The Method of Measuring Macromolecular Entanglements of Polymers Using Swelling Differential Scanning Calorimetry (DSC)

JIAN QIN,* PANPAN HU, JIONGXIN ZHAO, ZONGQUAN WU, and BAOJUN QIAN

Man-Made Fiber Research Institute, China Textile University, Shanghai, People's Republic of China

SYNOPSIS

Since Bueche, Graessley, Onogi, etc., advanced the concept of macromolecular entanglements, the subject has been studied extensively. So far, there are two kinds of methods of measuring the entanglements in a polymer system: One is the measurement of viscosity or other related properties of polymer fluids, either melts or solutions; the other is the measurement of modulus or other related properties of completely amorphous polymers. Until now, the effective method of measuring macromolecular entanglements for crystalline or semicrystalline polymers and fibers has not been developed. We report here a new method of measuring macromolecular entanglements of polymeric solids—using swelling differential scanning calorimetry (swelling DSC or SDSC), and we prove that the entanglements in fibers and polymeric materials can be measured quickly and conveniently with this method.

INTRODUCTION

As far as the polymer texture is concerned, scientists are quite familiar with its crystalline, amorphous, and orientation structures, but less familiar with its entanglement structure. Recently, it has been found that many results from experiments cannot be explained by the crystalline, amorphous, and orientation structures, but are in agreement with the concept of entanglement. More and more attention is being paid to the macromolecular entanglement research, and more and more papers on the subject have been published.[1-12] However, due to the restrictions of the research methods, the current research on entanglements remains at the qualitative level. In this work, we establish and experimentally prove a new method—swelling differential scanning calorimetry, which can be used to conveniently and rapidly measure entanglements of polymers in the solid state, especially of polymer fibers.

In this article, we include the results from a detailed study of swelling behavior of several polymers, particularly, acrylic fibers. The method that we used is differential scanning calorimetry (DSC). It is confirmed by a series of tests that the protrusion peak on the tail part of the DSC thermogram of swelling polymers is closely associated with the macromolecular entanglements.[13] The swelling DSC method is shown to be very effective for studying polymer entanglements. It is also proved that the second and third peaks on the swelling DSC thermogram are directly related to crystalline and amorphous structures, respectively. In our previous articles,[14-16] we discussed many results from the swelling DSC that led us to the interpretation of entanglement structure and the formation of the entanglement points in polyacrylonitrile copolymer fibers. This article focuses on providing all the evidence that supports our conclusion that the protrusion peak on the tail part of the swelling DSC thermogram represents the energy consumed during the separation of macromolecular entanglements.

* To whom correspondence should be addressed at Kimberly-Clark Corp., KC-WRE, 2100 Winchester Road, Neenah, WI 54956.

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EXPERIMENTAL

Samples Preparation

For our experiments, we used polyacrylonitrile copolymer (PAC) fibers produced in a large scale by the Jinsan Petrochemical Works, commercially termed Qinglun. Chemical composition of Qinglun is 91.7% acrylonitrile (AN), 7% methylacrylate (MA), and 1.3% methallylsulfonate (MAS). Some samples were taken directly from the production line immediately after the drawing stage, followed by an air-drying process in the laboratory, and then by a post-heat treatment designated as drying at a specified temperature, or a setting process in saturated steam at a specified temperature for a specified period of time.

Other fibers such as poly(vinyl alcohol), poly(vinyl chloride), polyethylene, polypropylene, polyester, and nylon 66 were all directly taken from different synthetic fiber plants. A completely amorphous polyacrylonitrile powder was prepared by dissolving an air-dried polyacrylic (PAC) fiber or as-synthesized polymer into a dope in a hot 80% aqueous dimethylformamide (DMF) solution (about 120°C) that served as a solvent with a very dilute concentration, followed by cooling, precipitation, separation, washing, and air-drying. Such a sample has almost no crystalline structure and we believe it also to be almost free from entanglement if the dope concentration is below 3% (weight ratio of polymer to solvent).

Molecular Weight Measurement

Waters-150 gel permeation chromatography (GPC) was used to measure the number-average molecular weight of the PAC fibers. The fibers were dissolved into a 0.065% solution with DMF. The solution, 250 μL, was injected into the GPC column (Shodex AD80M/S type) that was operated at 55°C. The measurement time was 27 min. The washing solvent was DMF, containing about 0.065% $NaNO_3$ and at a rate of 1 mL per min.

Swelling DSC Test

Instruments employed were a DuPont DSC System 99 and a Perkin-Elmer Series 7 thermal analysis system. It is important to conduct the DSC scan of a polymer sample under swelling conditions with no leakage of the solvent vapor from the DSC cell. The aluminum cell and cover used must be carefully annealed beforehand. Unlike in the conventional DSC experiment, in the swelling DSC, we had to use both a polymer material and a swelling agent, e.g., an 80% DMF aqueous solution. Eighty percent aqueous DMF is a nonsolvent for acrylic polymer at room temperature but will be a solvent at a temperature higher than 100°C. In the preparation of the swelling DSC test, both the polymer sample and the swelling agent should be completely sealed in a pair of preannealed aluminum cells. If the sample is in the form of fiber, it should be precut into very fine powder. To prevent the agent from leaking, a special sealer shown in Figure 1 was used to seal the cells. The proper amount of polymer sample was weighed on a microbalance and the required amount of swelling agent was transferred into the cell using the micropipette. The pressing of the cover onto the cell was done by a hand screw press; when properly done, a reliable air-tight seal can be achieved.

The suitable swelling agent used for acrylic polymer is usually aqueous DMF of 80–90% concentration by weight. The concentration is usually determined in an Abbe refractometer. For a particular polymer, a specific solvent mixture consisting of a good solvent and a poor solvent in the right composition must be used to obtain well-resolved thermogram peaks.

The DSC scan starts from room temperature and is conducted up to the temperature of complete fusion of the polymer. The rate of temperature increase is usually 5–10°C/min. The range of temperatures scanned depends largely on the nature of both polymer and swelling agent.

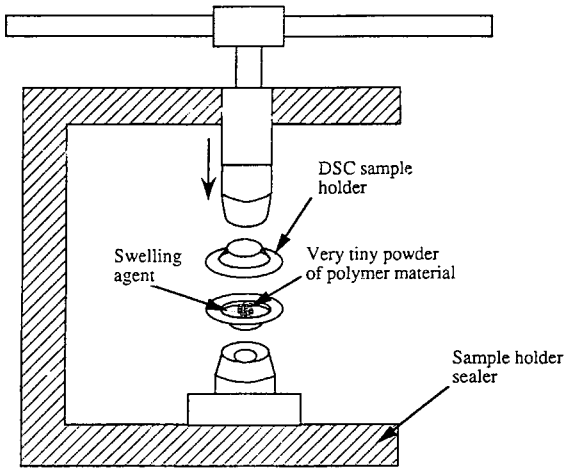

Figure 1 A diagram of the high-pressure sample holder sealer.

X-ray Diffraction Test

Fiber samples were wound around aluminum sample holders in such a manner as to make the individual strands parallel or the samples were cut into small pieces and then pressed on aluminum sample holders. Wide-angle data were obtained in transmission on a Rigaku-3015 X-ray diffractometer using Ni-filtered CuKα radiation. The diffracted beam was detected with a scintillation counter and the resulting signal was exhibited on a chart recorder. The samples on the X-ray diffractometer were rotated to average orientation effects of the fibers, whereas a 2Θ scan was made from 6° to 36°. The X-ray scan curve was divided into "crystalline" and "noncrystalline" regions. The ratio of the "crystalline" area to the total area under the curve was taken as the index of crystallinity.[13]

Viscosity Measurement

A Rheotest 2 Viscometer (made in Germany) was used to measure viscosity of the polyacrylonitrile copolymer solutions. Measurements were conducted at 25°C.

Dynamic Mechanical Measurement

Dynamic mechanical measurements of the fiber samples were made using a Rheovibron Model DDV-II (Toyo Instrument Co.) at a frequency of 110 Hz over the temperature range from −50 to +200°C. The rate of temperature increase was 2°C/min.

RESULTS AND DISCUSSION

Swelling DSC Thermograms of Polyacrylonitrile Copolymer Fibers

When the surrounding gaseous medium is replaced with a suitable swelling agent, several advantages are gained in the thermal analysis, such as:

1. The action of heat is enhanced, making the responses of fiber to heat quicker and more sensitive.
2. The temperature of transition is lowered by the action of solvents; thus, certain chemical reactions (like degradation and cyclization) are avoided. This makes the thermal analysis of swollen fibers particularly suitable for studying the original texture of the fiber step by step without premature modification by the heating program of the thermal analysis itself.
3. Detrimental effects of oxygen are automatically avoided due to the presence of solvents.
4. In the case of DSC, the test can be conducted in a sealed capsule, thus raising the temperature to a point above the boiling point of the solvent without vaporization and also extending the range of analysis up to complete disruption of the fiber texture. This makes it possible to measure disassociation energy of different structures such as physical bonding (coupling, interaction) and macromolecular entanglements (internal friction energy between molecular chains).

Figure 2 shows a typical swelling DSC (SDSC) thermogram of acrylic fiber in an 80% aqueous DMF solution. Between the start at the room temperature and the end at 110°C, there are four endothermic peaks upon swelling of the acrylic fiber in the aqueous DMF solution. The peaks represent the disassociation energies of different regions in the acrylic fiber's texture as proven by the swelling DSC thermal analytical data. Based on our extensive examination of swelling DSC thermograms, we attribute the four peaks to the four different regions in the texture of acrylic fibers:

1. The first peak represents the disassociation energy of *mesomorphous structure,* which is a kind of intermediate structure between the crystalline lattice and the amorphous background.
2. The second peak originates from the swelling of *crystalline lattice structure,* which reveals itself as a sharp endothermic peak in the thermogram and is strongly supported by the wide-angle X-ray diffraction (WAXD)

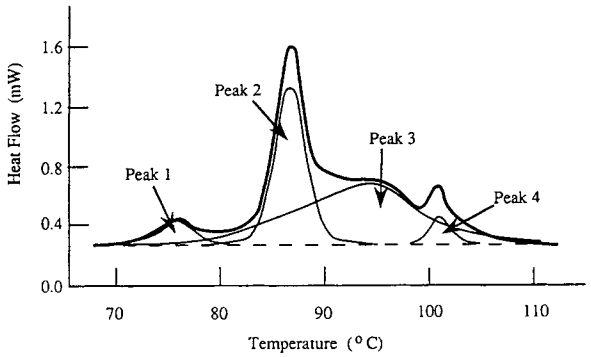

Figure 2 A typical swelling DSC thermogram of polyacrylic fiber in 80% DMF.

method. A good correlation between WAXD and swelling DSC methods is illustrated in Figure 3.

3. The third peak apparently represents the *amorphous background,* which contains a large number of intermolecular junction points from the weakest bond energy to the highest. The broad peak (so-called background) in the thermogram of the swelling DSC is also seen in the WAXD graph. The same correlation between WAXD and swelling DSC methods is also obtained (Fig. 4), which further supports our hypothesis.
4. The last peak is tentatively attributed to the *entanglement structure* of the macromolecular chains, the loosening of which requires a definite amount of energy, called a disentanglement energy. An entangled coupling may be a short-range local loop of neighboring chains or a long-range contour loop.

Crystalline, amorphous, and entanglement structures are three chief textural units common in most fibers. Mesomorphous structure is not a common textural unit and it appears only under certain conditions.

Evidence Related to the Existence of Entanglement Structures in SDSC

The Molecular Weight Effect

Figure 5 shows the swelling DSC thermograms of acrylic fibers that have different number-average molecular weights. As we know that the number of entangled points of macromolecular chains is directly proportional to the length of macromolecular chains, the longer the length of the macromolecular chain, the more numerous are entangled points in the polymer system. The number of entanglements as represented by the protrusion peak in Figure 4 indeed increases with the increasing molecular weight of the polymer chains.

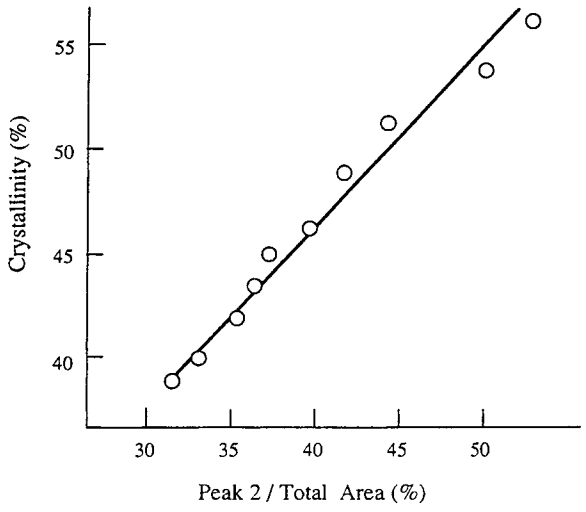

Figure 3 Relation between crystallinity from WAXD and the second peak on the swelling DSC thermograms of polyacrylic fibers in 80% DMF.

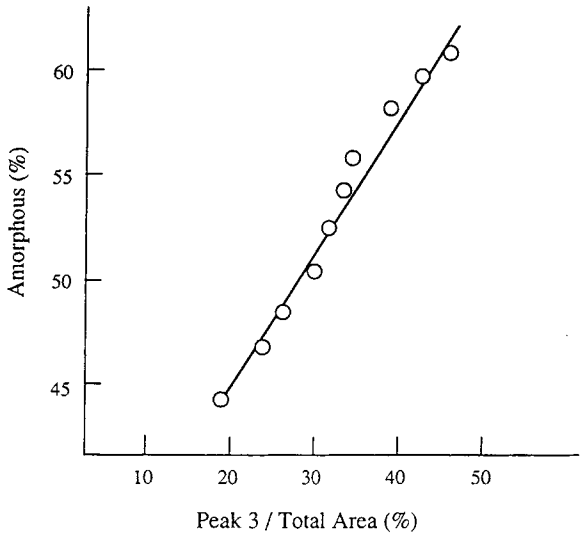

Figure 4 Relation between amorphous content from WAXD and the third peak on the swelling DSC thermograms of polyacrylic fibers in 80% DMF.

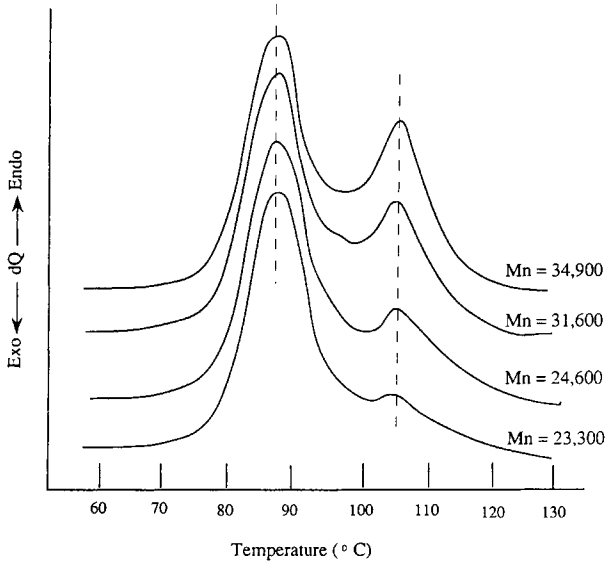

Figure 5 Swelling thermograms of polyacrylic fiber with different number-average molecular weight and in 80% DMF.

The Concentration Effect

In the polymer solution, concentration is inversely proportional to the distance between macromolecular chains. The higher the concentration, the shorter the distance between chains, which is favorable for creation of more entanglements. A special experiment was designed to investigate the concentration effect. A polyacrylonitrile copolymer was mixed with 80% DMF in different concentrations ranging from 1 to 25 wt %. At room temperature, 80% DMF is a nonsolvent for the acrylic polymer. However, the polymer is completely dissolved in the 80% DMF if the solution is heated up to 120°C. The hot solution is then slowly cooled to the room temperature with a gradual precipitation of the polymer. Precipitated polymer is finally washed by water and air-dried at room temperature without change of its texture. Figure 6 shows swelling DSC thermograms of the air-dried precipitated acrylic polymers. It is interesting to note that the thermograms show a broad background peak when the polymer is precipitated from the solutions with a concentration equal or less than 3 wt %, which indicates that the precipitated polymer only has an amorphous structure. On the other hand, the thermograms have a sharp protrusion peak when the precipitated polymer comes out of the solution with a concentration equal or higher than 5 wt %. This is in agreement with the usual concept of increasing entanglements in polymer solution at higher concentrations.

The Cross-linking Effect

Entanglements can only be taken apart when the polymer chain is linear and uncross-linked. To directly demonstrate that the last peak on the swelling DSC thermogram is related to disassociation of

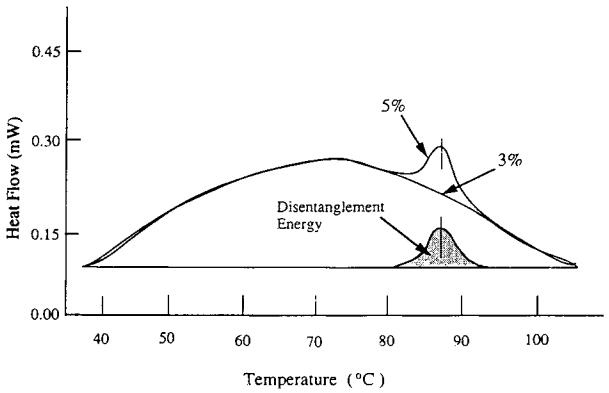

Figure 6 DSC thermograms of swelling polyacrylic precipitated from dopes of different concentrations.

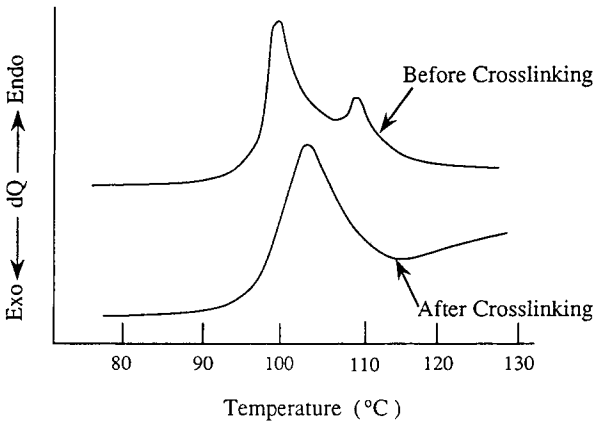

Figure 7 DSC of swelling poly(vinyl alcohol) fibers in 50% aqueous ethanol.

macromolecular entanglements, comparison of the thermograms of a polymer before and after the cross-linking reaction is very helpful and meaningful. Figure 7 contains two SDSC thermograms of poly(vinyl alcohol) fibers before and after aldolization (swelling agent: 50% aqueous ethanol). The aldolization intermolecularly cross-links poly(vinyl alcohol) chains and converts water-soluble polymer into insoluble polymer networks. Before cross-linking, poly(vinyl alcohol) fiber has three endothermic peaks corresponding to the crystalline, amorphous, and entanglement structures. After cross-linking, entanglements inside the fiber are no longer separable. The last peak disappears from the thermogram, which also indicates that the last peak represents the total energy consumed in the process of disentanglement.

Comparisons of the Results Measured by SDSC and by the Rheological Test

The Molecular Weight Effect

Figure 8 is another piece of evidence to support the hypothesis that swelling DSC is a valid method to measure macromolecular entanglements. In Figure 8, we illustrate a comparison of the results from both swelling DSC and rheological test. Both the disentanglement energy and viscosity of the polyacrylonitrile copolymer have a similar relation to its number-average molecular weight (M_n). Critical M_n of the polyacrylonitrile copolymer, below which there is no entanglement points in the polymer texture, appears in a very narrow molecular weight range (around 35,000 to 40,000), which indicates that two measurements are in agreement with each other.

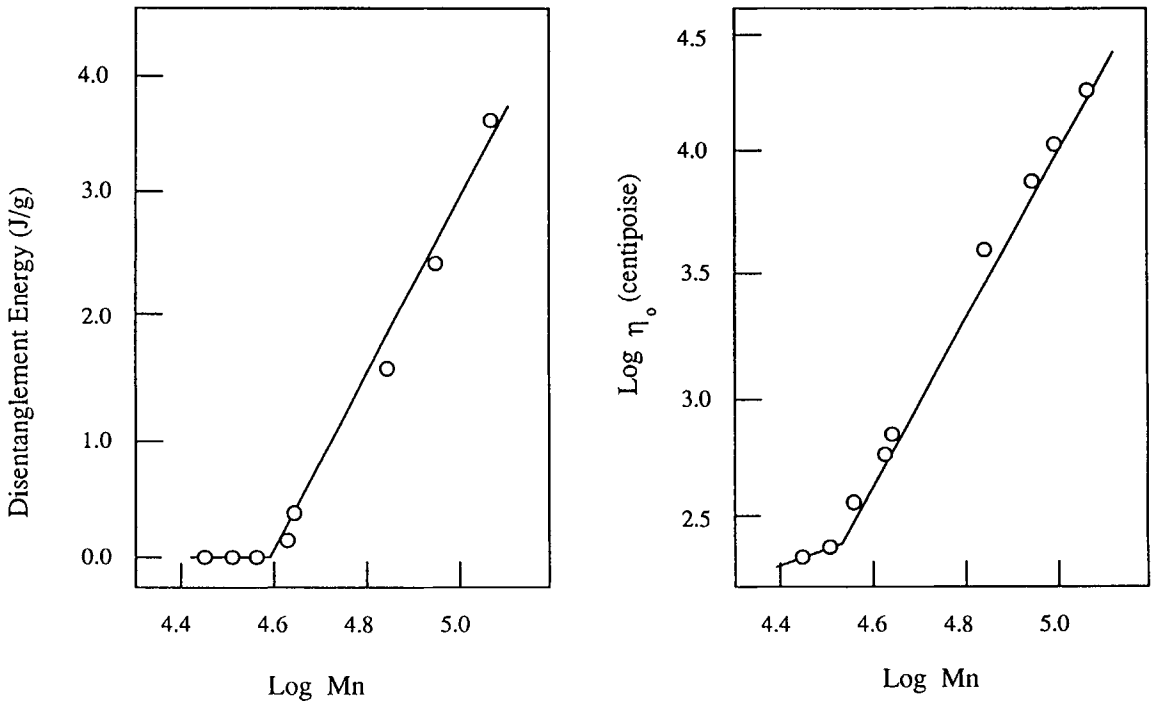

Figure 8 A comparison of the results measured by swelling DSC and the rheological test—molecular weight effect.

The Concentration Effect

If we keep the same molecular weight and change the concentration of the acrylic polymer solution, we can also see a similar transition from nonentanglement texture to entanglement texture as the concentration increases. Figure 9 shows the results from SDSC and the rheological test. The critical concentration is located between 3% and 5%.

Comparison of Results from SDSC and from the Dynamic Modulus Test

The viscosity of a polymer solution is proportional to the number of entanglements in the solution. An elastic modulus of a solid polymer is another indicator of the number of entanglements. To determine the relationship between the elastic modulus and entanglements, a group of acrylic fibers was chosen that have a very similar crystallinity but quite different disentanglement energy. The elastic modulus of the fibers was measured by dynamic mechanical measurement on a rheovibron at a frequency of 110 Hz. The modulus at 150°C was used as the elastic modulus and correlated with the disentanglement energy. A good linear relationship was obtained (as shown in Fig. 10), which again confirms that the disentanglement energy measured by swelling DSC really indicates the number of entangled points in the polymer.

Swelling DSC Thermograms of Some Common Fibers

Through a long period of study of the fibers' texture using the swelling DSC, much data have been accumulated and their general nature became known. Thus, the three chief textural units are common to most fibers. Swelling DSC texture curves for eight common man-made fibers are given in Figures 11 and 12. The respective swelling agents used in the swelling DSC test are listed in Table I. Usually, we prefer to choose a mixture of a solvent and a nonsolvent as a swelling agent for a polymer sample. The key to selecting a swelling agent for a certain polymer material is based on the following four requirements:

1. The swelling agent must be a nonsolvent for the sample to be tested at the room temperature so that there is very little penetration of the agent before DSC scanning.
2. When heated, the swelling agent must be able to gradually penetrate the structures of the sample with higher and higher structure in

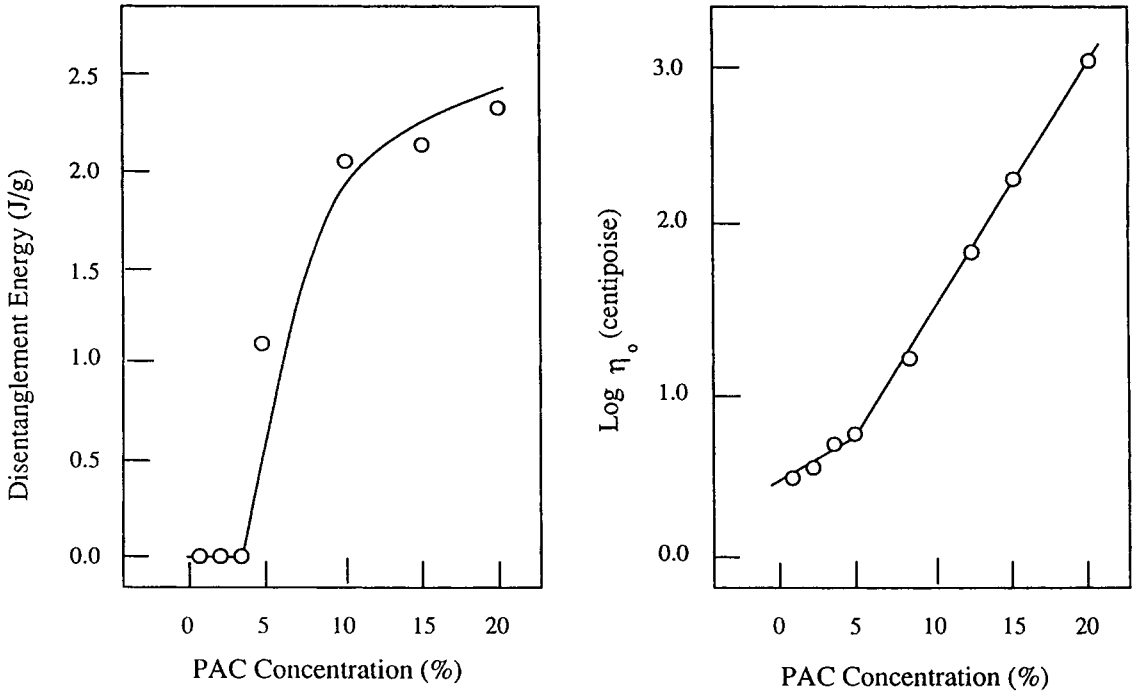

Figure 9 A comparison of the results measured by swelling DSC and the rheological test—concentration effect.

terms of order and strength until the sample is completely dissolved.

3. The boiling point of the swelling agent must be higher than the dissolution temperature of the sample in it; otherwise, the sample is not guaranteed to have a complete sealing of sample cell at a higher temperature.
4. The viscosity of the swelling agent should not be too high, or it will be very difficult for it to wet and to penetrate the sample.

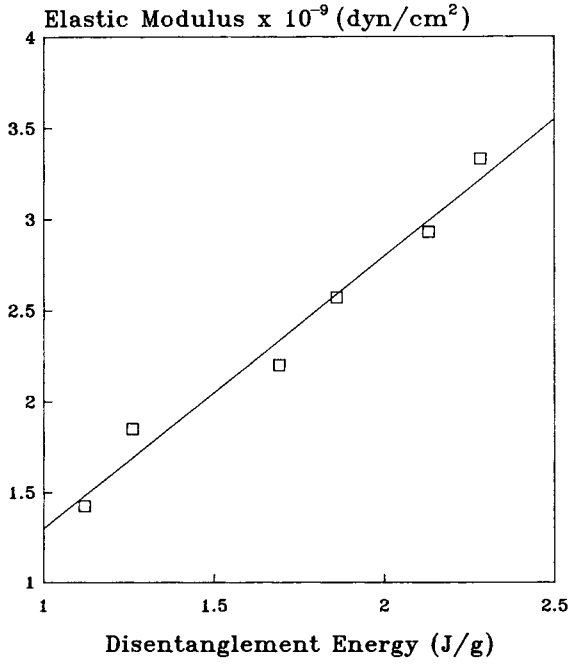

Figure 10 Relationship between elastic modulus and disentanglement energy of acrylic fibers.

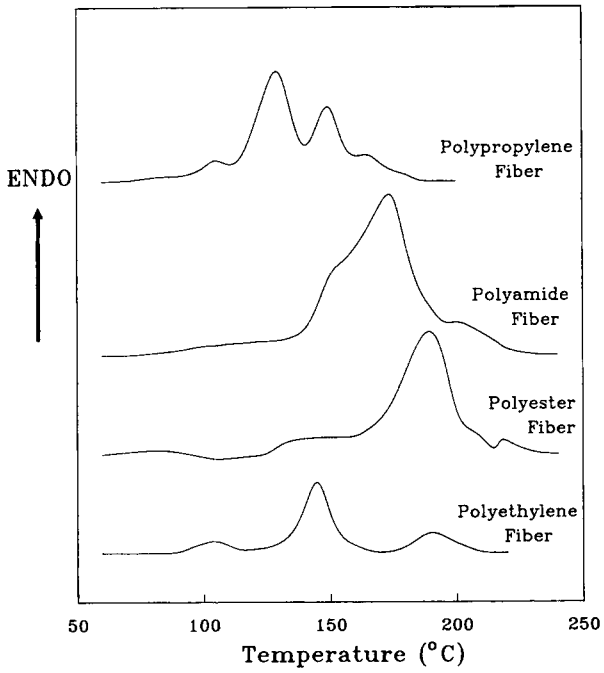

Figure 11 Swelling DSC thermograms of some melt-spun synthetic fibers.

CONCLUSIONS

1. There are usually four endothermic peaks appearing on the swelling DSC thermograms of synthetic polymer fibers whether they are made by melt spinning or solution spinning. The four peaks represent the total bond strength of amorphous, mesomorphous, crystalline, and entanglement structures in the presence of swelling agents at certain temperatures. The height and width of each peak can also indicate the energy distribution of bonds in the corresponding structural region.
2. The last endothermic peak on the swelling DSC thermograms of synthetic polymer fibers is usually attributed to disassociation of the macromolecular entanglement structure, which has been proved by several other tests and correlations.
3. The entanglement structure of a polymer is largely dependent on both its intrinsic properties, such as molecular weight, chemical composition, and crystallinity, and extrinsic properties, such as temperature, concentration, stress, and presence of low molecular weight chemicals.
4. Swelling DSC is a quick and convenient method of measuring macromolecular entanglements of polymeric solids. Swelling DSC is also independent on form (liquid/solid) and texture (amorphous/crystalline) of a polymer to be tested. Other existing methods (viscometry and mechanical property measurement) do depend on both the form and texture of the polymers.

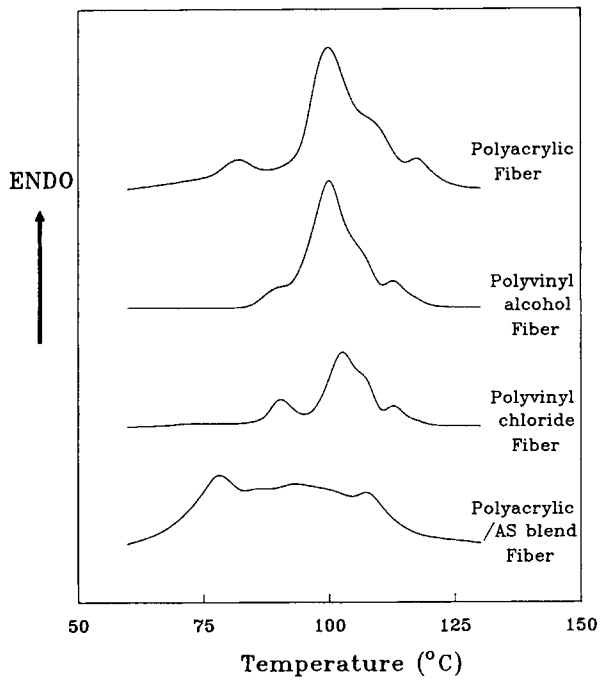

Figure 12 Swelling DSC thermograms of some solution-spun synthetic fibers.

Table I Swelling Agents Used for SDSC Tests of Some Common Fibers

Fibers	Swelling Agent
Polyethylene fiber	Paraffin oil
Polypropylene fiber	Paraffin oil
Polyester fiber	*o*-Chlorophenol/ethylene glycol (1 : 3)
Polyamide fiber	Ethylene glycol
Acrylic fiber	80% aqueous DMF
Polyacrylic/AS blend fiber	80% aqueous DMF
Polyvinyl alcohol fiber	50% ethylalcohol
Polyvinyl chloride fiber	93% DMF or tetrachloroethane

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