Macromolecular Entanglement. III. Textural Development of Acrylic Fibers

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SYNOPSIS

The texture of a polymer (or fiber) is effectively developed by heat and stress. In this article, the chief material studied is acrylics, usually polyacrylonitile copolymer (PAC fiber) produced by Jingshan Jinglun Fiber Production Plant. In industry, the Jinglun acrylic fiber is heat treated, using saturated steam, at a temperature of 120–130°C to enhance its loop strength, reduce shrinkage, and stabilize crimp. At 140°C, the fiber becomes tacky and its good textile properties seem to deteriorate. At 150–160°C, the texture of the fiber seems to be deeply modified. Tested by differential scanning calorimetry (DSC) with the fiber immersed in a swelling agent (usually termed swelling DSC, abbreviated as SDSC), in addition to the entanglement peaks situated on the latter part of the thermogram of the Jinglun fiber, a new endothermic peak before the crystalline peak (actually, paracrystalline in the case of acrylic fiber) was discovered. The elastic recovery properties of the treated fiber under partially swelling conditions were improved. This seems to indicate that this preparacrystalline peak might also be concerned with entanglements.

INTRODUCTION

The texture or supermolecular structure of a polymer is usually considered as consisting of the following structural units.[1]

Intermolecular Bond Structure

1. *Crystalline lattice structure* is most effectively studied by the wide-angle X-ray diffraction (WAXD) method, but will not be dealt with in this article.
2. *Mesomorphous structure* is a kind of structure intermediate between the crystalline lattice and the amorphous background.
3. *Amorphous background* exhibits as a broad peak in the thermogram of the swelling differential scanning calorimetry (SDSC) and as a halo in the WAXD diagram. The term background is further explained below.
4. *Entanglement structure* an entangled coupling may be a short-range local loop of neighboring chains or a long-range contour loop.[2]

Orientation

Orientation is an important structural unit of texture for fibers and films. It exists both in the crystalline and amorphous regions. Orientation, however, unlike other structural units of texture, is not an entity, but a relation pertaining to direction.

Morphological Structure

Morphological structure is observed by optical and electron microscopy. We will omit this item in the present article.

Texture is a structure common to all high polymers, whether in bulk or in fibers and films. In this article, the examples are mostly related to acrylic polymers, although in some cases other polymers are also referred to.

It would be advisable here to briefly summarize our previous work. In parts 1 and 2 of this series,[3,4] we pointed out that the presence of entanglements

in polyacrylonitrile copolymer (PAC) fibers is characterized by the appearance of a small peak or "protrusion" on the latter part of the SDSC thermogram. This peak can be modified (enhanced or reduced) by heat treatment either in a dry atmosphere or in saturated steam; the extent of modification depends upon the time and temperature of heat treatments. Also, the degree of entanglement is much influenced by the concentration of the polymer solution (dope) from which the bulk polymer and fiber are coagulated or precipitated, and also by the time and temperature of heat treatments. The influence of stress, either internal stress frozen in the texture during processing, which can be released upon heating, or motive stress generated in the chain molecules during crystallization, is important in the process of disentanglement.

With respect to the study of texture by multiendotherms using conventional differential scanning calorimetry (DSC), we have made an extensive survey of the existing literature. Mead and Porter[5] have shown that crystallized polyethylene after annealing above 210°C at pressure of 0.49 GPa produces multiple endothermic peaks in DSC. Multiple and overlapping endotherms in conventional DSC are also observed by others[6] and generally explained as associated with the melting of the chain-folded fraction, or imperfect, smaller lamellar crystals or low-molecular-weight portion of polymers.[6] In the case of nylon-6, polymorphic crystal forms, α and γ, are shown by conventional DSC thermogram.[7,8] So far, we failed to get any result in which the presence of entanglement in the texture of a polymer is revealed. The existence of macromolecular entanglements in the polymer texture, irrespective of whether the polymer is swollen or not, is quite certain. The difference might be due to the fact that macromolecular entanglements act as an integral part of the whole swollen network structure, which can resist rupture until the maximum degree of swelling is reached. At this moment, macromolecular entanglement bonds will be broken all at once and the summative energy of all the entanglement bonds must be absorbed in a short interval of temperature change, resulting in a sharp protrusion peak on the swelling differential scanning calorimetry (SDSC) thermogram.[3] This explains why our SDSC method is a powerful tool for studying macromolecular entanglements. If the polymer is subjected to a conventional DSC, the situation will be entirely different.

Before proceeding to the experimental part, expositions of some terms seems appropriate.

1. *Crystalline or paracrystalline* A substance whose lattice structure is regular in three dimensions is usually crystalline when examined by WAXD. If regularity is present in the lattice structure only in one or two dimensions, then the materials may be regarded as paracrystalline.[9] Acrylic polymer usually shows axial irregularity; its X-ray diffraction diagram shows no meridional spots. Hence, PAN or PAC is paracrystalline, while polyester, polyamide, and polyolefin etc., are crystalline, sometimes even with two or more crystalline forms.

2. *Amorphous phase or background* The term amorphous background was borrowed from X-ray diffraction.[9] This diffuse scattered intensity is due to amorphous material and also in part due to axial irregularity. The term "background" correctly describes the situation since the crystalline region is actually formed on the basis of the amorphous background during the crystallization processes.

The diffraction angle 2θ is governed by the distance between crystalline planes (wide angle), and in small-angle scattering the distance between the scattering particles plays the same role. Hence, in both cases, the density of the scattering material determines scattering angle. On the other hand, the SDSC thermogram describes the distribution of bond energy between the neighboring macromolecules as a function of the temperature of the thermogram. The crystalline (or paracrystalline) peak represents the maximum average energy density, but it does not deny the presence of privileged pairs of macromolecules in the amorphous phase that possess greater bond energy than the maximum average value of the paracrystalline peak. The amorphous material is glassy or liquid in nature; it has no melting point. On the contrary, its melting range spreads over the whole SDSC thermogram. The whole swelling and melting process of a polymer fiber during heating can be visually observed under a polarized thermomicroscope.[3]

Concerning semicrystalline polymers, the two-phase theory is generally accepted. But, for acrylic polymer, the single-phase double-bonded theory is more attractive.[10,11] The structure of an acrylic polymer may be looked upon as a network structure of amorphous and paracrystalline regions, some long macromolecular chains, interpenetrating both regions without any sharp phase boundary between the two regions. In swollen fibers, the entanglements play the role of network crosslinks just like those in a rubber. The amounts of bond energy in the two regions are distinctively different (see discussion below).

EXPERIMENTAL AND RESULTS

SDSC Method for Studying Texture

There exist a multitude of methods for studying texture, including the most widely applied method, WAXD. Here, only the SDSC method described below will be recommended since it possesses certain advantages. It is simple, quick, and direct.[12] The method is, however, still in the process of development. In Part 1 of this series, this method has already been applied.[3]

The sample should be cut into fine powders. For acrylic polymer, 80–85% aqueous dimethyl formamide (DMF) is preferably used as the swelling agent. Two mg polymer are used in each test; a polymer/solvent ratio of 2 mg to 10 μL is preferred. The rate of temperature rise of 5 or 10°C/min is usually chosen. A perfect hermatic seal of the DSC cell is necessary for obtaining reliable, reproducible thermograms.

Preparation of Experimental Polymer Materials

1. PAC fiber (PAC, with comonomer composition of acrylonitrile/methyl acrylate/methallylsulfonate, 91.5/8.1/0.4) is freshly spun and steam stretched, followed by washing and air drying. The sample was taken from Jingshan Jinglun Production Plant at the stage after washing and before drying. It is of low crystallinity and fair orientation.
2. PAC bulk polymer is obtained directly from emulsion polymerization.
3. PAC polymer is dissolved in hot 80% DMF, followed by cooling and precipitation.
4. PAC polymer is solution spun into water to form a model fiber.

With the exception of sample 1, the samples are very nearly amorphous, which is necessary to help understanding the process of texture development.

After a SDSC test is finished and the cell is left to cool quickly, a second scan is done as usual; the obtained thermogram is also very nearly amorphous.

The SDSC thermograms of the several acrylic polymer samples mentioned above are shown in Figure 1, which exhibits the general shape of a more or less flat Gaussian probability curve containing no entanglement protrusion peak.

### Development of Texture in a Bulk Polymer by Heating in Dry Air and in Saturated Steam

Heating in dry air and in saturated steam yield quite different textures in the resulting polymers.

The starting samples are PAC bulk polymer obtained by dissolving PAC polymer in hot 80% aqueous DMF solution, followed by precipitation upon cooling, separation, washing, and air drying, as mentioned above. Dry heating was done in an oven of the forced air-circulation type and steam heating done in an autoclave, both with automatic temperature control.

The SDSC thermograms of the precipitated samples and the change of entanglement protrusion peak with concentration of dope were already given in
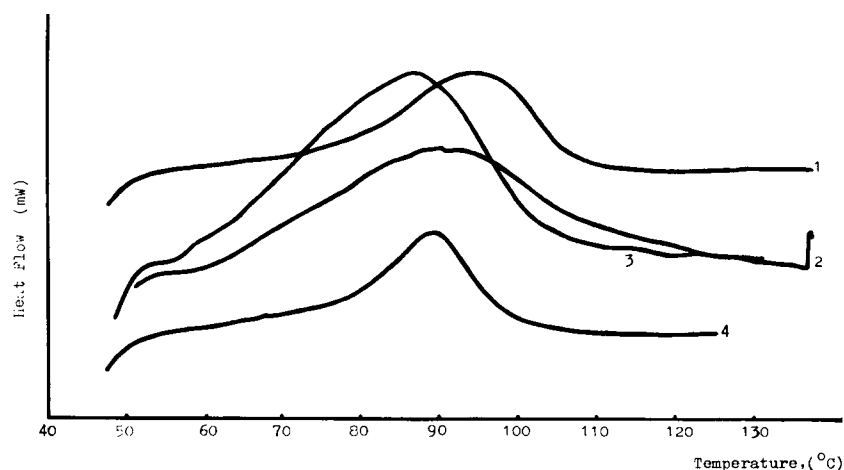
Figure 1   Amorphous background of a PAC swelling DSC thermogram. (1), PAC polymer precipitated from 2% dope (80% aqueous DMF); (2), model fiber from 30% PAC dope (pure DMF); (3), bulk polymer precipitated from 30% dope (pure DMF); (4), second scan of a PAC SDSC test.
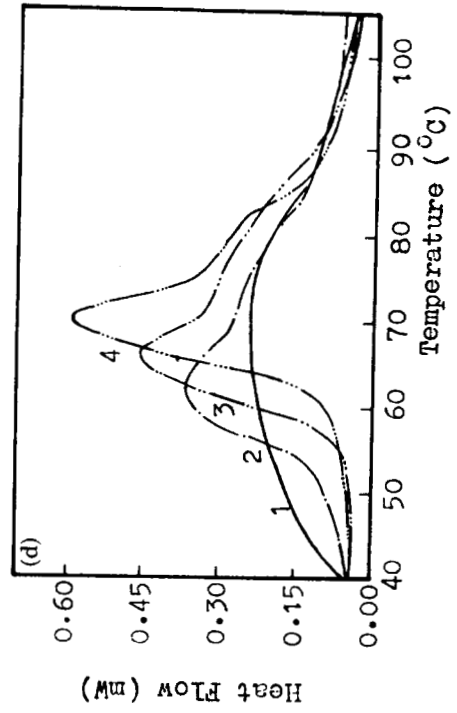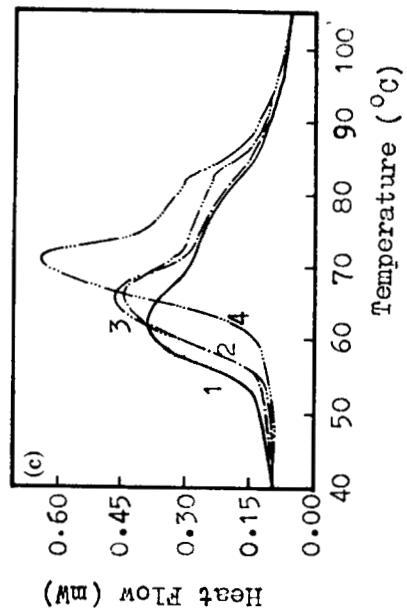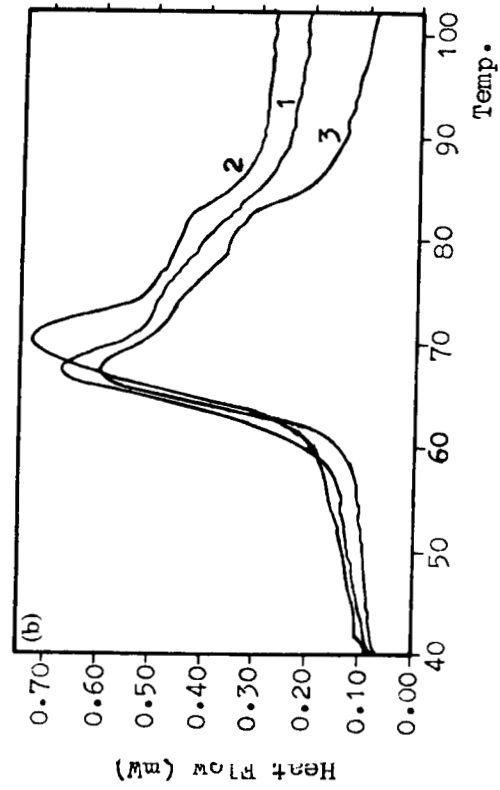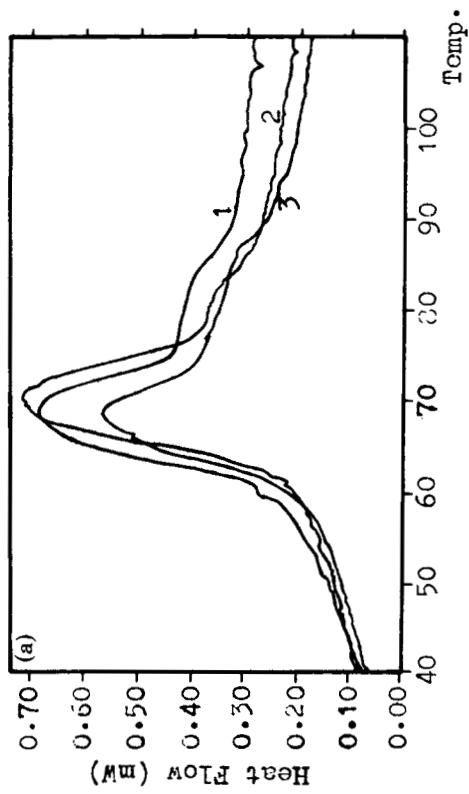
part 1.[3] Three percent of polymer concentration in the dope is a limit below which entanglement network seems no longer present. Steam heating seems to be somewhat more efficient to produce entanglements than dry heating. The influence of dope concentration on entanglement formation seems to persist into the precipitated polymer samples, as can be observed in Figure 2. The temperature and time of steam heat setting will enhance entanglements. All processes of heating, whether dry or in saturated steam, will enhance greatly the paracrystalline peak, as shown in Figure 2.

## Development of Fiber Texture by Heat and Stress

The starting materials are the same as that mentioned in sample 1 above.

Development of Fiber Texture by Dry Heating

Certain fiber-like acrylics will be subjected to oxidation when heated in air above 180°C. The effects of heating acrylics in air at temperatures between 100–140°C on their texture can be illustrated by their SDSC thermograms, as shown in Figure 3.

Although the meaning of the SDSC thermograms with respect to texture is still not entirely clear, their general significance can be stated with little doubt. Nevertheless, individual types require some explanation.

In Figure 3, each SDSC texture curve exhibits four distinct peaks. For fibers that had been air dried or dried at a temperature not higher than 105°C, there may exist in the beginning portion of the thermogram a small peak that will disappear upon further heating to 110°C. This phenomenon is probably due to glass transition. Upon heating to 120°C or higher, a new peak (close to peak 2 and designated in Fig. 3 as peak 1′) gradually grows up and rises in temperature, approaching peak 2 but never uniting with it. Since peak 2 is recognized quite certainly as the paracrystalline peak, peaks 1 and 1′ situated before peak 2 are designated as preparacrystalline peaks, the nature of which is not entirely clear yet.
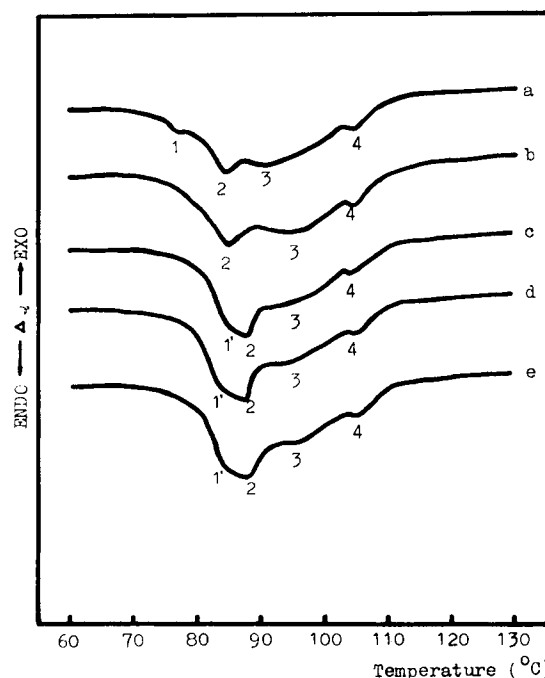
Figure 3   SDSC thermograms of PAC fibers dried at different temperatures. (a), 105°C; (b), 110°C; (c), 120°C; (d), 130°C; (e), 140°C. SDSC test, 80% DMF; polymer: solvent ratio, 2 mg/10 μL.

In later paragraphs in connection with the steam heating of fibers, other types of preparacrystalline peaks will be discussed.

Peak 2 also rises in temperature upon heating; at the same time, both the area and height of peak 2 seem to grow upon heating. From prolonged previous experience, which has been verified by WAXD, peak 2 is due to the paracrystalline structure.

Peak 3, the nature of which has puzzled us much previously, can now be assigned to the amorphous background, which does not shift much in position (temperature) upon heating.

Peak 4 has been shown with certainty to be due to entanglement,[3] the magnitude of which changes with the previous heating history of the sample.

The changes of peak temperature by dry heating are plotted in Figure 4.

Figure 2   Effects of heat treatments on the texture of PAC fibers. (a), dry heating at 105°C for 15 min on precipitated PAC bulk polymer: (1), 3%; (2), 5%; (3), 10% dope concentration. (b), steam heating at 105°C for 15 min on precipitated PAC bulk polymer: (1), 2%; (2), 3%; (3), 5% dope (86% aqueous DMF). (c), steam-heating temperature on bulk PAC polymer precipitated from 3% dope (86% aqueous DMF): (1), 110°C; (2), 115°C; (3), 120°C; (4), 126°C. Heating rate of SDSC test, 5°C/min. (d), steam-heating time on bulk PAC polymer precipitated from 3% dope (86% aqueous DMF): (1), 0′; (2), 2′; (3), 10′; (4), 30′.
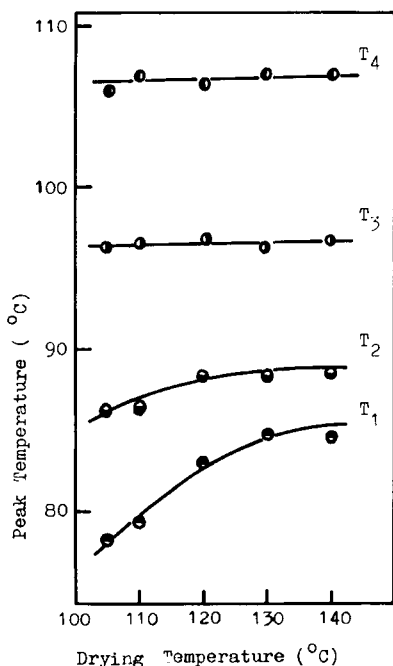
Figure 4   Effects of drying temperature on peak temperature. (T), temperature of the peak; subscripts designate peak number.

Texture Development of Fibers by Heating in Saturated Steam

PAC fiber can be heated safely in saturated steam at a temperature below 140°C; above this temperature, it will become tacky. This is the range of temperature usually employed for heat setting in saturated steam.

Figure 5 shows a set of SDSC curves of PAC fibers that has been heated in saturated steam of different temperatures, from which the following textural characteristics can be noted: The paracrystalline peak temperature increases from 87–98°C when the steam heating temperature is raised step by step from 90–140°C. At the same time, the amorphous background peak changes from 98–102°C only. The preparacrystalline peak at 78°C first appears when the steam heating temperature reaches 130°C, and it reaches a temperature of 77°C when the heating temperature is 140°C. The change of preparacrystalline peak temperature is only 1°C. Finally, the entanglement peak temperature changes also very little. The nature of the preparacrystalline peak will be discussed later.

Texture Modification of PAC Fiber by Steam Heating at Unusually High Temperatures

It was long known in industry that steam heat setting of PAC fiber can improve greatly the loop

strength of the fiber, but the true reason was not ascertained before the cause was traced to entanglements.[4]

Setting in saturated steam at temperatures above 140°C was unusual and seldom employed technically. Nevertheless, to understand better the nature of steam heat setting it is appropriate to do experiments of saturated steam heat setting at such unusually high temperatures.

A series of seven PAC fiber samples, heated beforehand to different temperatures from 125–162°C in saturated steam, were subjected to SDSC tests. The resulting thermograms are shown in Figure 6, from which the following characteristics can be observed:

1. The steam setting temperature and the three peak temperatures together with WAXD data are all listed in Table I; the last entanglement peak is lacking since the samples had been steam heated for 10 min only and hence were disentangled, as already demonstrated previously.[4]

Since the development processes of the different textural units are now fairly certain, we can resolve these peaks by a computer program, or even by a manual program, al-
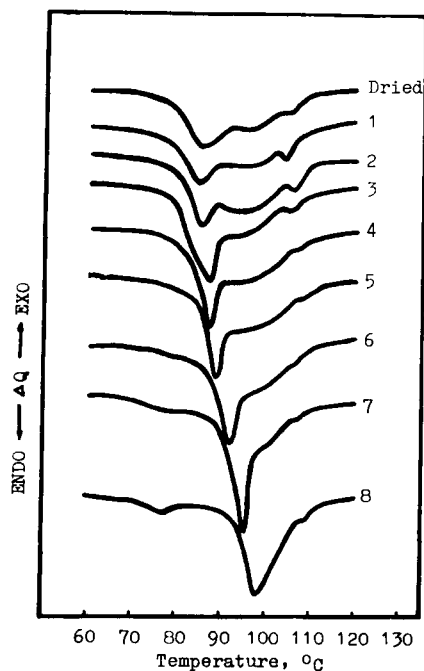
Figure 5   SDSC thermograms of PAC fibers heat set in saturated steam of different temperatures: (1), 90°C; (2), 95°C; (3), 100°C; (4), 105°C; (5), 110°C; (6), 120°C; (7), 130°C; (8), 140°C.
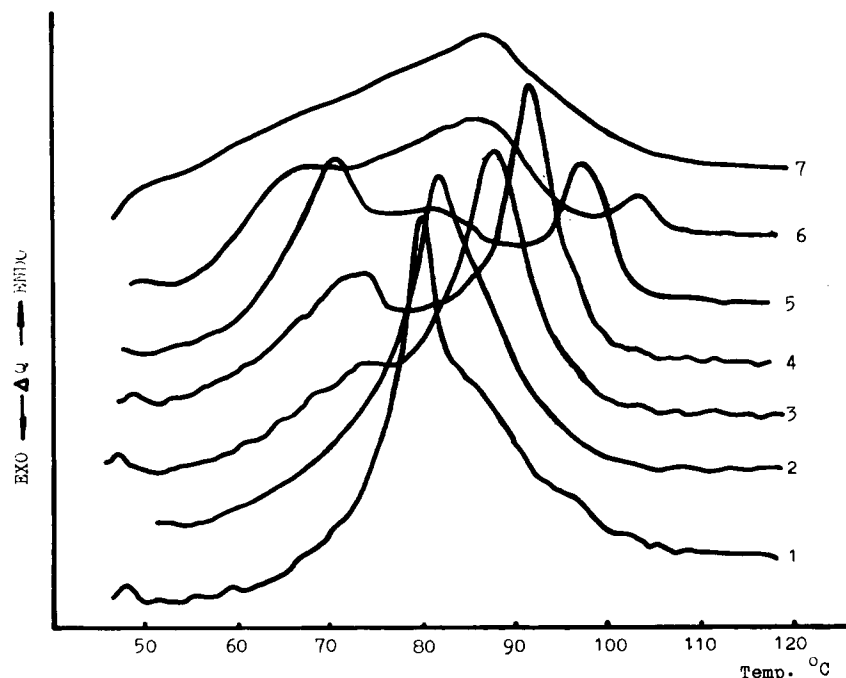
Figure 6 SDSC thermograms of PAC fibers heated in saturated steam of unusually high temperatures. Steam temperature: (1), 125°C; (2), 133°C; (3), 139°C; (4), 144.2°C; (5), 149.8°C; (6), 153.7°C; (7), 162°C. *Note:* The sequence of the amorphous background peak and the paracrystalline peak in Fig. 9 is different from that in Fig. 6.

though the latter is more laborious. We cannot enter into the details of peak resolution here since it will be too lengthy.

2. When the fiber texture is developed at unusually high temperatures, existing textural units will be damaged to a certain degree. For example, in Figure 6, if the temperature of saturated steam exceeds 145°C the degree of paracrystallinity will drop sharply, as shown by the WAXD data obtained experimentally and given in Table I.
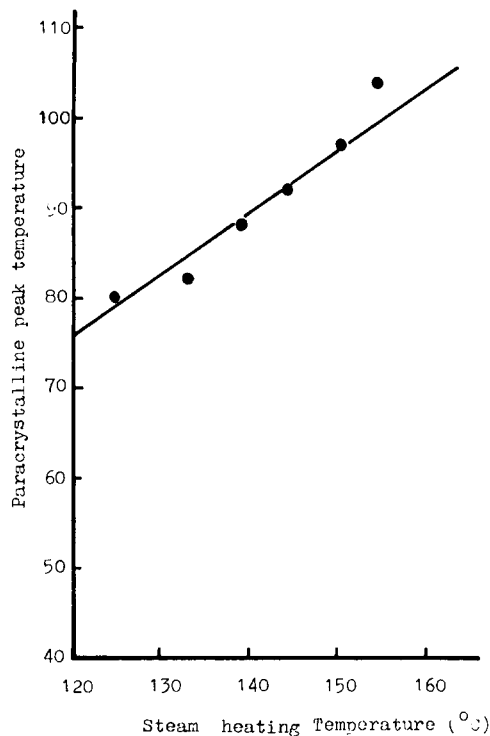
3. The relation between the setting temperature (T_s) of saturated steam and the temperature of the resulting paracrystalline peak (T_c) is shown in Figure 7 and can be expressed by the empirical equation:

$$T_c = 0.7(T_s - 120) + 76.$$

4. It is worthwhile to note that in the paracrystalline region a new prominent peak comes into existence. It is actually the same

Table I   Results of Saturated Steam Heat Setting of PAC Fiber at Unusually High Temperatures

	Sample					
	1	2	3	4	5	6
Gauge pressure (kg/cm²) (heat setting time: 10 min)	1.5	2	2.5	3	3.5	4
Setting temperature (°C)	125	133	139	144	150	154
1st (preparacrystalline) peak temperature (°C)	—	—	75	75	71	67
2nd (amorphous background) peak temperature (°C)	—	—	—	—	82	87
3rd (paracrystalline) peak temperature (°C)	80	82	88	92	97	104
WAXD crystallinity index (%)	30.9	29.7	22.0	22.6	15.0	10.5
Total endotherm of the SDSC thermogram, ΔH_T (J/g)	60.0	60.6	55.5	58.2	60.3	51.4
WAXD half-breadth of (100) peak (degree)	1.36	1.36	1.35	1.30	1.29	1.37

Heat content of the SDSC thermogram
 (2nd scan $\doteq$ 30 J/g)

Figure 7 Relation between unusually high temperatures employed in steam heat setting and the resulting paracrystalline peak temperature. Empirical equation: $T_c = 0.7\ (T_s - 120) + 76$.

peak as that on the last curve of Figure 5 (140°C), the nature of which was actually entirely unknown to us at the time of its first discovery.

To understand better the nature of this new pre-paracrystalline peak, tests on the elastic recovery of the treated samples were done in 80% aqueous DMF at 45°C (see Fig. 8). The reason for conducting this test under 45°C is to loosen the dissociable bonds in the amorphous region so that the swelling Young's modulus is lowered but the entanglement loops are not affected. In so doing, the elastic recovery properties in 80% aqueous DMF of the samples are much enhanced. Therefore, the presence of these peaks must point to the fact that these peaks are associated with macromolecular entanglements in the amorphous regions (see results given in Fig. 8 and Table II). These results will be discussed later.

Development of Fiber and Film Orientation by Hot or Cold Drawing

This important polymer textural unit usually produced by drawing was profusely explored in fiber scientific and technical literatures.

Complex Example of Texture Modification by Heating and Stretching

The chief factors governing the development and modification of texture are temperature, time, and stress. In Figure 9, the SDSC thermograms of a set of fibers are given. The disappearance of the small preparacrystalline peak in going through from curve 1 to curve 2 is due to glass transition, as has already been pointed out. In curve 3, enhancement of the paracrystalline peak by saturated steam heat setting in the relaxed state is very marked.

In curve 4, partial deterioration of crystallinity by hot stretching is quite evident. This is restored by a further steam heating in the relaxed state (curve 5). The disentangling effect of heating and reentangling by hot stretching can also be clearly visible.

Postparacrystalline Peaks Associated with Entanglements

The term postparacrystalline peak means that this peak is situated after the paracrystalline peak on
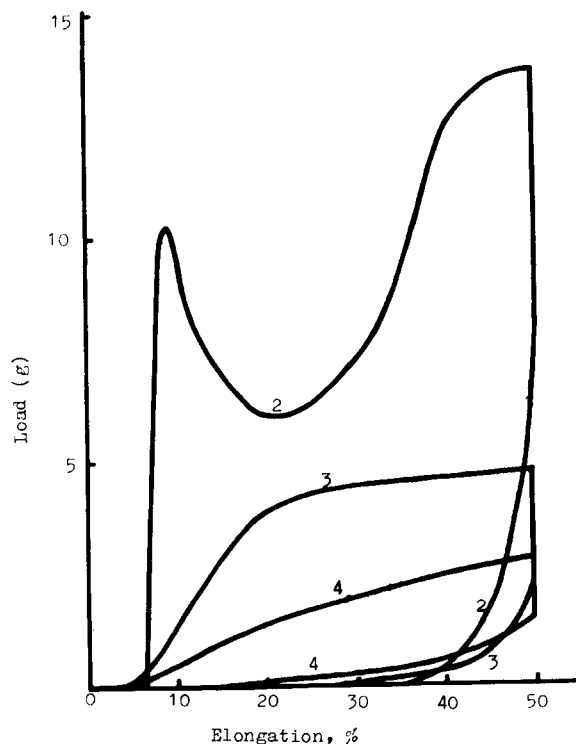
Figure 8 Enhancement of elastic recovery properties of PAC fibers by the new prominent preparacrystalline peak; TMA test done in 80% aqueous DMF at 45°C. Experimental procedure: Draw 50%, let stay 1 min, and relax completely to zero load.
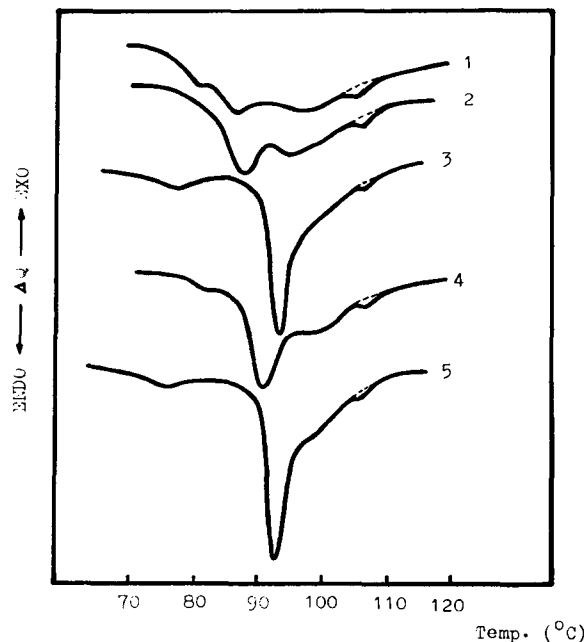
Sample number	2	3	4
Fineness (dtex)	3.6	4.6	5.9
Steam temp. (°C)	133	139	144

Table II   Mechanical Properties of Swelling PAC Fibers Heat Set in Unusually High Temperature Steam, Tested in 80% Aqueous DMF

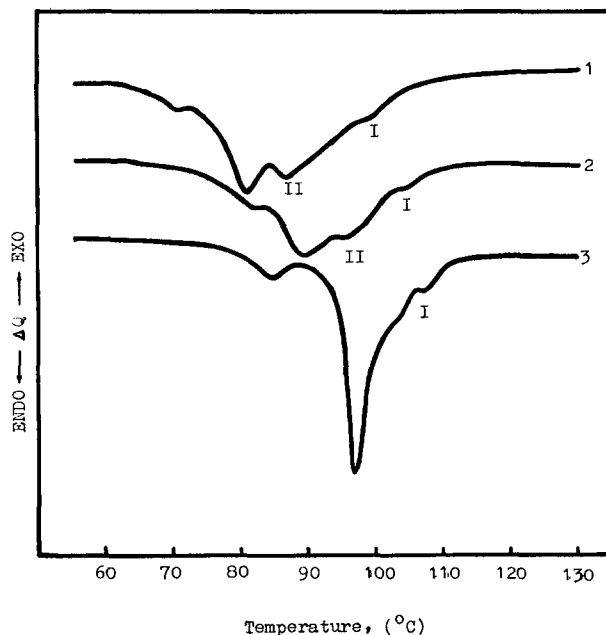|	Sample			
	1	2	3	4
Steam heating temperature (°C)	125	133	139	144
Initial modulus at different temp. (°C) (g/cm^2)				
20	4.24×10^6		2.15×10^6	6.49×10^5
25	4.02×10^6			6.25×10^5
30			2.15×10^6	6.51×10^5
35	2.47×10^6		2.00×10^6	6.53×10^5
40	2.34×10^6		2.15×10^6	7.80×10^5
45	1.84×10^6		2.34×10^6	8.75×10^5
50	2.01×10^6		2.04×10^6	2.24×10^5
55	1.75×10^6		3.29×10^6	6.84×10^4
60	1.75×10^6		2.38×10^5	5.00×10^4
65	1.41×10^6		1.67×10^5	
70	2.44×10^5			
75	1.54×10^4			
Elastic recovery (%) tested at room temp.		38.5	25.7	23.0
Elastic recovery (%) (tested in 80% DMF at 45°C)		47.0	51.0	88.8

the SDSC thermogram. One kind of such peak ordinarily encountered is termed type I. There is another kind, termed type II, that is usually closer to

the paracrystalline peak. Two cases have been observed:

1. Samples of acrylic fiber that possess a relatively higher second monomer methylacrylate


Figure 9   Complex example of texture modification by heating and stretching. Sample: PAC fiber. (1), air dried; (2), dried at 100°C; (3), steam set relaxed; (4), hot drawing; (5), steam set relaxed again. Entanglement energy (J/g): (1), 2.6; (2), 2.1; (3), 1.1; (4), 1.6; (5), 1.3. Note the fall of entanglement by hot drying and steam heat setting and the increase of the same by hot drawing.

Figure 10   Effect of chain flexibility on entanglement. Second monomer (MA) content: (1), 9.5 wt %; (2), 8.8 wt %; (3), 7.3 wt %.
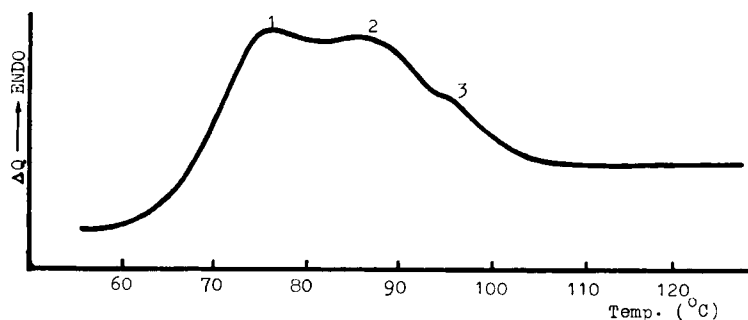
Figure 11(a)   SDSC thermogram of PAC fiber in 80% aqueous DMF. (1), paracrystalline peak; (2), amorphous background; (3), entanglement. Sample: PAC fiber taken from the production line of Jingshan Jinglun Plant. Total heat content of the SDSC thermogram: 54 J/g.

(MA) content, and hence chains, are of greater flexibility and liability to entangle (Fig. 10).

2. From a consideration of the order of coagulation during spinning, the entanglement (chain looping) must have been formed before crystallization.

The problem of entanglement as a unit of texture will be discussed in greater detail below.

SDSC Thermograms and Conventional DSC Thermogram of a PAC Fiber Sample Compared

The sample was taken from the production line of a Jinglun manufacturing plant. The thermograms
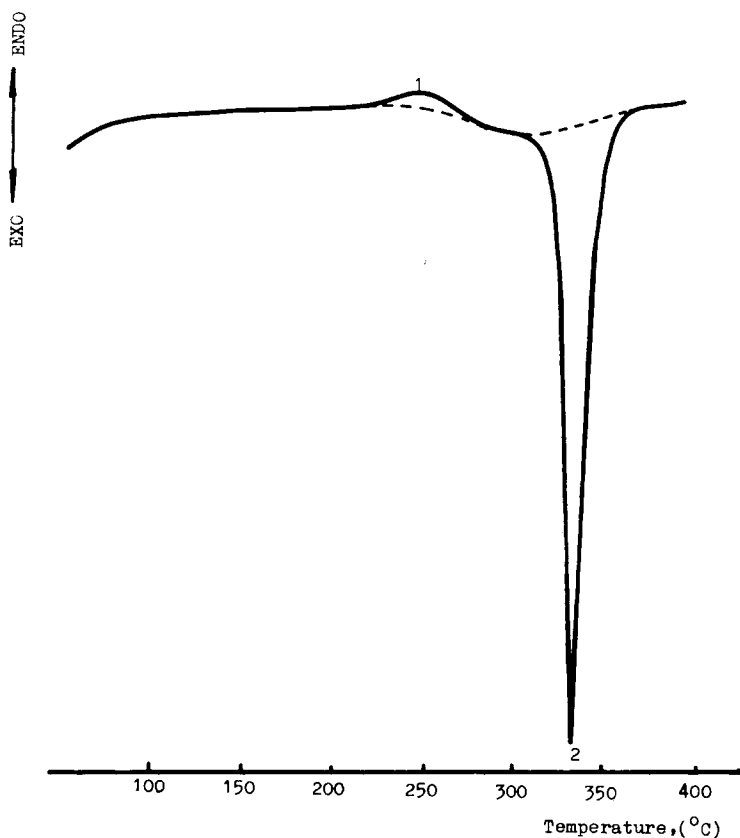
Figure 11(b)   PAC fiber, dry DSC thermogram; sample is the same as in Fig. 11(a). (1), endothermic peak; (2), exothermic peak. *Note:* Heat content (J/g): swelling DSC, 54.0 J/g; dry DSC (endothermic peak 1), 35.0 J/g; the difference is heat of solvation 19.0 J/g; heat of cyclization (peak 2), 700 J/g.
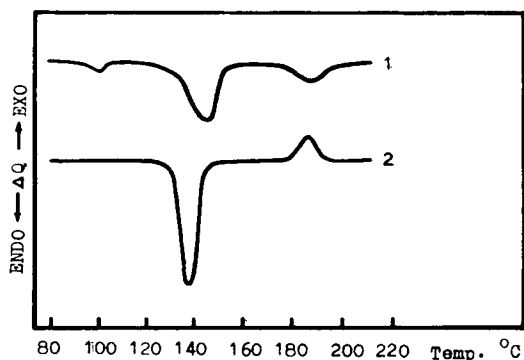
Figure 12(a)   SDSC texture of polyethylene fiber: (1), melt spun; (2), gel spun. *Note:* The appearance of an exothermic peak on the SDSC thermogram of the gel-spun PE fiber is quite interesting. It might possibly originate from the extended chain nature of the gel-spun PE fiber. When the crystalline structure of the fiber has been disrupted (melt dissolution), the extended chains will turn into random coiled chains, evolving a certain amount of heat and hence forming a small exothermic peak. The problem is worthy of further study.

are shown in Figures 11(a) and 11(b). The differences between the two thermograms are very marked indeed. These will be further discussed below.

SDSC Textural Units of Some Common Fibers

Through a long period of study of the texture of fibers by SDSC, many data have been accumulated and their general nature becomes known. Thus, the three chief textural units are common to most fibers. The SDSC texture curves for six common manmade fibers are given in Figures 12-16.[13] The respective

swelling agents used in SDSC test are listed in Table III. In some cases, the procedure for developing the texture of fibers is also given. Some notes are given in the figure legends.

DISCUSSION

### Significance of the SDSC Thermograms

There exist two kinds of DSC, the dry and the swelling DSC. They differ basically in principle and practice. Dry DSC of a polymer is usually carried out with the material in pure condition, i.e., without the addition of a swelling agent. The main effect of a solvent on the polymer is swelling and a subsequent depression of melting temperature. The DSC thermogram of the original polymer then becomes that of a swelling polymer.

Referring to Figures 11(a) and 11(b), the differences between the behavior of PAC fiber in swelling DSC (80% DMF) and conventional DSC can be clearly seen:

1. The peak melting point of a PAC fiber is depressed from around 250 to 80°C, a depression of about 170°C. The complex side reactions of oxidation and cyclization are avoided.
2. In SDSC, the fine textural characteristics of PAC fiber show the paracrystalline peak, the amorphous background, and the entanglement protrusion peak in detail. In conventional DSC, the textural endothermic peak is very small because the amount of energy absorbed by texture resolution is small in com-
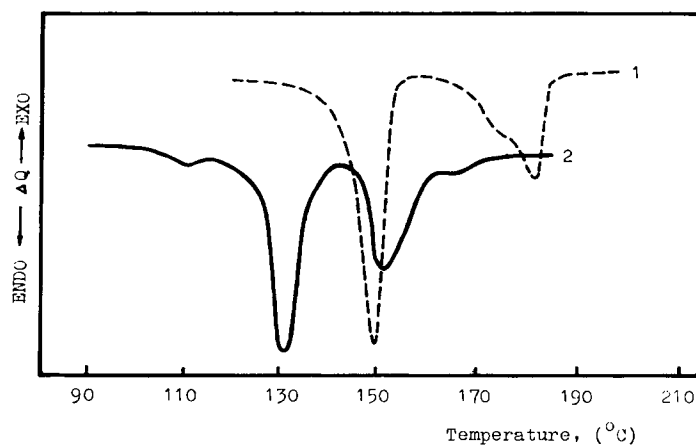
Figure 12(b)   Texture of polypropylene fiber. (1), ordinary DSC; (2), swelling DSC. Higher-temperature peak, α-crystalline form; lower-temperature peak, β-crystalline form.
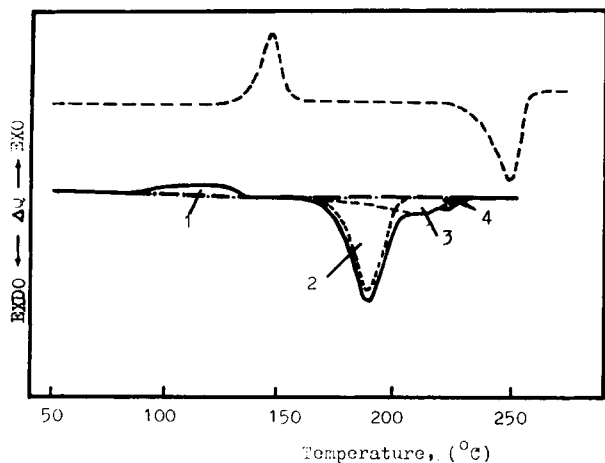
Figure 13(a) Texture of PET fiber. (1), crystallization peak; (2), melting peak; (3), amorphous background peak; (4), disentanglement peak. (———), swelling DSC; (– – – –), ordinary DSC. Peak separation is done manually and is rather rough.

parison with the enormous cyclization exotherm. It is a happy accident that these two peaks of PAC fiber can be separated in conventional DSC. In the case of PAN fiber, the small textural endotherm will overlap the big cyclization exotherm, and hence will be completely overwhelmed and nondiscernible.[14] Even when the textural endotherm in Figure 11(b) is much enlarged, no details can be detected.

3. The results obtained from SDSC thermograms can be further employed for quantitative calculation of textural content (e.g., crystallinity) of a PAC fiber. The last point will be presented in a separate article in the future.

### Entropy Changes Produced by Saturated Steam Heat Setting

When a PAC fiber sample was previously annealed under a relaxed condition for a sufficiently long time, its texture would be in a stable or quasistable condition. Upon heating at a certain temperature, the segments of the macromolecules in such a fiber will be set into rapid motion (both translation and rotation) and the intermolecular bonds in the amorphous region will first be dissociated. The material would turn pliable; its tensile modulus would drop suddenly one to two orders of magnitudes (glass transition). With PAC fiber, this temperature is around 100°C.

The existence of saturated steam will lower the transition temperature by about 30°C. Referring to Figure 5, it can be seen that maximum crystallinity was attained by saturated steam heating at about 130°C. The material is then at its most stable state. Saturated steam heating at temperatures higher than this will impair the crystallinity already existing.

Upon further rise of saturated-steam-heating temperature to a value of above 140°C, a part of the
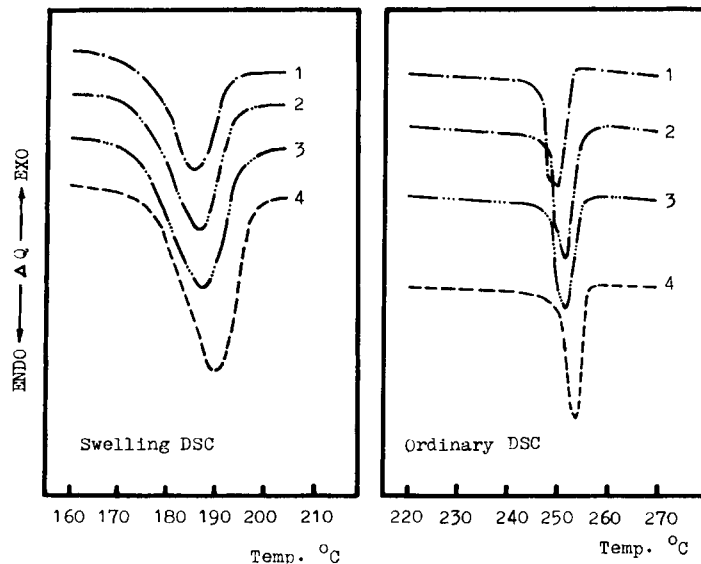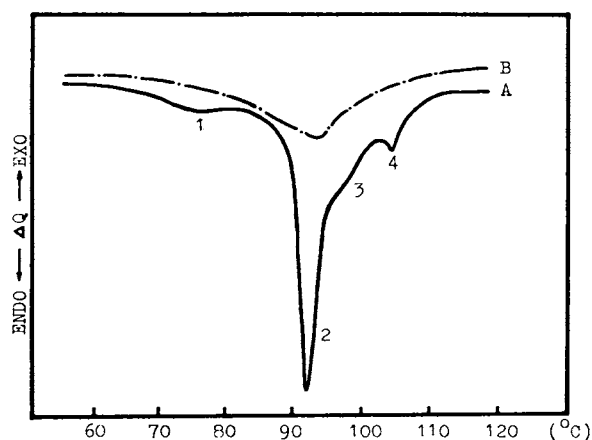

Figure 13(b) PET-POY SDSC thermogram. Winding speeds: (1), 2000 m/min; (2), 3000 m/min; (3), 4000 m/min; (4), 5000 m/min.
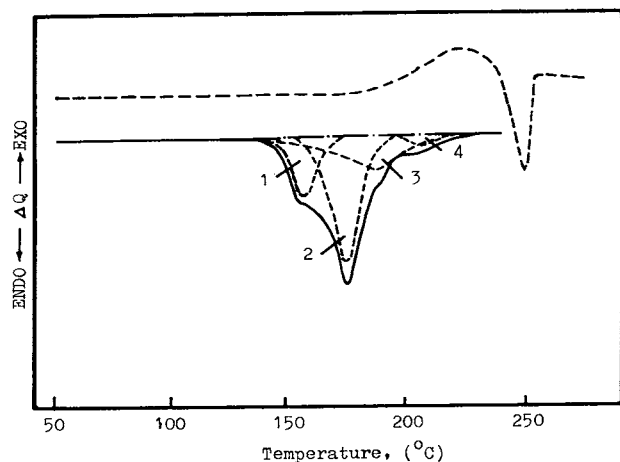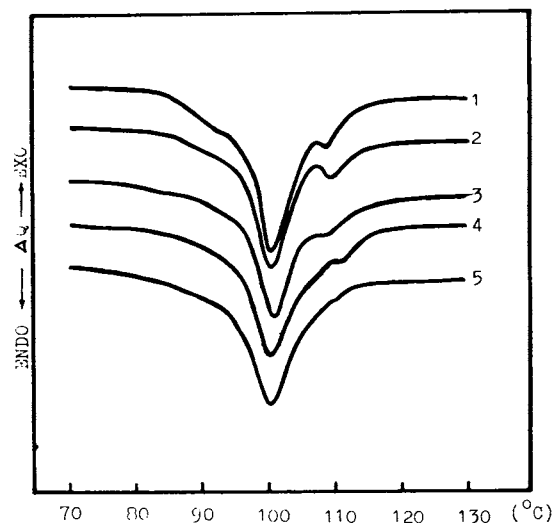
Figure 14   Swelling DSC thermograms of polyamide fibers. (1, 2), crystalline peaks; (3), amorphous background peak; (4), entanglement peak. (——), swelling DSC; (– – – –), ordinary DSC.

Figure 16   Texture of PVA fiber by SDSC. Drying temperatures: (1), 110°C; (2), 120°C; (3), 130°C; (4), 140°C; (5), 150°C. *Note:* The entanglement peaks and their change during heating are evident.

macromolecules in the amorphous region will attain a state of very high kinetic energy. These macromolecules are in a state of macro-Brownian motion, i.e., the center of gravity of the whole macromolecule shifts in position. These specially privileged macromolecules would then be able to interweave the amorphous region, forming a preparacrystalline texture, as shown in Figure 6.

When the steam-heating temperature reaches a value above 160°C, the macromolecular motion becomes so violent that all types of textural units are destroyed. The material is nearly in a molten state

Figure 15   Texture of PAC fiber. (A), SDSC thermogram of a high-ordered PAC sample; (B), SDSC thermogram of a low-ordered PAC sample. (1), preparacrystalline peak; (2), paracrystalline peak; (3), amorphous background; (4), entanglement.

that upon cooling rapidly forms an amorphous texture. What will result if the cooling is done very slowly remains to be verified by further experimentation.

Through all these processes of heating in saturated steam of ever-increasing temperature, it seems that heat was continuously absorbed into the system. Textural bonds including entanglements were dissociated, and entropy of the system was brought to a higher and higher level. The material finally was converted into a molten mass of high viscosity. This is the principle upon which the melt, spinning process of acrylic fiber is based.[15]

Entanglements as Units of Texture

In the classical scheme of macromolecular structure,[1] long-chain molecular entanglements were placed in the third main group, "Strengthening and Loosening of Supermolecular Structure."[1] Based upon our recent experimental results, it might be more appropriate to place "Entanglements" directly under the fourth main category, "Texture," in the subgroup "Short-Range Structure of Neighboring Chains."

The criterion for placing a structural unit in this subgroup is its intermolecular bond energy. According to recent results,[16] the entanglement bond energy is about 1.75 Kcal/mol, a value intermediate between Van der Waals' and hydrogen bond. Furthermore, entanglement bonds can be conveniently studied by the same method of swelling DSC, just

Table III   Solvents Used for SDSC Tests of Some Common Fibers

Fiber	Solvent
Polyethylene fiber	Paraffin oil
Polypropylene fiber	Paraffin oil
Acrylic fiber	80–85% aqueous DMF
Polyamide fiber	Ethylene glycol
Polyester fiber	O-chlorophenol/ethylene glycol (1 : 3)
Poly(vinylalcohol) fiber	50% ethylalcohol
Poly(vinylchloride) fiber	93% DMF or tetrachloroethane

like the crystalline peak and the amorphous background.

Entanglement bonds might exist in the SDSC thermogram sometimes before the paracrystalline peak (preparacrystalline) and sometimes after the paracrystalline peak (postparacrystalline). These are further discussed below.

Preparacrystalline Peaks

Preparacrystalline peaks (bonds) can be more or less clearly seen from the thermograms given in Figures 3, 5, 6, and 9. The nature of the preparacrystalline peaks has puzzled us for a long time. Those small preparacrystalline peaks, which are usually present in as-spun fibers, can be removed by gentle dry heating at a temperature a little above the glass transition (100°C for PAC fiber). This phenomenon can be seen in Figures 3 and 9; it is concerned with glass transition and has nothing to do with entanglements.

Dry heating the PAC fiber to a temperature up to 180°C and also saturated steam heating up to 140°C will produce profound textural changes, well known technologically as heat setting, as can be seen from results given in Figure 3 (dry heating) and Figure 5 (steam heating).

However, a new result that had repeatedly appeared in our previous work (Figs. 5 and 9) escaped our serious attention. A new peak came into existence in the preparacrystalline region for PAC fibers heat set at 140°C in saturated steam. Upon heating at an unusually high steam temperature of 150°C or higher, this peak became very prominent, as shown in Figure 6. Under this condition, the fiber was under incipient fusion, became sticky, and seemed to be damaged. With further rise in steam temperature, the growth of this peak stopped. At 162°C, the texture of the fiber collapsed altogether. All these processes can be closely followed and clearly observed in Figure 6.

The preparacrystalline textural unit shown in Figure 6 is supposed to be formed at a rather higher temperature of more than 140°C in saturated steam, when the motion of some macromolecules (especially those of shorter length) is so violent that they are able to interweave the amorphous background to form an entangled textural unit. Such macromolecules might be free at both ends without anywhere being anchored on the crystalline region when the entanglement was formed.

If the picture suggested above was real and true, the treated fibers must reflect something in their mechanical properties, especially Young's modulus and elastic recovery. The samples were immersed in 80% DMF aqueous solution at 45°C during testing such that the dissociable bonds were largely broken but the entanglement bonds still intact. These two properties were actually experimentally measured and the results shown in Figure 8 and Table III. The samples were from Figures 6(2)–6(4), respectively, the former with no preparacrystalline peak and the latter with a big preparacrystalline peak. The enhancement of elastic recovery and the depression of Young's modulus are expected to be the properties of an entanglement texture.

One might naturally ask the question: What is the difference between the preparacrystalline entanglement peak as shown in Figure 6 and the postparacrystalline entanglement usually existing in SDSC thermograms of polymer fibers? The latter, as has been explained rather in detail in part 1 of this series,[3] is an integral part of the network structure, consisting of the crystallites, entanglements, and possibly also a part of the macromolecules in the amorphous region. It can be reasonably conceived that the entangled macromolecules must be somewhere tied with the crystallite and cannot be freed from the network before the melting of the crystalline structure, except by withdrawing chain ends from the entanglement (see below).
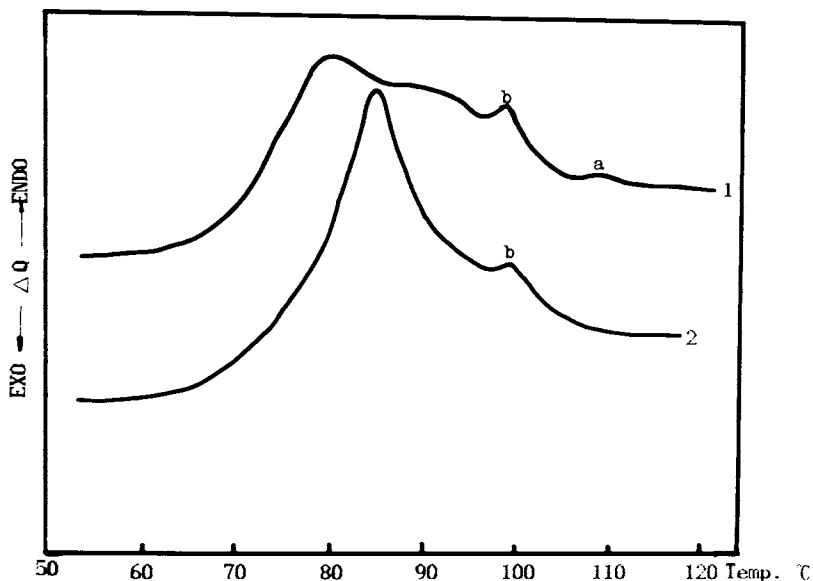
Figure 17   Effects of heating on postparacrystalline entanglement peak. (a), postpara-crystalline entanglement peak type I; (b), postparacrystalline entanglement peak type II. Curve 1, before heating; curve 2, after heating.

Postparacrystalline Entanglement Peaks

In the experimental results, we mentioned two types of postparacrystalline entanglement peaks, I and II (Fig. 10). Type I is situated farther from the par-acrystalline peak, i.e., the ordinary entanglement peaks that have been referred to often. Type II is situated nearer to the paracrystalline peak.

The cause of forming type II entanglements is possibly due to greater flexibility of macromolecular chains, hence greater liability of being entangled. For example, PAC fibers containing 9.5% MA instead of the ordinary 7.5% will exhibit such peaks in their SDSC thermograms.[13]

Under the above-mentioned conditions, the probability of forming entanglements is usually great. Moreover, entanglement formation would naturally occur before crystallization. Therefore, a part of the existing entanglements will have a greater chance of being tied on both sides by the newly formed crystallites during the process of formation. Therefore, such entanglement will never disentangle before the crystallites are disrupted.

Figure 17 shows the effect of heating on the two types of postcrystalline entanglements; type I is disentangled, while type II is not.

Figure 18 schematically represents the three types of entanglements (preparacrystalline, postpara-crystalline peak I, and postparacrystalline peak II). Postparacrystalline I is capable of disentangling by

chain withdrawing from the entanglement, while postparacrystalline II with both sides tied cannot, unless the paracrystallites are disrupted. Prepara-crystalline entanglement is formed at unusually high temperatures, but is free at both ends and easily eliminated at still higher temperatures.

In the amorphous region, dissociable intermacro-molecular bonds and entanglement bonds occur certainly side by side, the latter containing a loop
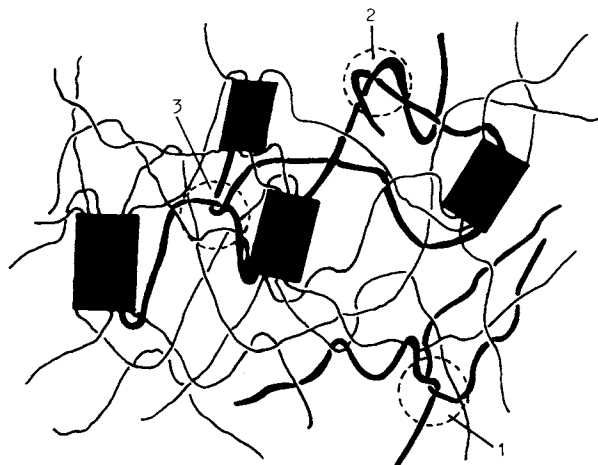
Figure 18   Schematic representation of three types of entanglements. (1), preparacrystalline entanglement peak; (2), postparacrystalline entanglement peak type I; (3), postparacrystalline entanglement peak type II.

in addition. The interaction nature of the two bonds are similar; the difference is topological only. The energy of the entanglement bonds might be modified by enhancement of dissociable macromolecular bonds.

We are just in the beginning stage of investigating such new types of macromolecular entanglements. Deeper understanding of their nature will certainly help us reveal the development of texture and open up a way leading to applications.

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