 80 min. (b) Heat-setting temperature 160°C. Setting time: (1) 0 min; (2) 1 min; (3) 10 min; (4) 40 min; (5) 60 min. (c) Heat setting temperature 170°C. Setting time: (1) 0 min; (2) 1 min; (3) 10 min; (4) 20 min; (5) 40 min. (d) Heat setting temperature 180°C. Setting time: (1) 0 min; (2) 1 min; (3) 10 min; (4) 20 min; (5) 40 min. (e) Effects of hot-air heating of less than 1 min around 120°C. Setting time: (1) 0 s; (2) 10 s; (3) 20 s; (4) 30 s; (5) 40 s. (f) Effects of frozen internal stress on entanglement. Setting time: (1) 0 s; (2) 10 s; (3) 20 s; (4) 30 s; (5) 40 s; (6) 50 s.



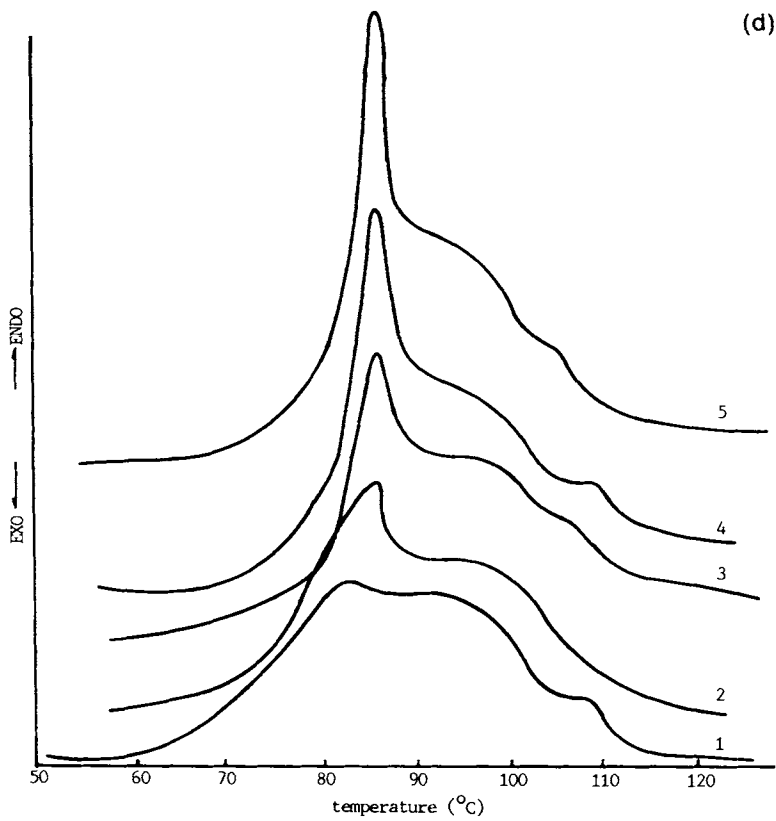
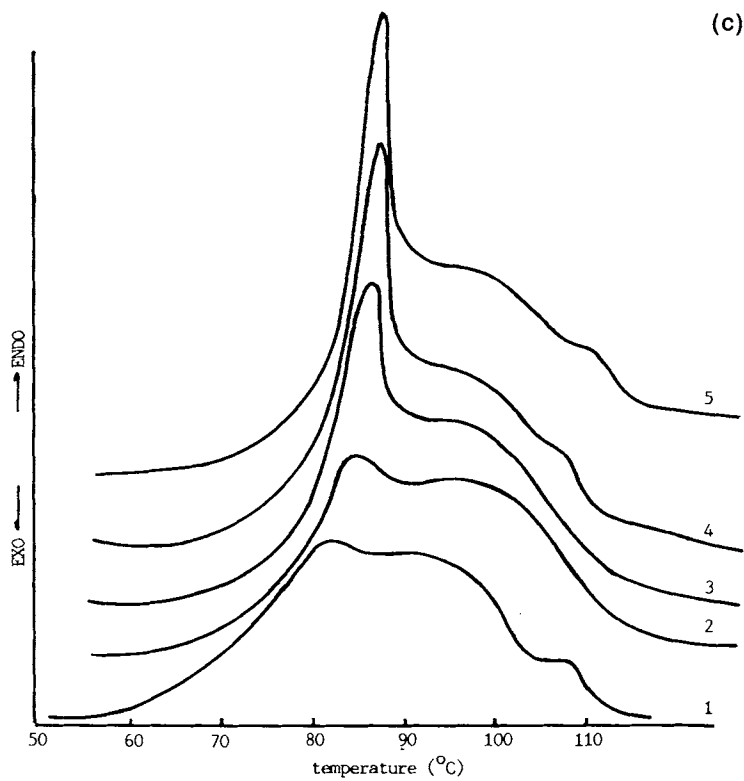


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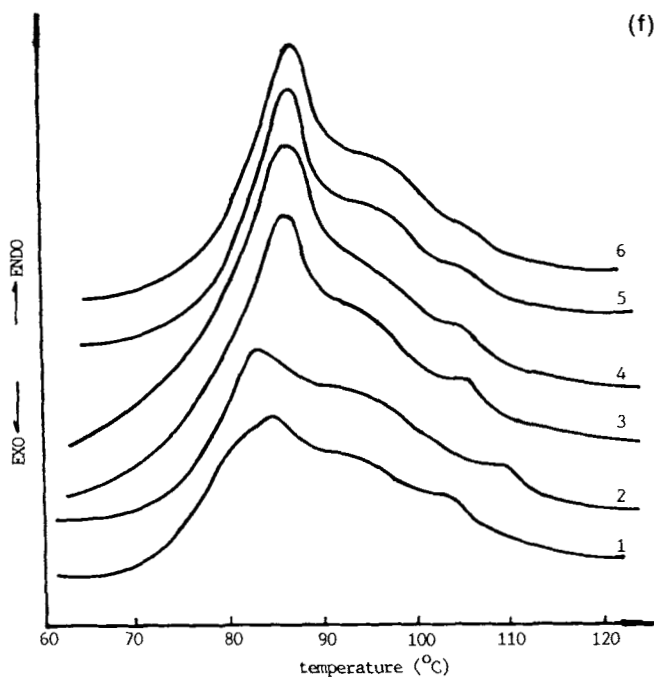
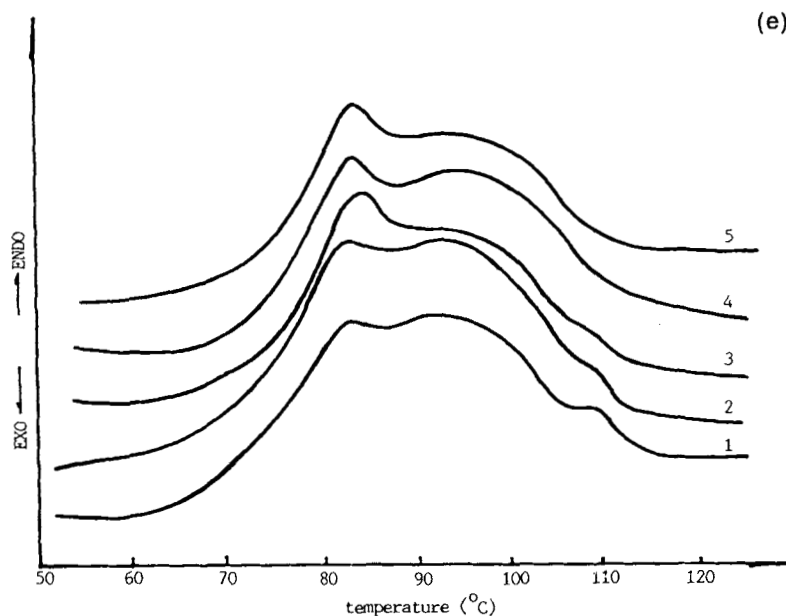


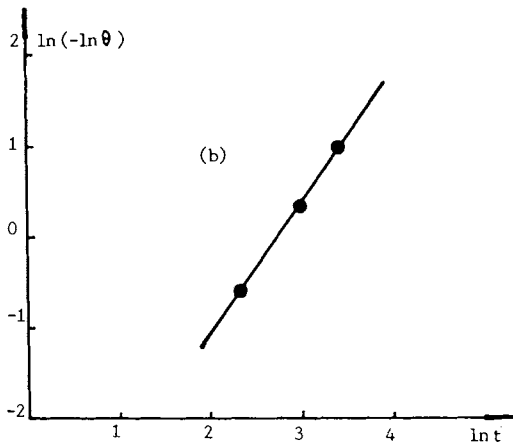
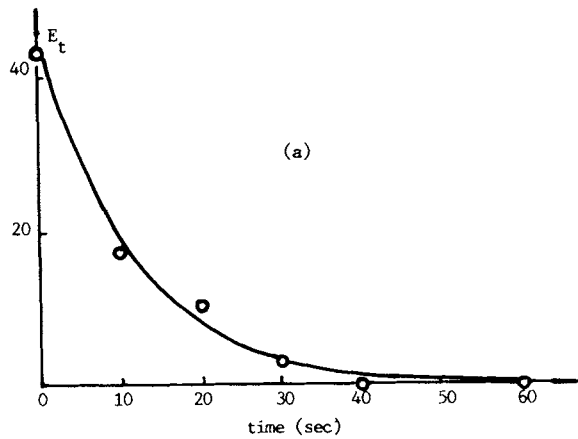
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number of seconds, the resulting DSC thermograms [Fig. 6(f)] will allow calculations similar to that illustrated above [see Fig. 8(a) and (b)], giving values of  $n = 1.091$ ,  $Kr = 0.024$ , and  $t_{1/2} = 28.9$  s.

Thus, it is definitely proved that the frozen internal stress when set free by gentle heating at a temperature slightly above the glass transition temperature of about  $100^{\circ}\text{C}$  will exert a big influence on disentanglement.

### c. Measurement of Stress Generated in the Fiber Sample during Heat setting in Air or Inert Liquid Medium at a Constant Temperature

To verify the proposition that the shrinking stress should be responsible for modifying the entanglements, it would be desirable to measure this stress in a TMA apparatus for fibers. A sample is placed in our TMA XRF-2 instrument at constant length



**Figure 7** Kinetic curve of disentanglement process in PAC fiber and kinetic analysis of disentanglement using Avrami's equation:  $[\theta = (E_\infty - E_t)/(E_\infty - E_0) = \exp(-K_r t^n)]$ ;  $K_r = 0.0927$ ,  $n = 0.9631$ ,  $r = 0.9652$ ,  $t_{1/2} = 7.18$  s).

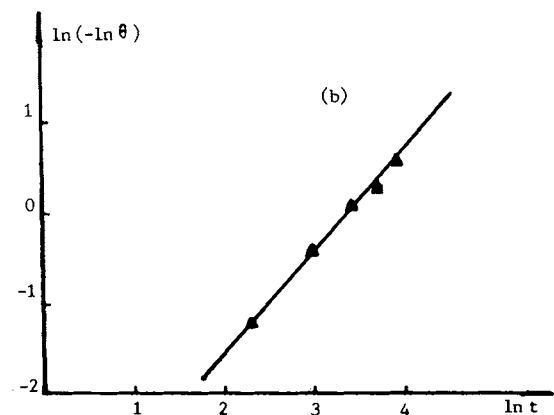
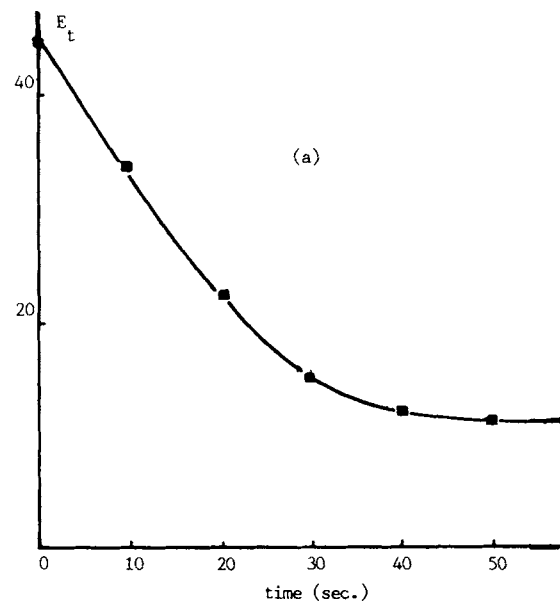
and heated in silicone oil at a constant temperature; the shrinking stress due to thermal shrinkage, crystallization, or other causes can be directly measured and recorded. The shrinking stress will grow and accumulate, but with its growing, it will always simultaneously be subjected to continual relaxation, so the record always exhibits a maximum and then falls off gradually, but the original zero value of measured stress is never recovered, probably due to some structural change during the shrinking or crystallizing process.

The time vs. shrinking stress curves under a constant temperature are shown in Figure 9(a) and (b). The maximum will be reached within 2 min when the temperature reaches its equilibrium value. This means that the stress during the beginning part of the curve is due to thermal shrinking stress, as crystallization is a process that requires more time to complete.

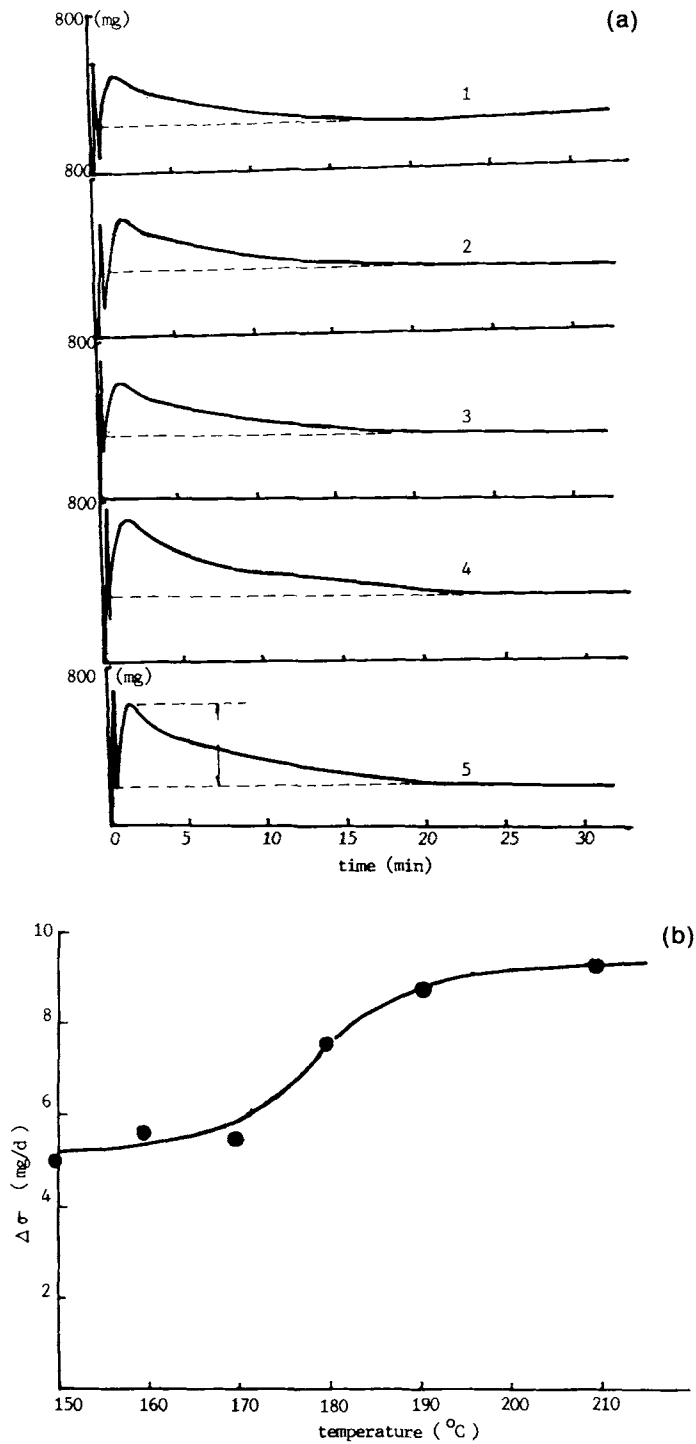
### III. DISCUSSION

#### 1. Distinction between Externally Applied Tension and Internal Stress Generated during Thermal Shrinkage and Crystallization Induced by Heat setting

In Fig. 2, it can be seen that the entanglement energy as measured by the protrusion peak area of the SDSC thermogram of the treated fibers will fall on both sides of the central maximum that corresponds to the zero effective stress when the externally applied tension is just compensated by the shrinking stress of the fiber. In general, the resulting effective



**Figure 8** Kinetic curve of disentanglement process in PAC fiber and kinetic analysis of disentanglement using Avrami's equation:  $(K_r = 0.024, n = 1.091, r = 0.996, t_{1/2} = 28.88$  s).



**Figure 9** (a) Time-shrinkage stress curve of PAC fibers at constant temperature: (1) 150°C; (2) 160°C; (3) 170°C; (4) 180°C; (5) 210°C; (b) the plot of  $\Delta\sigma$  vs. temperature.

stress is either a positive or a negative value, making the corresponding entanglement always smaller than the central maximum value. The results given in Figure 5 show, however, that entanglements can be completely removed by thermal shrinking and hot

recrystallization stress induced isotropically by steam heat setting.

In the case of externally applied tension, which acts in the direction of the fiber axis, the component is greatest in this direction and least in a direction

perpendicular to the fiber axis. Therefore, under the action of the externally applied tension, those linking macromolecular chains lying in and near the direction perpendicular to the fiber axis will be ineffective in modifying entanglements. Consequently, a portion of the entanglements can never be removed.

On the other hand, in the case of steam heat setting of the fiber sample in the relaxed condition, the linking molecules will transmit the shrinking stress induced by crystallization and thermal shrinkage in all directions, thus acting on all entangled chains whatever their orientation assumed and causing their complete removal if the time of action is long enough.

We can approximately evaluate the distinction between the two cases: Let the fraction of external applied tension that is effective to cause disentanglement be  $\alpha$ ; then, on average, we have

$$\alpha = \frac{\int_0^{\pi/2} \cos \phi d\phi}{\int_0^{\pi/2} d\phi} = 0.637$$

where  $\phi$  is the angle between the applied tension and entangled chains. From the data in Figure 2, the effective disentanglement fraction for external applied tension  $\alpha = 1.6/2.4 = 0.667$ . These two values agrees approximately.

## 2. The Mechanism of Disentanglement and Entanglement

### a. General Statements

If original entanglement energy of both coupling and looping is less than its equilibrium value, upon heating, the growth of entanglements will occur spontaneously from a thermodynamic point of view. The reverse process or disentanglement is favored by the presence of stresses tending to pull the chains out of its entangled state. The magnitude of this stress needed is quite small, being a matter of only a few mg/den. This view is in harmony with the experimental facts described above.

The entanglement bond energy as represented by the protrusion peak on the tail portion of SDSC thermogram should include the energy of the entanglement loopings and the coupling association energy between neighboring chains forming the entanglement loopings. The first part consists of only a minor portion of the whole, although it strongly influences the latter. The dual nature of the entan-

glement energy as revealed by this small protrusion peak has been thoroughly propounded elsewhere.<sup>4</sup>

The chain entanglement loopings are physically real, not only conceptual. It can be certainly perceptible from the SDSC thermogram, but because of the small magnitude of looping energy, it can barely be measurable directly. Nevertheless, the presence of the entangled loopings will enhance or augment the coupling (association) energy between macromolecular chains, making the total energy of the small SDSC protrusion peak more easily measurable. In other words, looping energy is recognized through the accompanying coupling energy, the two being closely related.

It might be appropriate to trace here the mechanism of formation of an entanglement bond with a dual nature. The coupling energy part comes from interaction between macromolecular chains and is conformational, whereas the looping energy part is topological (might be similar to configurational). The former is easily affected by temperature, solvent, or stress to which the macromolecular chains are subjected, whereas the latter is resistant to moderate high temperature and stretch (stress). It must be emphasized that the coupling bond formation in a polymer during the heat-treatment process is accomplished not in the process of heating, but in the process of cooling; the former would disrupt the existing texture in order to provide room for forming new texture. However, the looping bonds whether removed or formed (disentanglement or entanglement) are accomplished during the process of heating, as exemplified in the Experimental part of this paper.

When the heat motion of the macromolecular chains is subsiding down upon cooling, couplings between chains are gradually formed. Where and how these couplings are formed is evidently a statistical process that will be affected by certain textural units already existing, like entanglement loopings, which will restrict the macromolecular motions of neighboring chains. This is probably the reason why coupling energy is augmented where entanglement loopings exist, resulting in a protrusion peak on the tail portion of the SDSC thermogram. This process would occur even under room temperature.<sup>4</sup>

During the DSC process, the disruption of bonds (including couplings in the amorphous background, in the crystalline region and entanglement loopings themselves) is endothermic. When the coupling is dissociated and replaced by a solvent molecule, the energy of dissociation is endothermic and the heat of swelling is exothermic, so the net result is a diminution of the heat of the DSC thermogram if the DSC process of the polymer is conducted in the

swelling condition. This will be further discussed in Part III of this paper.<sup>5</sup> Nevertheless, the existence of the heat of swelling will not affect our estimation of the relative amount of entanglement loopings present.

The specific nature of an entanglement looping will make it quite resistant to moderate high temperature and stress. It is self-tightening to mechanical stretching. It will persist in most processing conditions during fiber formation. This is a very important peculiarity of most polymers during fiber processing.

### **b. Effects of the Medium**

In the medium of hot air, the elimination of entanglements of the fibers under heat setting is very fast so that the action of the frozen internal stress alone will be sufficient to achieve complete disentanglement even at a rather low temperature of 120°C for a short duration of less than 1 min [see Fig. 6(e)].

On the other side, the disentanglement capacity of saturated steam as a heat-setting medium seems to be less than that of hot air. The cause of this difference might be due to the difference in viscosity of the hot air and of the saturated steam to hinder the motion of the macromolecules and in their power to relax stresses. The results given in Figures 3 and 6 showed the complexity of the nature of the medium on entanglement modification. Further studies are necessary.

### **c. Internal Stresses Generated during Heat Setting**

Internal stress consists of several kinds:

- (a) Frozen internal stress was kept in the macromolecular chains by the freezing action of the matrix, both in the amorphous and in the imperfectly crystallizing regions during the processing stages. As soon as the matrix was set into heat motions, the frozen stresses would be released and act on their neighboring chains.
- (b) The entropic shrinking stress was generated in chains in the amorphous region when the intermolecular bonds were broken by the heat-setting process. Similarly, the shrinking stress due to entropic contraction in the paracrystalline region will succeed sooner or later.

The above-mentioned entropic shrinking stress for PAC fiber occurred during heat setting in dry air in two stages: one at a temperature below 160°C and the other at a temper-

ature above 160°C.<sup>6</sup> The shrinking process is probably completed in rather short duration, and the hot recrystallization process that greatly enhanced the crystallite width occurred somewhat later than the shrinking stress development.

In the actual heat-setting process, the fiber sample was plunged all at once into the medium that was already adjusted to the required temperature. Therefore, the temperature of the fiber rose rather quickly to that of the medium. The frozen internal stress was released rather suddenly.

We are, at present, still unable to exactly ascertain and separate the effects of the various internal stresses on disentanglements, the investigation of which is still under way.

- (c) Effects of heat history. It must be noted that the initial response of a sample to heat modification of entanglements depends very much upon the previous heat history of the sample.

A sample at an intermediate state of entanglement will give a response of entanglement or disentanglement according to the relative intensity of the effects of internal stress or thermal motion.

### **d. Shear Modification**

The technique of shear modification has been applied in the polymer-processing industry for two to three decades although at first workers in this field were not clearly aware that the phenomenon was primarily concerned with the removal of entanglements by shearing stress.<sup>7,8</sup>

The analogy between disentanglement by internal stress and entanglement modification by shear is quite close. However, with the former, modification is brought about in solid polymer, whereas with the latter, entanglements usually in liquid polymer are modified.

### **Contemporary Theories of Entanglements**

This discussion on the mechanism of entanglement modification should not be brought to a close without some references to the contemporary theories of entanglements. The tube model and the theory of reptation for entanglement chains are well known.<sup>9,10</sup> The back-and-forth model of reptation of a macromolecule during disentanglement is also plausible.<sup>11</sup> Nevertheless, the experimental findings given in the present paper show some aspects worthwhile mentioning.

- (a) During disentanglements, some stress of one form or another is necessary to pull the chain out of its entangled state. Under heating in dry air, the disentangling speed is very fast, especially when frozen internal stress is present. The onward motion of the chains might be sporadic, instead of uniform, because of varying hindrance encountered.
- (b) During entanglement, the entangled chain must execute rapid thermal motions in constantly changing directions, thus interlacing their neighbors and forming topological entangled couplings. Most of the trial interlacings might be ineffective since their motion is also hindered. The theory of reptations basically applies here.
- (c) From the nature of disentanglement and entanglement as described in the experimental results above, the former could be expected to occur at very fast speed, especially in dry hot air.

### 3. The Effects of Macromolecular Entanglements on Mechanical Properties of Fibers

This topic will be the subject of our further studies. For the present, only loop strength and break loop extension will be discussed. The experimental results have already been given in Table III.

Why should looping and knotting of a fiber impair its loop strength to such a big extent? Entanglement is a microscopic looping of the macromolecular chains. Macroscopical looping of a fiber might cause excessive straining in the microscopically looped

macromolecules. This twofold looping may cause excessive high stress inside the looped macromolecule, thereby reducing greatly the capability of the fiber to sustain externally applied stress. The result is a big drop of the loop strength of the sample. The looped macromolecule in the sample becomes a weak spot during the loop-strength test.

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