

# Studies of Macromolecular Entanglements.\*

## I. Melting Behavior of Swelling Polymers with Macromolecular Entanglements

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### SYNOPSIS

In this paper the swelling and melting behavior of several polymers, particularly acrylic fibers, is studied by thermomicroscopy and differential scanning calorimetry in detail. It is confirmed that the protrusion peak on the tail part of the DSC thermogram of swelling polymers is closely associated with the macromolecular entanglements. The proposed swelling DSC method is proved to be very effective for studying polymer entanglements. It is also shown that the melting point, whether of the paracrystalline region or of entanglement structural unit, can be well fitted to Flory's melting point depression theory.

### INTRODUCTION

About a decade ago, in connection with the differential scanning calorimetry of acrylic fibers in aqueous DMF (dimethyl formamide) solutions, we discovered on the tail part of the resulting thermogram a small peak (or rather a protrusion or "kink").<sup>1</sup> At that time, the DSC instrument we employed was relatively crude; the result almost escaped our notice. Recurrence of this same result in our later experiments led us to inquire into the origin and essence of this protrusion. Since the DSC thermogram evidently represents a process of revealing the texture of a polymer,<sup>2</sup> we were induced to relate this protrusion to macromolecular entanglements which by its nature should be the last structural unit in a macromolecular texture to be dissociated during thermal analysis. However, this hypothesis seems to be a little too bold at that time, so that we only presented this idea in a few later publications as a probable proposition.<sup>3-5</sup>

Now, after more careful work on this subject, the nature of this protrusion became clearer and its sig-

nificance better understood. Meanwhile, more research results about entanglements emerged in an accelerating pace from different laboratories in the polymer field round the world.<sup>6-10</sup>

In this paper we will examine the swelling and melting behavior of several polymers in details by thermomicroscope and DSC methods, and the results obtained will be beneficial to the research of macromolecular entanglements.

First, it would be appropriate here to devote a few lines to polymer texture. Polymers usually exist in their texture composed of amorphous, mesomorphic, and crystalline (or paracrystalline) regions.<sup>2</sup> According to the size and flexibility of the macromolecules and the conditions of temperature, stress, time, and concentration to which the macromolecules are subjected during processing, varied structural units of texture of the polymer result. The macromolecules are usually oriented in a privileged direction according to the direction of the stress to which the polymer macromolecule is subjected during processing.

In the amorphous region, or even to some extent in the crystalline region, because of the long and flexible nature of the macromolecules, they are looped together to some extent, designated as "entanglement bonds or couplings." They may be looked upon as a special type of bonds formed from short or long range macromolecular interaction.

Since the various structural units of texture are

\* This work was done under the joint auspices of the National Foundation for the Promotion of Natural Sciences and the Doctorial Training Section of the National Education Commission, both of the Chinese Government.

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closely knitted together, their responses to temperature and stress changes are usually more or less mingled with each other, and are not easily separated when a polymer is subjected to thermal analysis in the dry state. However, if the thermal analysis is conducted with the polymer immersed in a suitable mixture of good and poor solvents and kept in properly swollen state, then the thermogram can be much better resolved into its component peaks. In the case of DSC, the thermogram of swelling fibers, like acrylic, polyamide, poly(vinyl alcohol), and poly(vinyl chloride) fibers, can all be resolved into a series of peaks representing amorphous, paracrystalline (or crystalline), and entanglement structures.

In several series of experiments in connection with DSC of swelling acrylic and other fibers, together with thermomicroscopic observations, we have gathered hitherto sufficient evidence to show that the last peak (or protrusion) in the DSC thermogram of swelling polymers is due to the entanglement in the polymer texture. Since the swelling polymer pending melting is in a state of highly swollen gel, we are naturally persuaded to devote at the start our attention to the study of the melting behavior of swelling polymers containing entanglements (both in bulk and in fibers).

## EXPERIMENTAL

### Samples Used

(1) Polyacrylonitrile copolymer (PAC) fibers produced in a large scale by the Jinsan Petrochemical Works, commercially termed Jinglun, were our chief samples. Chemical composition of Jinglun is 91.7% AN (acrylonitrile), 7% MA (methylacrylate), and 1.3% MAS (methallylsulfonate).

Some samples were taken directly from the production line immediately after the drawing stage, followed by air drying in the laboratory, and then heat treatment designated as drying at a specified temperature, or setting in saturated steam at a specified temperature for a specified period of time.

(2) A PAC bulk polymer of complete amorphous structure was prepared by dissolving an air-dried PAC fiber sample as described above into a dope in hot 80% aqueous DMF solution, followed by quick cooling, precipitation, separation, washing, and air drying. Such a sample is believed to be nearly free from macromolecular entanglement if the dope concentration is below 5% (weight ratio of polymer to solvent).

(3) Homogeneous PAN bulk polymer was prepared by a special polymerization process in the laboratory using a special fluorine containing catalyst.<sup>‡</sup>

(4) A special PAN fiber was prepared in the laboratory from a PAN polymer<sup>‡</sup> of about 400,000 weight average molecular weight, using a dilute dope of less than 4% concentration, followed by quenching and hot drawing. This product is termed gel-spun PAN fiber.<sup>11</sup>

(5) Other fibers used in this study are generally commercial products.

## Thermal Analytical Instruments and Processes

### DSC Study

The instruments employed are Dupont DSC System 99 and Perkin Elmer Series 7.

It is imperative to conduct the DSC scan of a polymer sample under swelling conditions without the least leakage of the solvent vapor from the DSC cell. The aluminum cell and cover used must be carefully annealed beforehand. The right amount of polymer used is weighed on a microbalance and the required amount of solvent transferred into the cell by means of micropipettes. The hard pressing of the cover onto the cell was done by a hand screw press; when properly done, a reliable hermetic seal can be obtained.

Suitable solvents used for acrylic polymer are usually aqueous DMF of 80–90% concentration by weight, the concentration being usually determined by an Abbe refractometer. For a particular polymer, a specific solvent mixture consisting of a good solvent and a poor solvent in right composition must be used in order to get well-resolved thermogram peaks. The DSC scan starts from room temperature up to complete fusion of the polymer. The rate of temperature rise is usually 5–10°C/min.

### Microscopic Observation of the Melting Behavior of Acrylic Fibers under a Polarizing Thermomicroscope

A concave slide with a cavity of small volume is used, and the required amount of polymer sample and solvents is added to the slide cavity and then covered

<sup>‡</sup> Thanks are due to Professor Xiangzhen Zhao of the Organic Chemistry Research Institute, Chinese Academy of Science for kindly giving us this polymer, known to be prepared by bulk polymerization, using a fluorine-containing catalyst.

and sealed with a glass cover using an epoxy resin as a sealing agent.

The melting behavior of a swelling polymer can be examined and photographed under the microscope and the melting temperature of the sample carefully observed and recorded. Changes in the crystallinity of the polymer sample can be judged visually or measured by a photoelectric probe attached to the crossed polarizing microscope.

A commercial acrylic fiber and a gel-spun PAN fiber were studied under a polarized thermomicroscope successively. Difference in the behavior of melting is obviously due to the nearly complete absence of entanglements and very high crystallinity in the texture of the gel-spun PAN fiber.

## RESULTS

### Morphological Changes of the Swelling PAC Fibers under an Optical Polarizing Thermomicroscope

Two series of acrylic fiber samples were compared. One is ordinary PAC fibers (Jinglun) which contains relatively great amount of macromolecular entanglements; the other is a high molecular weight PAN fiber, with an  $M_w$  of about 400,000, prepared by a

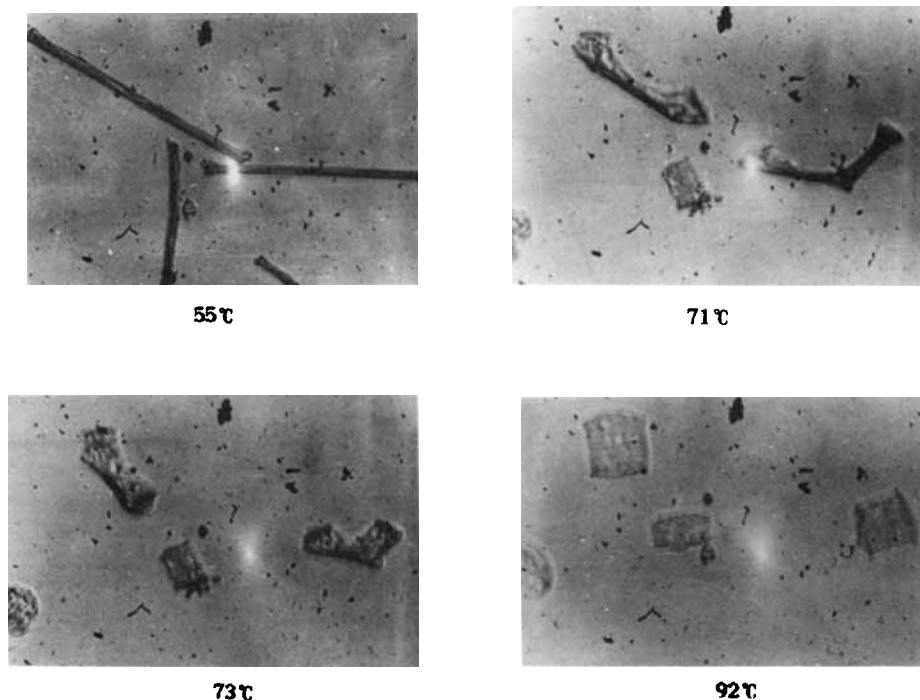
special polymerization process as described above and spun into fiber by the gel-spinning process, expected to contain relatively little entanglements.

Upon heating, the PAC fiber under the action of solvent swells gradually till a maximum swelling is reached in the eve of dissolution, and then disappears sharply. The continuing process observed is a melting or dissolution according to whether an excess of solvent is present or not. If the amount of solvent used is only sufficient to swell the fiber, then only one phase is present, and the process would be a true melting; otherwise, the change would be dissolution.

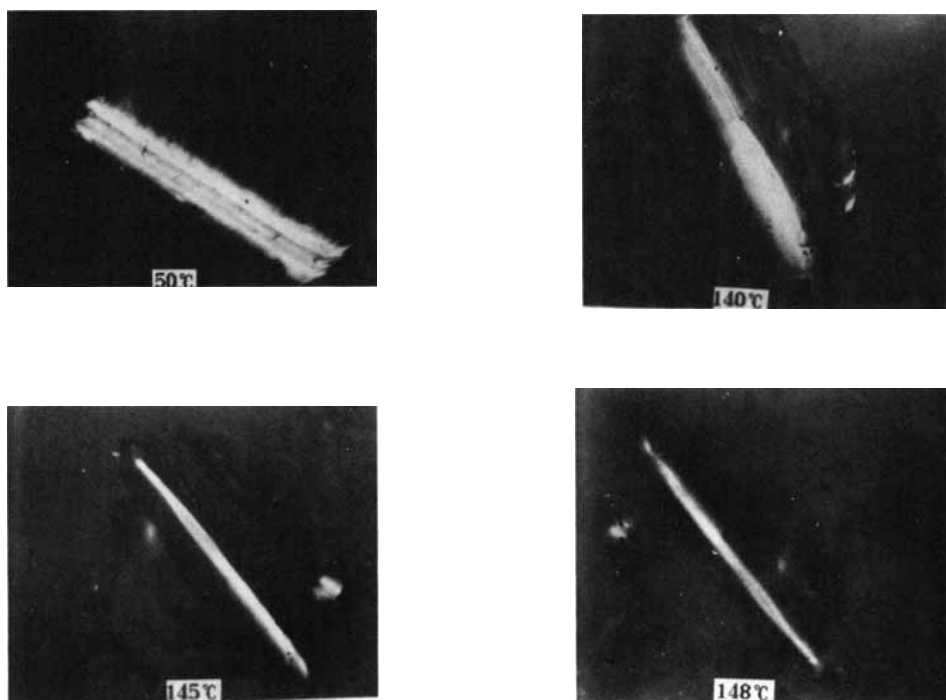
In the case of gel-spun PAN fiber, the morphological changes are entirely different. The degree of swelling is relatively low, and the fiber will peel off layer by layer, becoming thinner and thinner as dissolution continues until the whole fiber disappears finally.

The microphotos shown in Figures 1 and 2 illustrate clearly the morphological characteristics of the two samples. Their differences in nature lie in the presence and absence of entanglements and hence the formation of a network (gel) structure or not.

Under crosspolarized light the appearance of the gel-spun PAN fiber was very bright. This is an evidence of high crystallinity and low entanglements formed by the gel-spinning process. The entangle-



**Figure 1** Thermomicroscopic observations of the melting behavior of the fully swollen PAC fibers in 80% aqueous DMF.



**Figure 2** Thermomicroscopic and microphotometric examination of a gel-spun PAN fiber in 80% aqueous DMF solution.

ments will interfere with crystallization during processing in general.

In the case of gel-spun acrylic fiber, the amount of shrinkage at the end of temperature rising process, i.e., at about 148°C, is relatively lower because here the network structure due to entanglements is absent. It is also due to its high crystallinity that the dissolution temperature of the gel-spun acrylic fiber is much higher than that of the PAC fiber.

### The Swelling and Melting Behavior of PAC Fibers

It is well known that the absorption of a certain amount of solvent by a polymer will depress its melting point to a definite degree.<sup>12</sup> If the volume of the solvent present, here 80% aqueous DMF, is high, an excess of pure solvent will be present as a second phase in contact with the swelling polymer as a first phase. When such a system of swelling PAC fiber was observed under a polarized thermomicroscope in a process of rising temperature, the fiber will swell at first very slowly. However, when a certain temperature is approached, the rate of swelling will grow several tens of times greater in the direction transverse to the fiber axis, as well as the rapid contraction in length. At this moment, the

intensity of light under crosspolarized light will disappear completely, showing that the paracrystalline part in the PAC fiber has been destroyed by swelling. The phase boundary between the swelling fiber and the solvent will soon disappear in 1 or 2°C interval of temperature, and the fiber will be dissolved completely in the excess solvent. This temperature may be regarded as a melting point of the swelling paracrystalline portion of the fiber.

However, if the amount of solvent used is near or even less than the weight of the polymer, then only one swelling phase exists and the fiber will not dissolve immediately when the paracrystalline structure was destroyed, but instead will continue to exist in the swelling state till a much higher temperature (usually several tens of degrees centigrade higher). In this case, the measured melting temperature of the swelling PAC fiber, instead of being a sharp point, becomes a range. This seems to be quite reasonable since the object undergoing melting is a swollen gel consisting of all structural units of texture including amorphous region, paracrystalline region, and entanglements. The concept of a single melting temperature usually applicable to an unswollen highly crystalline polymer fails altogether. This behavior can be seen from results shown in Table I, derived from Figures 3(a), 3(b), and 1.

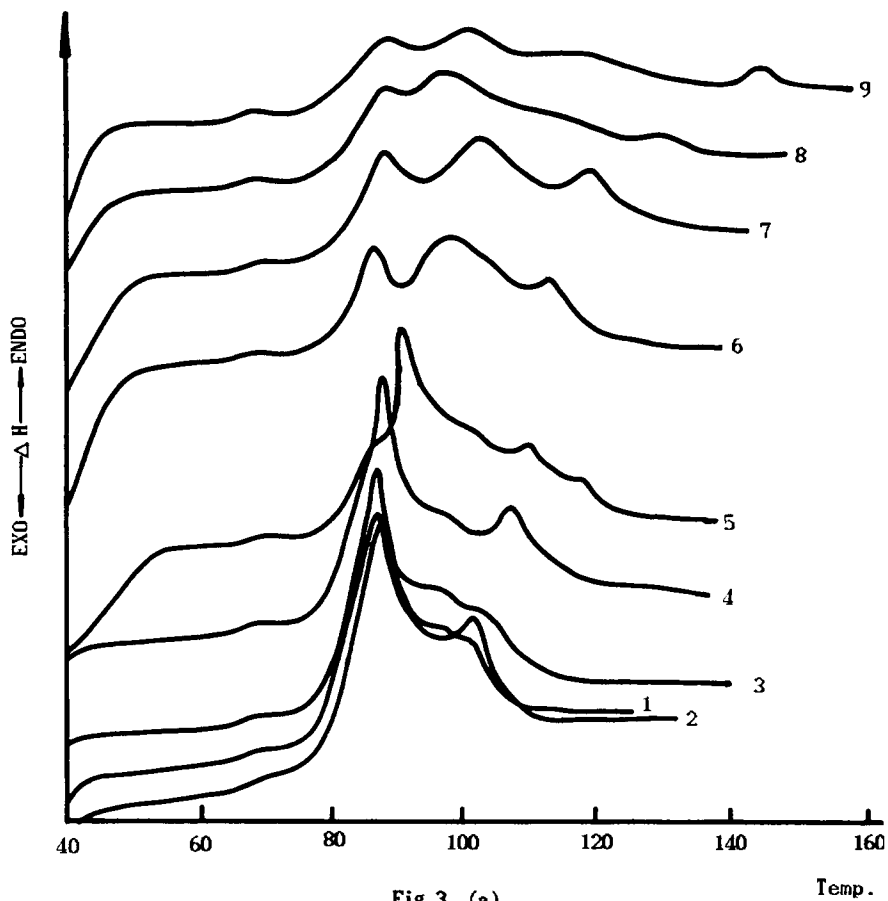


Fig.3 (a)

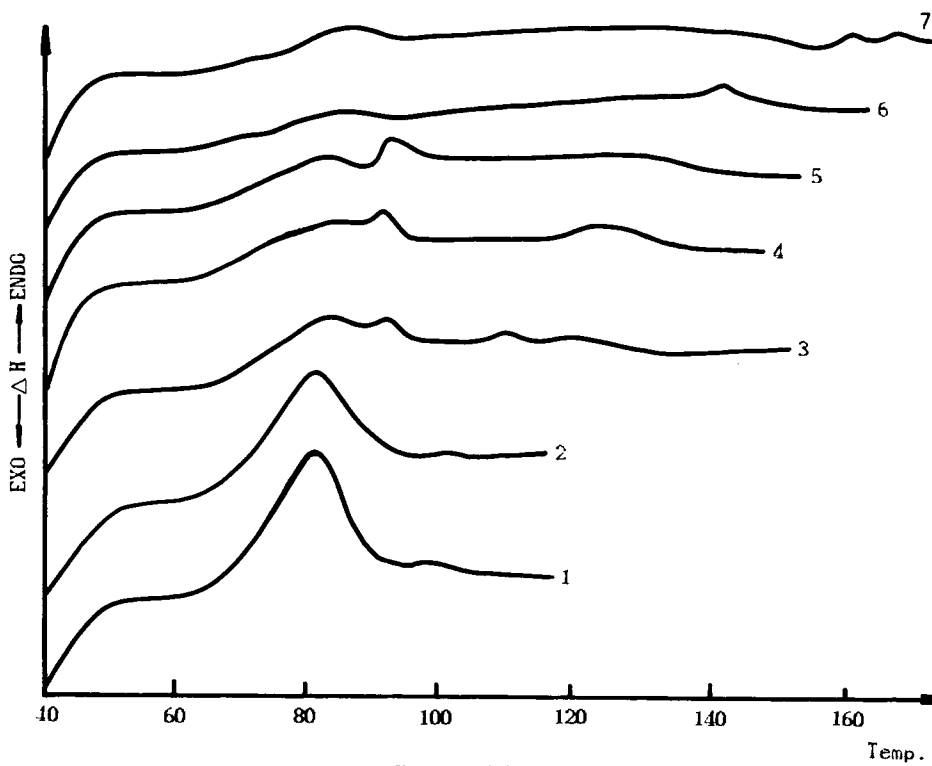


Fig.3 (b)

**Figure 3** DSC thermograms of swelling PAC fibers in aqueous DMF solution of (a) 80% and (b) 90% concentrations. For condition of DSC analysis. see Table I.

**Table I** Swelling DSC and Thermomicroscopic Data Derived from Figure 3a and Figure 1

Sample No.	Solvent/Polymer ( $\mu\text{L}/\text{mg}$ )	$\nu_1$	$T_{m1}$ (Opt.)	Temperature ( $^{\circ}\text{C}$ )						
				$T_c$		$\bar{T}_c$ Av.	$T_p$	$T_{m2}$ (opt.)		$\bar{T}_{m2}$ Av.
				1	2			Beginning	Ending	
9	0.75	0.47	98	89	102	96	144.0	138	147	143
8	1.00	0.54	97	89	97	93	129.0	128	135	132
7	1.50	0.63	97	88	103	95	119.5	117	125	121
6	2.00	0.70	95	87	98	92	113.5	113	118	116
5	2.50	0.74	90	91.0			109.0	105	116	111
4	3.00	0.78	81	88.0			106.5	98	108	103
3	4.00	0.82	78	87.0			102.0	98	105	102
2	5.00	0.85	79	87.5			101.0	97	103	100
1	10.00	0.92	79	87.5			101.0	96	102	99

Samples: PAC fiber, AN : MA : MAS = 91.7%: 7%: and 1.3%.

Solvent: Aqueous DMF solution.

$T_{m1}$  (opt.): temperature of rapid contraction;  $T_c$ : paracrystalline peak temperature, (1) 1st peak, (2) 2nd peak;  $T_p$ : temperature of protrusion peak;  $T_{m2}$  (opt.) temperature of melting;  $\nu_1$ : volume fraction of solvent =  $\frac{\text{Solvent}}{\text{Polymer}/1.15 + \text{Solvent}}$ , where 1.15 is the density of PAC fiber.

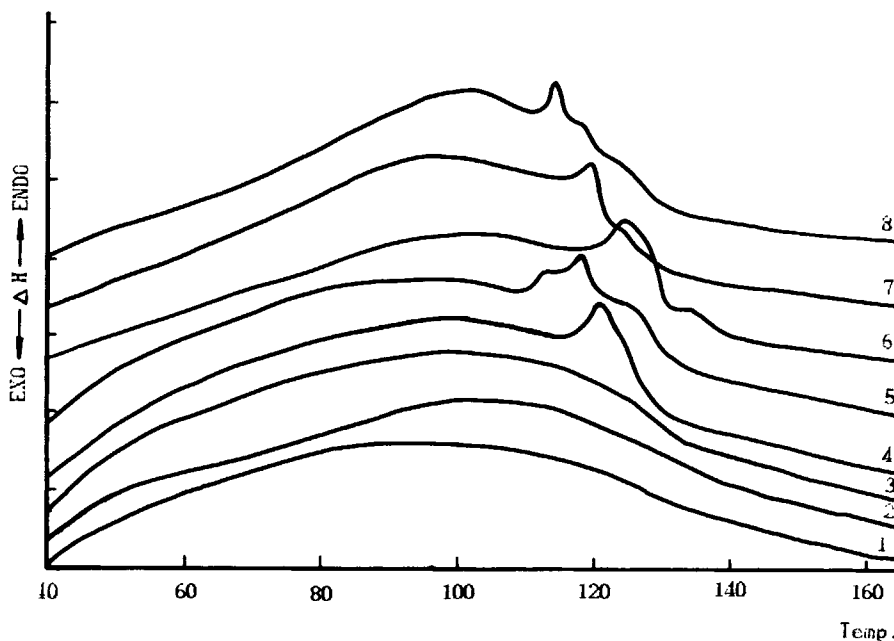
Rate of temperature scanning:  $5^{\circ}\text{C}/\text{min}$ .

### Results Obtained from DSC Thermograms of Swelling PAC Fibers

In parallel with the thermomicroscopic observation, we also conducted on the same PAC sample DSC tests with aqueous DMF swelling agents of concen-

trations 80% and 90%, using a wide range of polymer to solvent ratios during DSC analysis. The thermograms are shown in Figures 3(a) and 3(b). Part of the data from microscopic and DSC results are tabulated in Table I.

It should be noted that the temperature ( $T_m$ ) at



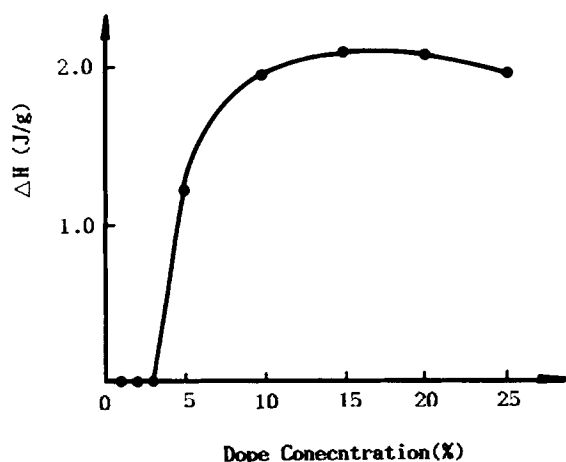
**Figure 4** DSC thermograms of swelling bulk PAC polymer coagulated from dopes of different concentrations. Sample number (concentration): 1 (1%); 2 (2%); 3 (3%); 4 (5%); 5 (10%); 6 (15%); 7 (20%); 8 (25%)

which the light intensity disappears during the above polarizing microscopic observation of the swelling PAC fiber coincides quite closely with the paracrystalline peak temperature ( $T_c$ ) on its DSC thermogram. It is more important to notice that the temperature ( $T_{m2}$ ) at which the swelling PAC fiber disappears during the microscopic observation (i.e., thoroughly dissolving or melting) also coincides quite nearly with the protrusion peak temperature ( $T_p$ ) on the tail part of the DSC thermogram. Since the existence of the fully swelling gel fiber, after its paracrystalline region being dissolved, depends upon the sole support of the network junctions formed by entanglements, the protrusion peak in DSC thermogram must be related to the energy absorbed by the dissociation of the entanglement bonds.

### Results Obtained from the DSC Thermogram of an Amorphous PAC Bulk Polymer

The amorphous PAC samples are prepared by dissolving in hot 80% aqueous DMF a PAC polymer into a dope of 1, 2, 3, 5, 10, 15, 20, and 25% concentration and then coagulated by cooling. The samples must be air-dried under room temperature without change of their texture.

The DSC thermograms of a series of samples coagulated from dopes of different concentrations are shown in Figure 4 and the entanglement energy as measured from the area of protrusion peaks vs. dope concentration are plotted in Figure 5. It is interesting to note that bulk acrylic polymers coagulated from dopes of low concentrations below 5% show no protrusion on their thermograms whereas those from dopes of concentration above 5% do show marked



**Figure 5** Relation between concentration of dopes and magnitude of entanglement protrusions.

protrusion, the magnitude of which (as represented by the area of the protrusions) increases with dope concentration until at a concentration of 15% the curve (Fig. 5) flattens and then falls off slightly with further increasing dope concentration. This is in agreement with the usual concept of increasing entanglements in dopes of higher concentration.

## DISCUSSIONS

### Some Results Derived from Melting Point Depression Data

From the data tabulated in Table I, it can be shown that both the paracrystalline peak and the protrusion peak can be used to check experimentally the rigidity of Flory's theory of melting point depression and hence prove that the protrusion peak is due to the absorption of energy during melting of entanglement structural unit of the swelling polymer and disruption of entanglement bonds, i.e., the complete collapse of the swelling gel structure. Strictly speaking, Flory's theory is sound for crystalline or semicrystalline polymer, whereas, in the present case, a single sharp melting point has been widened to a temperature range of several or even several tens of degrees centigrade. The paracrystalline peak temperature of the swelling DSC thermogram may be taken as the starting temperature of melting range and the protrusion at the end of the thermogram taken as the end point of the melting range. Both may be taken as fixed points characterizing the melting process. However, the end melting points can be utilized to yield greater differences of melting point depressions, and hence more precisely measured. The fitness of the experimental data to the theory is quite good and reasonable results of interaction parameter ( $\chi$ ) and the heat of fusion ( $\Delta H_u$ ) are obtained. These calculated results are given as an appendix to this paper.

### The Appropriateness of Assigning the Protrusion Peak to Entanglements

When we first proposed the assignment of this protrusion peak to entanglements, one might doubt about the appropriateness of this proposition and other alternatives would probably be suggested. For example, it might be a mesomorphous crystalline structure or a morphological structure like a skin of fiber. But experimental facts like the presence of such protrusions in the swelling DSC thermograms of poly(vinyl chloride) fiber, which is definitely

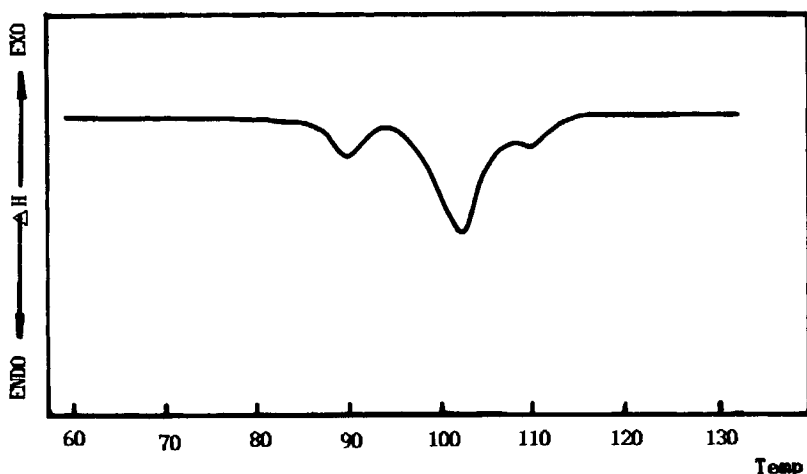


Figure 6 DSC thermogram of swelling polyvinylchloride fiber in tetrachloroethane.

known to be noncrystalline (see Fig. 6) and of precipitated bulk acrylic polymer which does not possess morphological structure (see Fig. 4) will at once exclude such suggestions. Of course, the first convincing evidence of the correctness of assigning the protrusion peak to entanglements is the close coincidence of this protrusion temperature with the melting temperature of the swelling gel under the microscope, as has already been pointed out above.

Indeed, in a multitude of DSC thermograms of a varied number of polymers prepared with different characteristics of molecular weight and macromolecular flexibility and formed or aftertreated under different conditions of dope concentration, temperature, tension, and time, no case has ever been encountered that is contradictory to the proposition that the protrusion peak is due to macromolecular entanglements. Instead, the entanglement proposition has always been helpful to the understanding or elucidating of the changes of polymer texture during processing. These detailed experimental results can not be released all at once in this short article. A few examples that are particularly interesting are given in Figure 7, which shows that the entanglements as represented by the protrusion peak increase indeed with the increasing molecular weight and flexibility of the polymer chains.

#### Detailed Examination of the Final Portion of the Swelling DSC Thermogram Where Protrusion Exists

When the polymer to solvent ratio used in the DSC test becomes greater than unity, the swelling agent would be only sufficient to form a swelling gel ca-

pable of melting; no excess solvent would be present to form a second phase consisting of pure solvent. So the tail part of the thermogram becomes very short and small in area, showing that there is little heat of dilution. This is shown in Figure 8, in which the two thermograms are related to the same fiber sample but with radically different polymer to solvent ratios, 2 : 10 and 10 : 10, respectively. The marked difference of magnitude of the tail part can be easily seen; the shaded portion could be looked upon as due to the heat of dilution.

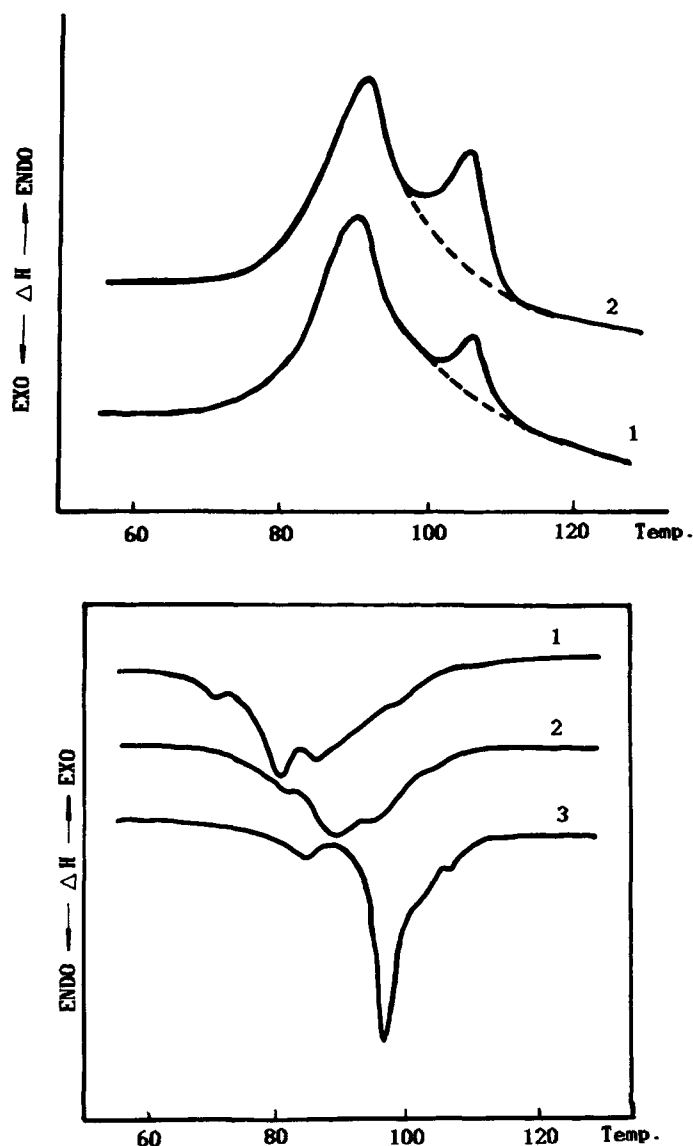
The presence of several fluctuations on the protrusion peak is apparently due to unevenness of the swelling polymer sample which always exists in the form of patches of gel particles throughout the swelling DSC process.

These details add further proof to the proposition that the end of the DSC thermogram is due to the melting of a swelling polymer.

#### The Splitting of the Paracrystalline Peak

The paracrystalline peak of the swelling DSC thermogram of the PAC fiber is the principal peak which sometimes is splitted into two peaks according to circumstances (cf.  $T_{c(1)}$  and  $T_{c(2)}$  in Table I). When the concentration of the aqueous DMF used is relatively low, e.g., below 85%, and when the polymer to solvent ratio used is high, e.g., above 4/10, such phenomenon can be distinctly seen [see Fig. 3(a): 6, 7, 8, and 9 thermograms]. The reason for this is that the amount of solvent (DMF) present is only sufficiently great to swell those portion of the paracrystalline materials which are relatively less ordered to get into full degree of swelling. The ther-





**Figure 7** DSC thermogram of PAC fibers of different molecular weight and chain flexibility. (a) The effects of macromolecular weight ( $M_n$ ) on entanglements: (1)  $M_n = 31,600$ ; (2)  $M_n = 34,100$ . (b) The effects of chain flexibility on entanglements: MA content = (1) 9.5 wt %; (2) 8.8 wt %; (3) 7.3 wt %.

mogram 5 in Figure 3(a) might be also the critical case, i.e., polymer versus solvent ratio 4 : 10, when the pure solvent phase just disappears.

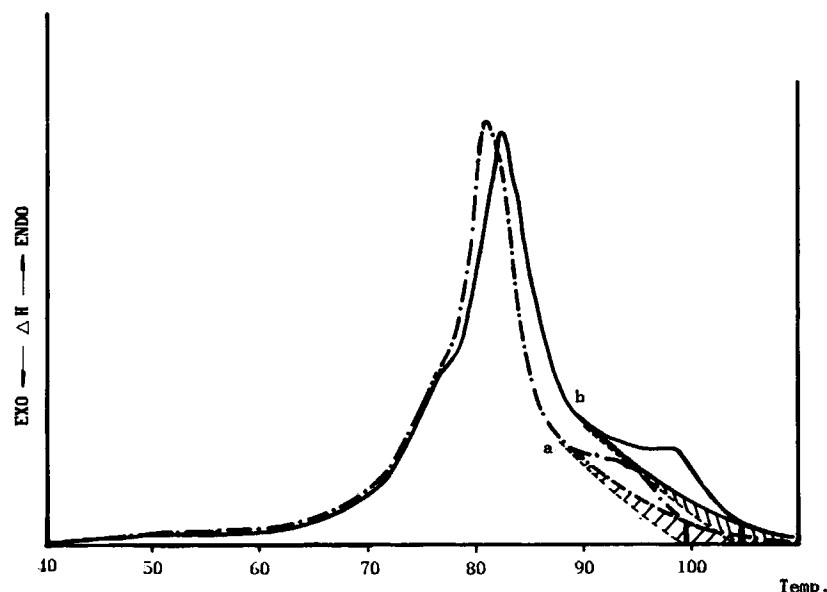
The paracrystalline peak temperature varies little throughout the range of changing polymer to solvent ratio, but when the peak is definitely split into two and if we take the higher one as the paracrystalline peak, it will jump about 10°C or higher.

Whether these two paracrystalline peaks exist as two separate structures or they are just the resolution peaks of one swelling paracrystalline structure remains to be studied further. At present it does

seem that they are two separate entities but are only resolved when the amount of solvent present is insufficient.

#### The Generality of the Melting Behavior of a Variety of Polymers under Swelling Conditions

Although most of the results given above are for PAC fibers, they are valid also for bulk polymers and PAN fibers and even other polymer fibers like vinylon, poly(vinyl chloride), nylon and polyester. When heated, all swelling polymers will become a



**Figure 8** Analysis of the tail portion of the DSC thermograms of swelling PAC fibers, using different polymer : solvent ratios: (a) 2 : 10; (b) 10 : 10.

gel before melting. Here the role of entanglements is to form a network structure which prevents a premature dissolution of the swelling polymer before melting. A PAN fiber prepared by gel spinning process is devoid of this entanglement or network structure and hence will dissolve directly without gelling and melting. With further release of our results, obtained from different varieties and forms of polymers, the generality of the behavior of swelling polymers would be finally verified.

## CONCLUDING REMARKS

- (1) The swelling and melting behavior of several polymers are examined in detail under a polarizing thermomicroscope, and also in parallel with DSC. The results so obtained demonstrate convincingly that the protrusion peaks on the ending portion of the swelling DSC thermogram are closely associated with the macromolecular chain entanglements.
- (2) A new experimental method for studying entanglements by swelling DSC is being developed which will be reported further in later publications. The method possesses the advantage of employing a solid sample directly without resorting to the preparation of a solution or gel beforehand.
- (3) The new method will be beneficial to other field of research, including theoretical and technological aspects of polymer entangle-

ments. In our laboratory, research work like the influence of entanglements on processing, the role of entanglements on the technology of the gel spinning of PE and PAN, the relation between shrinking stress and entanglements, the relation between entanglements and mechanical properties, etc., are all actively under way.

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Received April 6, 1990

Accepted April 23, 1990

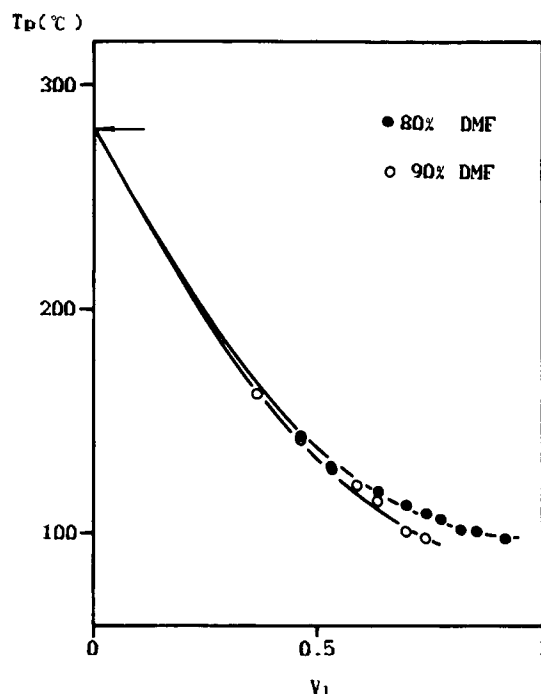
## APPENDIX

Flory<sup>12</sup> pointed out that the melting point of a polymer is depressed by the presence of a solvent according to the following equation:

$$\left( \frac{1}{T_m} - \frac{1}{T_m^0} \right) \frac{1}{v_1} = \frac{T_m^0 - T_m}{T_m T_m^0 v_1} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} (1 - \chi_1 v_1) \quad (\text{A.1})$$

in which  $T_m$  = the melting point of the polymer with solvent,  $T_m^0$  = the melting point of the polymer without solvent,  $v_1$  = volume fraction of solvent,  $\Delta H_u$  = heat of fusion,  $V_u$  = molar volume of polymer,  $V_1$  = molar volume of solvent,  $\chi_1$  = interaction parameter and  $R$  = gas constant.  $(1/T_m - 1/T_m^0)$  is approximately proportional to the melting point depression. When the left-hand member of eq. (A.1) is plotted against  $v_1$ , the resulting curve should be a straight line, with

$$\begin{aligned} \text{slope} &= - \left( \frac{R}{\Delta H_u} \right) \left( \frac{V_u}{V_1} \right) \chi_1 \\ \text{intercept} &= \left( \frac{R}{\Delta H_u} \right) \left( \frac{V_u}{V_1} \right) \end{aligned} \quad (\text{A.2})$$



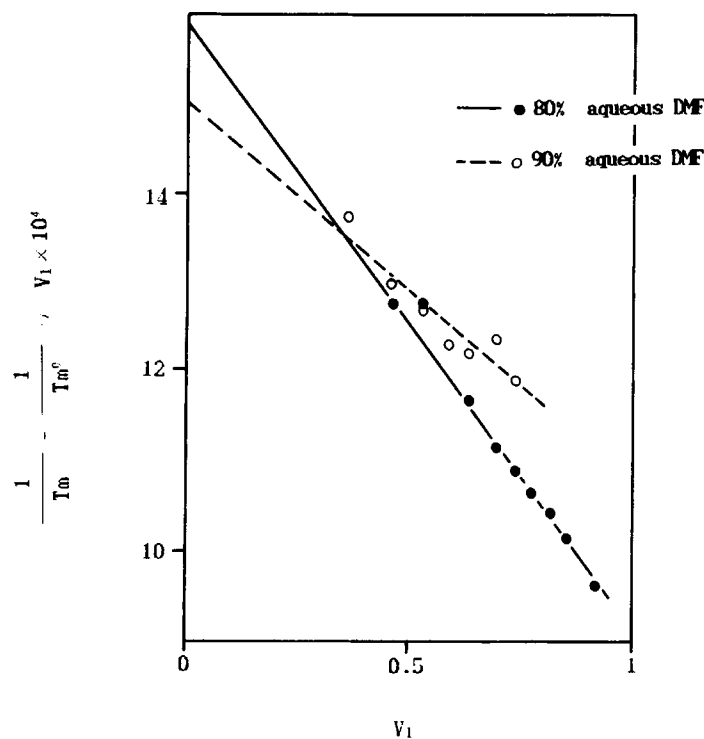
**Figure A.1** Extrapolation of the final melting temperature to  $v_1 = 0$ .

A plot of  $T_p$  vs.  $v_1$  (Fig. A.1) can be extrapolated by regression analysis to  $v_1 = 0$  to get  $T_m^0$ , but it is more accurate to get  $T_m^0$  by direct DSC test, using nitrogen as a protecting atmosphere.<sup>5</sup> The value of  $T_m^0$  for PAC fiber so found is 270°C, which is very nearly equal to the value obtained from the above regression method.

**Table A.I** Data for Swelling DSC of PAC Fiber in 80% and 90% DMF

$v_1$	Polymer/Solvent	80% DMF		90% DMF	
		$T_p$	$(1/T_m - 1/T_m^0)/v_1$	$T_p$	$(1/T_m - 1/T_m^0)/v_1$
0.920	2/20	98.0	$9.632 \times 10^{-4}$		
0.852	2/10	101.0	10.15		
0.821	2/8	102.0	10.46		
0.775	2/6	106.5	10.67		
0.742	4/10	109.0	10.91	98.5	$11.91 \times 10^{-4}$
0.697	4/8	113.5	11.17	101.5	12.37
0.633	4/6	119.5	11.68	114.5	12.19
0.590	4/5			122.0	12.26
0.535	4/4	128.5	12.75	129.0	12.68
0.463	4/3	144.0	12.74	142.0	12.99
0.365	4/2			162.5	13.73

$T_p$ : temperature of protrusion, taken as  $T_m$  in calculation;  $v_1 = \frac{\text{Solvent}}{\text{Polymer}/1.15 + \text{Solvent}}$ , where 1.15 is the density of PAC fiber. In Polymer/Solvent, the units are in mg/ $\mu$ L.



**Figure A.2** Melting point depression analysis of PAC fibers under varying degree of swelling.

Calculated  $(1/T_m - 1/T_m^0)/v_1$  and  $T_p$  values are listed in Table A.1 ( $T_p$  is taken as  $T_m$ ). The former is then plotted vs.  $v_1$  in Figure A.2 to get a straight line which serves as an experimental verification of Flory's theory of melting point depression.

The numerical values of the slope and intercept are taken from Figure A.2, and then  $\chi_1$  and  $\Delta H_u$  values are calculated by eq. (A.2).

**Table A.II** Calculated Value of  $\chi$  and  $\Delta H_u$

Solvent	80% DMF	90% DMF
Intercept $(R/\Delta H_u)(V_u/V_1)$	$15.9 \times 10^{-4}$	$14.85 \times 10^{-4}$
Heat of fusion $\Delta H_u$ (kJ/mol)	5.38	4.67
Slope $(R/\Delta H_u)(V_u/V_1)\chi$	$6.81 \times 10^{-4}$	$4.01 \times 10^{-4}$
Interaction parameter $\chi$	0.428	0.270

The  $V_1$  value is calculated by the equation

$$V_1 = \left( \frac{C_{\text{DMF}}}{0.95} + \frac{1 - C_{\text{DMF}}}{1} \right) / \left( \frac{C_{\text{DMF}}}{73} + \frac{1 - C_{\text{DMF}}}{18} \right)$$

where  $C_{\text{DMF}}$  = concentration of DMF, here 80% or 90%; 0.95 and 1 are the densities of DMF and  $\text{H}_2\text{O}$ ; 73 and 18 are molecular weights of DMF and  $\text{H}_2\text{O}$ . Calculated  $V_1$  values for 80 and 90% DMF are then 47.2 and 58.6, respectively. Molecular weight for PAC fiber is taken as 56 and density 1.15, so that  $V_u = 56/1.15 = 48.7$ . The calculated values of  $\chi_1$  and  $\Delta H_u$  are listed in Table A.II.

The  $\Delta H_u$  value measured directly from thermogram of swelling PAC fibers in 80% DMF is 53 J/g. The  $\Delta H_u$  value given in Table A.II as calculated from eq. (A.2) is 5.38 kJ/mol or 96 J/g, taking the molecular weight of PAC as 56. The difference between these two  $\Delta H_u$  values may be due to the heat of solvation, which would make the  $\Delta H_u$  value from DSC thermogram smaller.