

Effect of Comonomer Content and Annealing on Morphological Changes in Acrylic Copolymers and Fibers*

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Synopsis

A better understanding of internal microstructure is necessary to understand various properties of acrylic fibers, such as dyeability, mechanical properties, and comfort. In the present paper, the application of x-ray methods for the investigation of fiber microstructural parameters, namely, crystallinity and crystallite size, is demonstrated. Effect of comonomer incorporation on acrylic copolymer microstructure is assessed in the present work. Influence of annealing aftertreatment on the changes in structure is investigated using the evidence presented by x-ray and DSC studies. Introduction of small amounts of a comonomer (methyl acrylate, MA) results in diminishing crystallinity. Annealing of acrylic copolymers causes the onset of an intramolecular cyclization, as well as an increase in segmental mobility; both these factors lead to an increase in crystallinity and crystallite size. With increasing comonomer content, the exothermic peak in the thermogram is found to shift toward higher temperatures. Some evidence is presented that shows the effect of spinning process variables on acrylic fiber microstructure. The results and findings of the present work have been interpreted in terms of a two-phase structure for acrylic fibers.

INTRODUCTION

Research into the physical structure of fibers is of vital importance because it is the physical structure that determines the properties observed and the fields of application of fibers. Textile fibers derived from polyacrylonitrile (PAN) containing a small amount of comonomer, methyl acrylate (MA), have a physical structure very different from that of other synthetic fibers.¹⁻³ The physical structure of acrylic fibers is not only dependent upon the type and amount of comonomer present but is also a function of conditions prevailing during fiber manufacture. Slight variations in fiber microstructure, namely, the degree of crystallinity, crystallite size, and orientation, can markedly influence the dyeing behavior of acrylic fibers.

Attempts have been made to study the interrelationship between fiber microstructure and the physics involved in the dyeing process.

It is known that the dyeing rate of acrylic fibers increases considerably¹ as the temperature of the dyebath is raised from 110 to 140°C. This is attributed to the pronounced accelerating effect of annealing on internal

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motions in the fiber. Introduction of small amounts of a comonomer⁴ likewise greatly enhances the mobility of polymer segments. As a consequence, dyes diffuse much faster and dyeing can be carried out at relatively lower temperatures.

As part of our broader objective of elucidating the relationships among microstructure and mechanical properties and dyeability of acrylic fibers, the present paper seeks to establish (1) methods for the characterization of the microstructure of acrylic fibers, and (2) the nature of the influence of comonomer content, and the manufacturing conditions on fiber microstructural parameters.

EXPERIMENTAL

Materials

The present investigations were carried out on acrylic fibers removed at four different stages (1, 2, 3 and 4) of the fiber manufacturing sequence shown schematically in Figure 1. Copolymer powders with different ratios of acrylonitrile to methyl acrylate were also subjected to structural and thermal characterization. Annealing of acrylic fibers was carried out in an inert (N_2) atmosphere at 210°C for 10 min.

Preparation of Crystalline and Amorphous Standards

The amorphous standard was prepared by dissolving commercial acrylic fibers in dimethyl sulfoxide (DMSO) and rapidly reprecipitating the polymer with water and drying the precipitate in air. The reference crystalline standard was prepared by annealing the 100% polyacrylonitrile sample at 210°C for 10 min in a nitrogen atmosphere.

X-ray Measurements

The setup for measuring crystallinity employs a vertical Philips x-ray diffractometer in the transmission mode, in conjunction with a curved crystal focalizer. This focalizer eliminates the defocusing of the x-ray beam inherent in transmission and considerably reduces the instrumental line broadening. The diffracted beam is monitored by a scintillation counter in conjunction with a pulse-height discriminator, and intensities are recorded on chart at a scanning speed of $1^\circ (2\theta)/\text{min}$ and a chart speed of 200 mm/

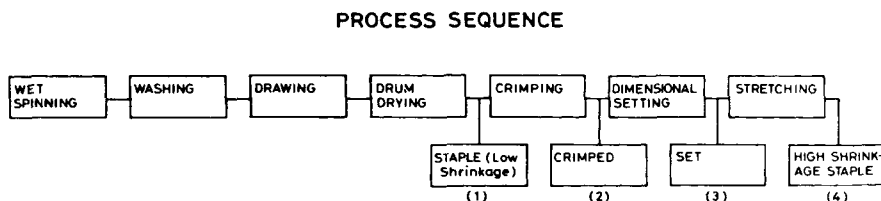


Fig. 1. Various processing stages involved in the production of acrylic fibers. Fibers from outlets (1), (2), (3), and (4) were selected for study.

h. The slit system used includes a divergence slit of 4° and a receiving slit 3 mm in width.

X-ray diffraction from a Cu target is employed at 35 kV, 15 mA. The pellet thickness is adjusted at an optimum level (≈ 1 mm) to obtain maximum intensity of the strongest reflections. The instrumental line broadening, measured using quartz powder, is less than 0.2° (2θ). The sample pellet is rotated in its own plane during a scan. The sample is perpendicular to the x-ray beam at 0° (2θ) and the usual $\theta/2\theta$ ratio is maintained between the movements of the sample and the counter throughout the scan.

DSC Measurements

Thermograms of the acrylic polymers were obtained using a Perkin-Elmer differential scanning calorimeter, Model DSC-2C, equipped with a data station. Samples were heated under nitrogen purge at a heating rate of $80^\circ\text{C}/\text{min}$.

Determination of Crystallinity

The x-ray degree of crystallinity of acrylic fiber and powder samples was estimated using the correlation method,^{5,6} which employs intensity data of the sample, as well as the crystalline and amorphous standards to carry out normalization and regression analysis on differential intensities, and yields the degree of crystallinity. The degree of crystallinity thus computed, however, is not an absolute value but is a relative parameter for comparing the order in different polymer samples. The advantages of this correlation method of calculating the degree of crystallinity are that no additive and multiplicative corrections are necessary for intensity data and no resolution of the diffractogram into crystalline peaks and amorphous halo is required.

Determination of Crystallite Size

The crystallite size D_{100} was calculated from the measured breadth β of the (100) equatorial reflection by employing the Scherrer formula⁷

$$D_{100} = \frac{0.9\lambda}{\beta \cos \theta_0}$$

where, λ is the wavelength of $\text{CuK}\alpha$ x-rays and $2\theta_0$ is the position of the maximum peak intensity of the 100 reflection of PAN.

RESULTS

The bimodal characteristics of the x-ray diffractogram of the amorphous standard prepared in this study (top curve) are compared with those of amorphous polyacrylonitrile⁸ prepared by synthesis (lower curve) in Figure 2. This broad liquidlike appearance and the similarity between the x-ray maxima of the two materials provides justification for the choice of the present amorphous standard.

The normalized x-ray diffractograms of the crystalline and amorphous standards prepared for this study are compared in Figure 3. Intensity data

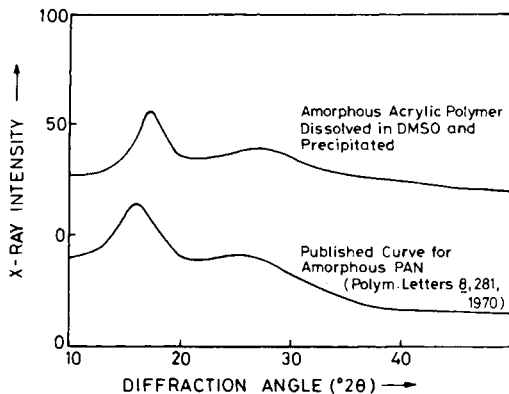


Fig. 2. A comparison of the random powder x-ray diffractogram of amorphous acrylic polymer with that of amorphous PAN.

of these reference standards for acrylic copolymer have been used in estimating⁶ x-ray crystallinities of various polymer samples (Tables I to III).

The effect of variation of the comonomer content on the diffraction curves of acrylic polymers is shown in Figure 4, before (Fig. 4a) as well as after thermal annealing at 210°C for 10 min (Fig. 4b). It can be seen that the x-ray intensity maxima become broader with increasing comonomer content. Further, the influence of annealing makes the x-ray diffractograms sharper and improves the peak-to-background ratio considerably. Even in the series of annealed samples, an increase in comonomer content causes a broadening of the x-ray diffractograms (Fig. 4b).

Crystallinities of dissolved and reprecipitated acrylic fibers are compared in Table I. It can be seen that all regenerated acrylic polymer precipitates have pronounced amorphous characteristics (i.e., crystallinity < 10%). Among the different precipitates, the polymer precipitated from DMSO solution with water is the most amorphous in character and has therefore been used as the experimental amorphous standard.

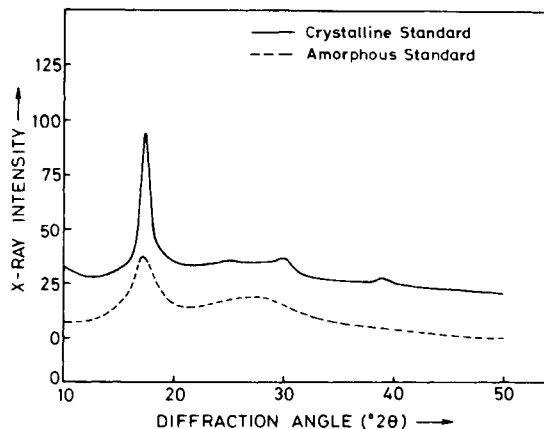


Fig. 3. Normalized x-ray diffractograms of crystalline standard (————) and amorphous standard (-----) for acrylic fibers.

TABLE I
Crystallinity of Dissolved and Subsequently Reprecipitated Acrylic Copolymer Fibers

No.	Sample particulars	Degree of crystallinity (%)
1.	Acrylic fiber dissolved in DMSO and reprecipitated ^a with H ₂ O	0
2.	Acrylic fiber dissolved in HNO ₃ and reprecipitated with H ₂ O (heavier fraction)	4
3.	Acrylic fiber dissolved in HNO ₃ and reprecipitated with H ₂ O (lighter fraction)	6

^aPresent amorphous standard.

Results given in Table II and Figure 5 highlight the role played by the composition of the copolymer, as well as by the thermal aftertreatment,⁹ in determining the level of crystallinity attained by the copolymer. In as-polymerized acrylic polymers, the crystallinity drops considerably from 34 to 3%, as the methyl acrylate content rises from 0 to 20%. This is due to the steric hindrance introduced because of the addition of the comonomer. As the comonomer content increases, the steric hindrance is also increased and the material remains more amorphous. In fact, the polymer with a comonomer content of 20% can be considered practically amorphous for most purposes. Thermal annealing¹⁰ causes an appreciable increase in x-ray crystallinity of all copolymer samples (Fig. 5 and Table II). This suggests a very large improvement in macromolecular packing and order within the lattice. However, samples of the copolymer do not crystallize to the same extent on slack thermal annealing at 210°C as the pure polyacrylonitrile material. Again, this can be attributed to the steric hindrances introduced into the macromolecular chain structure because of the addition of comonomer, appearing as side groups. It is therefore observed from Table II and Figure 5 that the higher the comonomer concentration in the poly-

TABLE II
Effect of Comonomer Content and Heat Treatment on the Crystallinity of Acrylic Polymers^a

No.	Sample	PAN-MA ratio	Degree of Crystallinity (%)	
			Before heat treatment	After slack heat treatment at 210°C for 10 min
1.	Acrylic polymer (pure PAN)	100:0	34	100 ^b
2.	Acrylic polymer	92:8	6	76
3.	Acrylic polymer	80:20	3	61

^aPAN = polyacrylonitrile; MA = methylacrylate

^bPresent crystalline standard.

TABLE III
Crystallinity of Acrylic Fiber Removed at Various Production Outlets During Manufacture

No.	Sample	Degree of crystallinity (%)
1.	Acrylic fiber from the staple outlet (1)	11
2.	Acrylic fiber from the crimping outlet (2)	25
3.	Acrylic fiber from the thermosetting outlet (3)	28
4.	Acrylic fiber, highly shrinkable, staple (4)	34

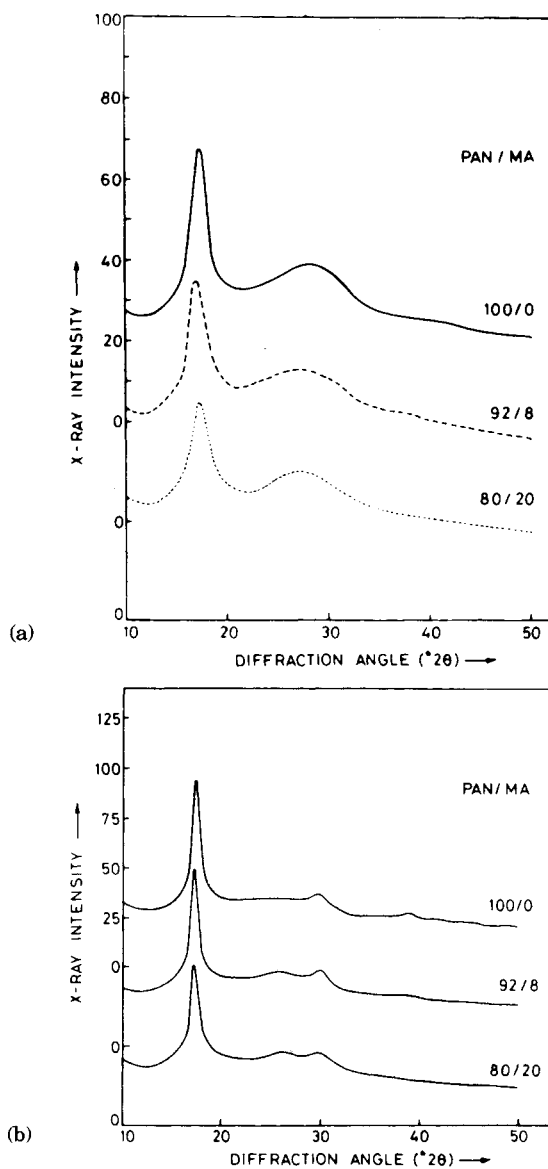


Fig. 4. Effect of comonomer content on the x-ray diffractograms of acrylic copolymers (a) before and (b) after annealing (210°C , 10 min).

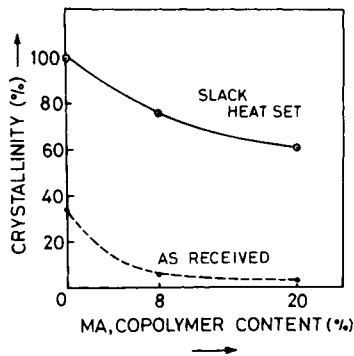


Fig. 5. Effect of comonomer content on observed x-ray crystallinity of as-received and heat-set samples.

mer, the lower is the attainable crystallinity of the polymeric material. A similar trend was observed⁴ in PAN copolymerized with HEMA (hydroxyethyl methacrylate).

Table III gives the degree of crystallinity of different acrylic fibers, collected during the successive and parallel stages of fiber production, listed in Figure 1. There is a spread in crystallinity values over the range from 11 to 34% for different acrylic fibers. Since the various additives, as well as the comonomer content, remain the same for all the fiber samples included in Table III, it is reasonable to infer that this variation or increase in crystallinity is a direct manifestation of the influence that various processing stages exert upon fiber microstructure. During fiber production,¹ the most significant influences on fiber microstructure would be exerted by the following stages: stretching, drying, steaming, and thermosetting.

The line profiles of the equatorial 100 diffraction peak are shown in Figure

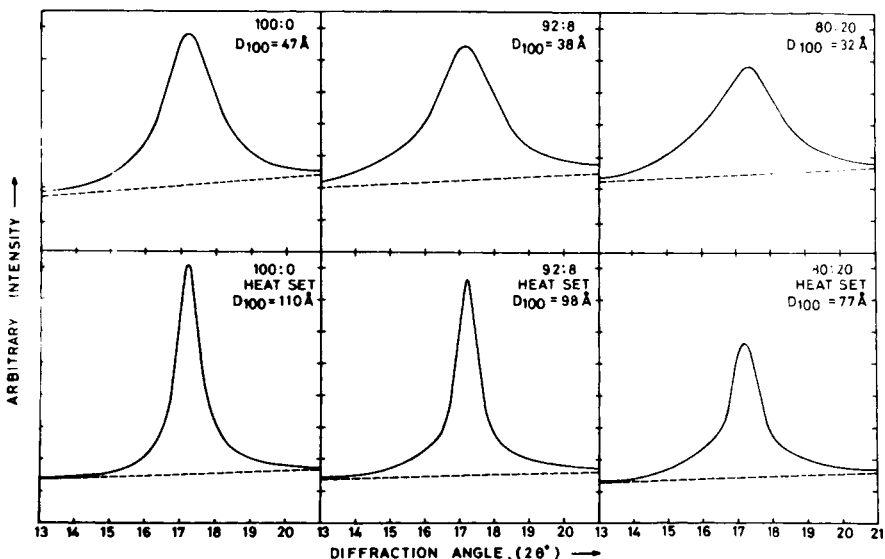


Fig. 6. X-ray radial line profiles of 100 equatorial reflection, showing the influence of copolymer composition and annealing on line broadening.

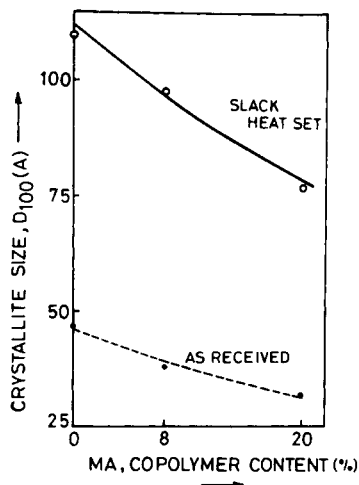


Fig. 7. Effect of comonomer content on the crystallite size of as-received and heat-set samples.

6 for acrylic copolymers with different copolymer composition, taken before as well as after annealing. With increasing comonomer content, a progressive broadening of the line profile occurs (Fig. 6, top row), whereas for a sample of any given composition, annealing causes a very noticeable reduction in line breadth (Fig. 6, top to bottom). The influence of copolymer composition on crystallite widths D_{100} of as-received and heat-set acrylic copolymer is shown in Figure 7. Crystallite size increases with decreasing comonomer content and also because of slack annealing.

Figure 8 shows the DSC thermograms of acrylic polymers with varying comonomer content recorded under identical conditions. The DSC ther-

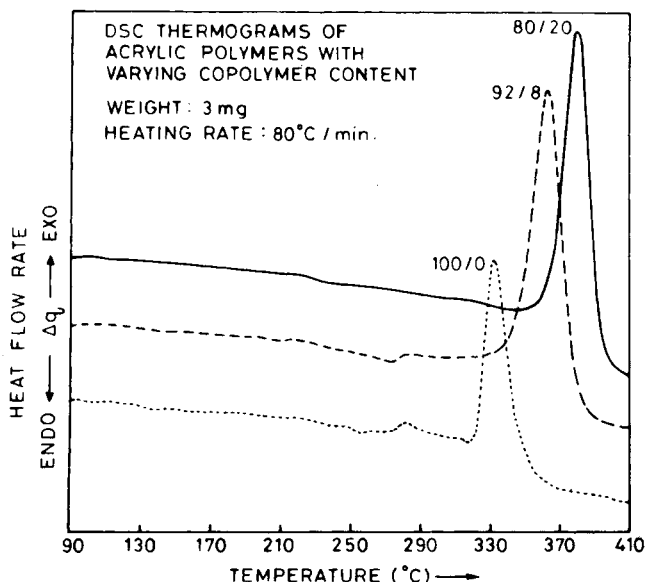


Fig. 8. Effect of comonomer content on DSC thermograms of acrylic polymers.

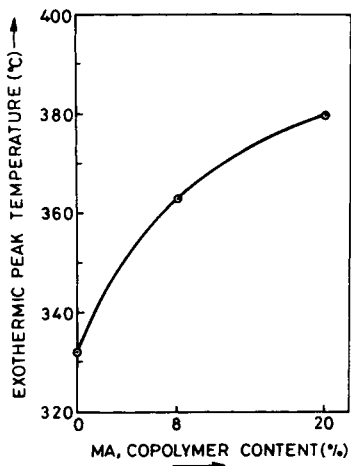


Fig. 9. Influence of comonomer content on the exothermic peak temperature.

mogram of pure PAN is characterized by two exotherms—a feeble one at about 275°C and the other a strong one at 330°C. With increasing comonomer content, the second exotherm becomes more and more intense and shifts progressively to higher temperatures (Fig. 9), whereas the first exotherm diminishes simultaneously. The feeble exotherm at the lower temperature very likely arises from the cross-linking, which is gradually inhibited as the comonomer content increases. On the other hand, the strong exotherm at the higher temperature is attributed to chemical changes due to cyclization, or due to thermal decomposition and a destruction of three-dimensional order. As the comonomer content is increased, this temperature is raised (Figs. 8 and 9), as the copolymer sites may inhibit cyclization. No

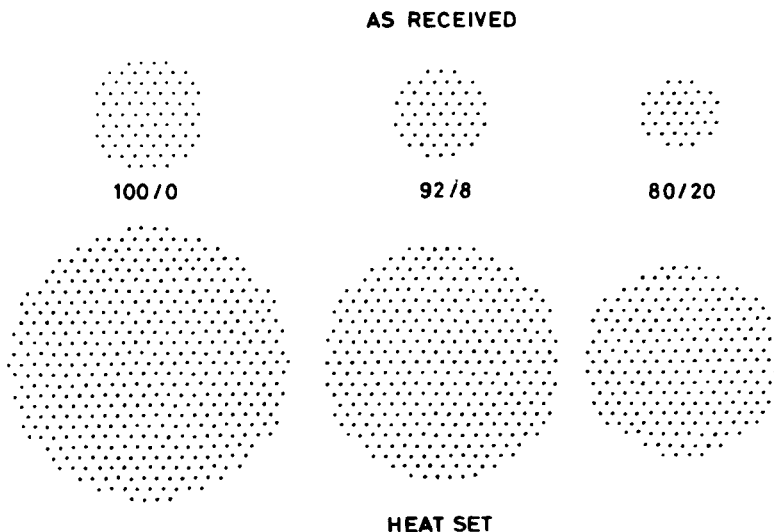


Fig. 10. Effect of copolymer composition and heat setting on crystallite cross section in acrylic copolymers. A dot represents one helical chain as in Figure 11.

endothermic peaks are seen in the thermograms, and no real or true melting of the polymer is believed to take place.

It seems likely that, at higher temperatures and prolonged periods of annealing, the formation of a new chemical structure occurs because of cyclization of neighboring polymer chains and some interchain cross-linking.^{11,12} Results shown in Table II and Figures 5 and 7 indicate that the changes in structure of PAN-MA copolymers are accompanied by a decrease in the degree of crystallinity and crystallite diameter (Fig. 10) with increasing comonomer content. It is interesting to note that heatsetting improves the crystallinity and crystallite size (Fig. 10).

DISCUSSION

Equatorial reflections at 17.4 and 30.3° (2θ) are predominant in the x-ray diffractograms of acrylic polymers (Fig. 4b). These can be explained in terms of a hexagonal lattice¹³ in which the helical PAN molecules (Fig. 11) are packed together, with a chain-to-chain separation of 6 Å. In fact, the macromolecular helices can be considered¹⁴ symmetrical rods (Fig. 12) with a diameter of 6 Å. Interchain attraction is low, and there are no reflections other than equatorial. Commercial acrylic fiber contains about 92% acrylonitrile units, and the balance, 8%, consists of methyl acrylate (the so-called comonomer), which is added to improve dyeability as well as mechanical and structural properties. The x-ray diffraction investigation (Fig. 4) on polyacrylonitrile and the effect of comonomer concentration on crystallinity (Fig. 5) and crystallite size (Fig. 7) indicate that there exist¹⁴ two well-defined phases, namely, crystalline and noncrystalline, in PAN (Fig. 12). An examination of these results in terms of I (intensity) versus 2θ (θ the diffraction angle) curves (Fig. 4) leads to a quantitative estimation of the changes produced by variation in the comonomer content. Results of x-ray analysis are given in Table II. The introduction of small amounts of a comonomer reduces the sequences of acrylonitrile molecules capable of interacting with neighboring sequences and therefore results in diminishing crystallinity (Fig. 5). Acrylic polymers with 20% MA or above can be considered amorphous, for practical purposes, since their crystallinity is extremely low (Table II). It therefore appears probable that a slight compositional variation in the PAN-MA copolymer balance will introduce profound changes in the microstructure of acrylic fibers.

It is well known¹² that the prolonged heat treatment of acrylic fibers (for 24–48 h at temperatures higher than 200°C) leads to a stepladder structure consisting of cyclized rings. Oxygen present in the pores of the fibers acts as a catalyst and causes cross-linking of adjacent polymer molecules and

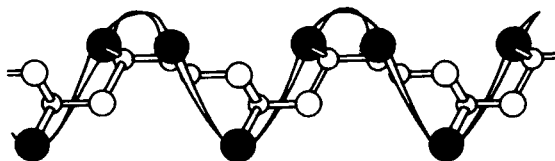


Fig. 11. Helical arrangement of atoms along a PAN chain molecule.

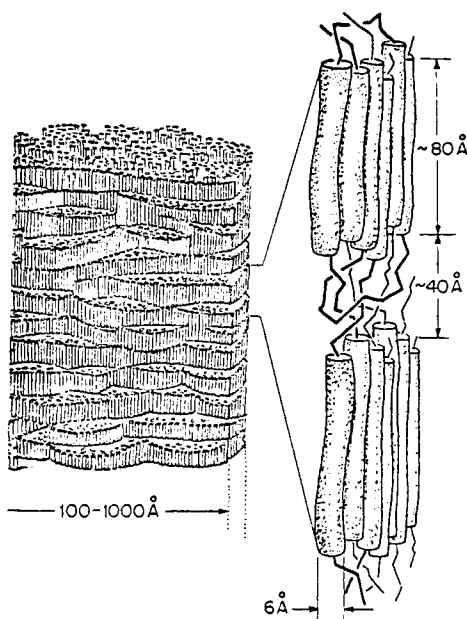


Fig. 12. Liquid-crystalline molecular structure in highly oriented acrylic fibers.¹⁴

increases the degree of cyclization (Fig. 13). In the present work, the duration of heat treatment on fibers is very short (10 min). Results obtained in the present work indicate that this conversion of the structure of acrylic fibers from the open chain form to the closed chain form has hardly begun, but it still causes enough segmental mobility to induce an increase in crystallinity (Fig. 5). Removal of the sterically most active nitrile groups leaves the remaining groups more ordered. There is no evidence of any structural (unit cell or crystal) transformation available since no new x-ray peak appears and the positions of the two main equatorial reflections remain unchanged.

The exotherms in the DSC thermograms shown in Figure 8 are interpreted as reflecting the formation of a new chemical structure,¹⁰⁻¹² believed to involve cyclization (Fig. 13, case I) along the polymer chains, as well as interchain cross-linking (Fig. 13, case II). Evolution of HCN and NH₃ is believed to occur during this process. Some random chain scission may also take place.

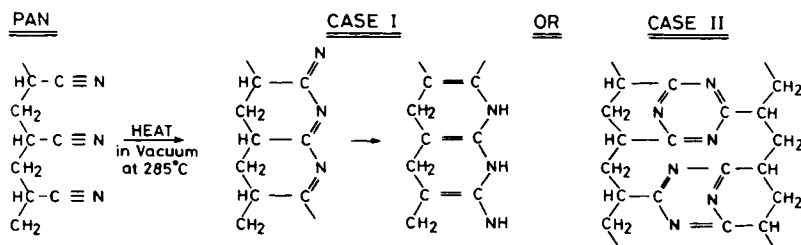


Fig. 13. Chemical transformation in acrylic fibers due to thermal annealing at high temperatures (> 200°C, 20–40 h).

CONCLUSIONS

As evident from the crystallinity and crystallite size data, the microstructure of acrylic copolymer is very much dependent on its chemical composition. With increasing comonomer content, the following microstructural changes are observed:

1. A decrease in crystallinity and crystallite width (D_{110})
2. An increase in the exothermic DSC critical decomposition peak temperature.

The thermal behavior of acrylic fibers is markedly influenced by their chemical composition. During thermal treatment of acrylic fibers, both morphological as well as chemical transformations take place.

Changes in the heat-setting conditions profoundly influence the microstructural parameters of acrylic copolymers.

As seen from the crystallinity data, the microstructure of acrylic fibers is strongly affected by the manufacturing processing conditions, such as stretching, crimping, drying, and thermosetting.

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