

Thermal Behavior and Fiber Studies of Certain Azoaromatic Polyamides

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Synopsis

Two aromatic polyamides containing azo linkage in the main chain were synthesized and characterized by TGA, DTA, and pyrolysis-GC-chemical ionization mass spectra. Fibers were also spun using a laboratory scale wet spinning unit and their mechanical and morphological properties studied. The results were correlated with structure and spinning conditions.

INTRODUCTION

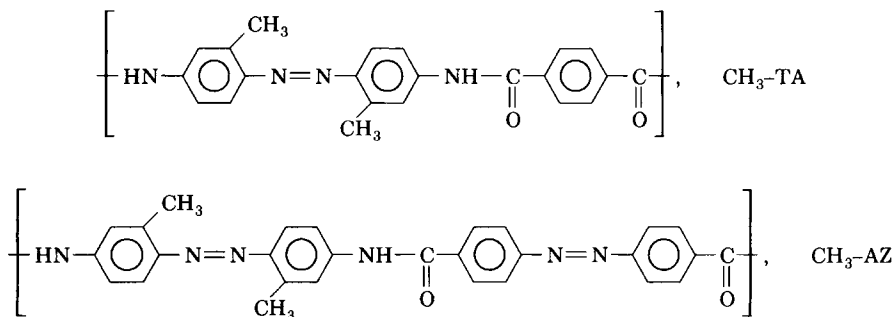
In recent years attention has been given to the synthesis of wholly aromatic polyamides with suitable substituents and flexible linkages in the main chain so that these polymers are easily processed.^{1,2} Incorporation of electron-releasing alkyl group in the aromatic nucleus has been shown to increase the solubility leading to tractable and spinnable solutions.¹ Azopolymers are of interest not only due to their possible use as high grade pigments of good fastness to light but also as materials to study the photochromic and photocontractible behavior.³ Our earlier report describes the synthesis and characterization of several aromatic polyamides containing the azo linkage in the main chain.⁴ In this article, we report the characterization of two azoaromatic polyamides derived from 2,2'-dimethyl-4,4'-diaminoazobenzene [benzenamine(3,3'-dimethyl-4,4'-azobis)] with terephthaloyl chloride and 4,4'-azodibenzoyl chloride. TGA, DTA, and pyrolysis-GC-chemical ionization mass spectral studies were carried out to study their thermal behavior. Fibers were also spun by using the wet spinning method and their tensile and morphological properties evaluated. The results were correlated with structure and spinning conditions.

EXPERIMENTAL

Materials

The structures and the codes of the polyamides used in the present investigation are shown on the following page:

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The detailed procedure of their preparation has already been reported.⁴

Thermal Studies

TGA and DTA were recorded in nitrogen for the polymers using Stanton-Redcroft simultaneous TG-DTA apparatus at a heating rate of 10°C/min. A Pt-Rh thermocouple was used to measure the temperature. Chemical ionization mass spectra was recorded with Fennigan MAT 112 S GC/MS (with Varian system) at 70 eV as ionizing voltage.

Fiber Studies

Fibers were spun from polymer dopes (20%) in 98% concn H₂SO₄ (AR) using a laboratory-scale wet spinning unit. The dopes were kept under dry nitrogen because moist air promoted clouding and eventual polymer precipitation from the bright and clear solutions. Ice-cold water was used as the coagulation bath. The fibers spun were washed, dried, and hot-stretched. The tensile properties of the fibers were determined with an Instron tensile strength testing machine.

Fiber cross sections were investigated with a Sterioscan Model S-150 scanning electron microscope. Wide-angle X-ray scattering (WAXS) patterns of the fibers were recorded with a Philips PW 1130 X-ray generator. A 35 kV and 25 mA nickel filtered CuK_α (λ = 1.54 Å) radiation was employed.

RESULTS AND DISCUSSION

The TG and DTA curves of the polymers are given in Figure 1 and the data in Table I. The TG curves show a small weight loss (about 5%) around 100–200°C, due to the loss of water absorbed by the polymers. A weight loss around 200°C is also likely due to the chain extension that may take place by the condensations of end groups resulting in the loss of water molecules.⁵ After 250°C, a deep fall in the TG curve is noticed. Above 600°C, the weight loss is steady. This is also supported by a number of broad exothermic peaks observed in the DTA curves, possibly due to crosslinking reactions. It is observed that CH₃-AZ is more stable than CH₃-TA. The azo group present in both the diamine and the diacid part perhaps enhances the rigidity of the polymer when compared to CH₃-TA. A comparison of TGA of these polymers in nitrogen and in air shows that *T*_{max} is low in air, indicating the low thermooxidative stability of these polymers. The polymers suffer a maximum

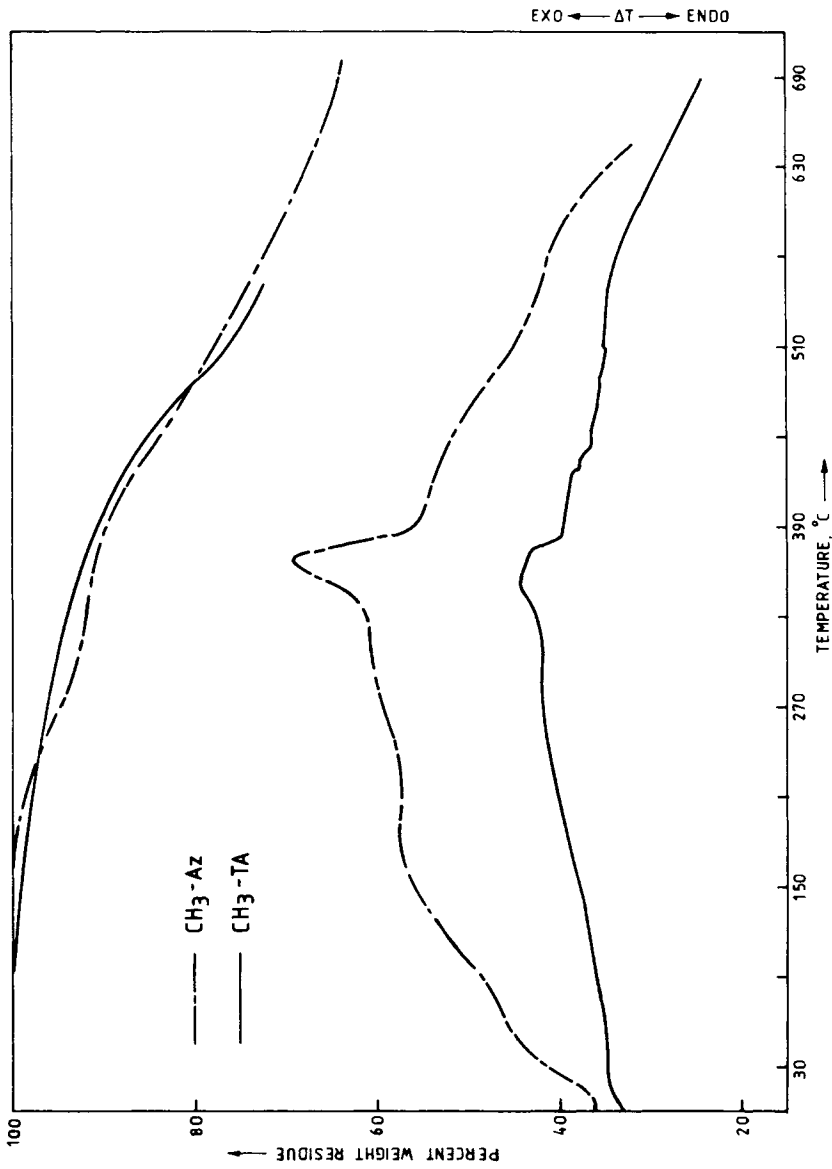


Fig. 1. TGA and DTA curves of polyamides in N₂: (---) CH₃-AZ; (—) CH₃-TA.

TABLE I
 Thermal Properties of the Polyamides^a

Polymer	Atmos	Percent weight loss								T_{\max} (°C)	No. of stages of weight loss	Exotherm temp(°C)
		10	20	30	40	60	80	100				
CH ₃ -TA	In N ₂	405	480	508	765	—	—	—	365	2	365,570	
	In air ⁴	150	390	420	466	492	540	608	360	5	530,580	
CH ₃ -AZ	In N ₂	420	460	635	—	—	—	—	370	3	165,370	
	In air ⁴	426	494	522	538	590	657	720	365	3	365,450, 590	

^a Heating rate 10°C/min.

weight loss of 70% in the temperature range 900–1000°C in N₂ atmosphere. The TG curves show that weight loss in air and in nitrogen are not comparable, thus indicating that the mechanism of decomposition is not the same. Interestingly, the last and penultimate steps of degradation occur rather very rapidly, and the maximum weight loss occur over a small temperature range. The TG curves of CH₃-TA show degradations in two and five phases in nitrogen and air, respectively, whereas CH₃-AZ shows a clear three-phase degradation. This indicates that the degradation mechanism is somewhat complicated in CH₃-TA. The first phase is possibly due to the cleavage of the bond between N and C of the amide group. The second phase may be due to the cleavage of the azo group as seen in TG curves in the temperature range of 470–530°C and DTA exotherms. No endotherms, indicating glass transition (T_g) or melting (T_m), were observed for the polyamides. It is seen that the first exotherm temperature in DTA corresponds to 20% decomposition and the successive exothermic peaks represent the second phase, third phase, etc. The exotherm observed in the region $370 \pm 10^\circ\text{C}$ is well defined and has the maximum peak area proportional to the enthalpy change.

Pyrolysis–Mass Spectral Studies

The pathways through which a polymer degrades thermally can be investigated by pyrolysis–mass spectral studies. In these studies bond scission can, however, take place at any point in the chain. The pathways are, therefore, complex and competitive. A wide range of total number of peaks due to the fragmentation products with respect to its maximum intensity were recorded for the two polymers. Only limited readings were chosen for analyses wherein intensity maximum and number of peaks were high. The pyrolysis mass spectrum recorded for the polymer CH₃-TA is given in Figure 2. In the two polymers studied, the major step is due to hydrolytic scission. In general, it may be pointed out that in polyamides, the most facile degradation route is the cleavage of the C–N bond of the amide group, leading to the formation of —NH₂ and —COOH as the end-capped units. The next route is the expulsion of the azo group present in the diamine moiety as nitrogen gas. The major primary process involves loss of CO₂. Minor competing processes involve loss of H, CH₃, NH₂, and C₂H₂. The azo group plays a central role in determining the course of degradation of the polymer.

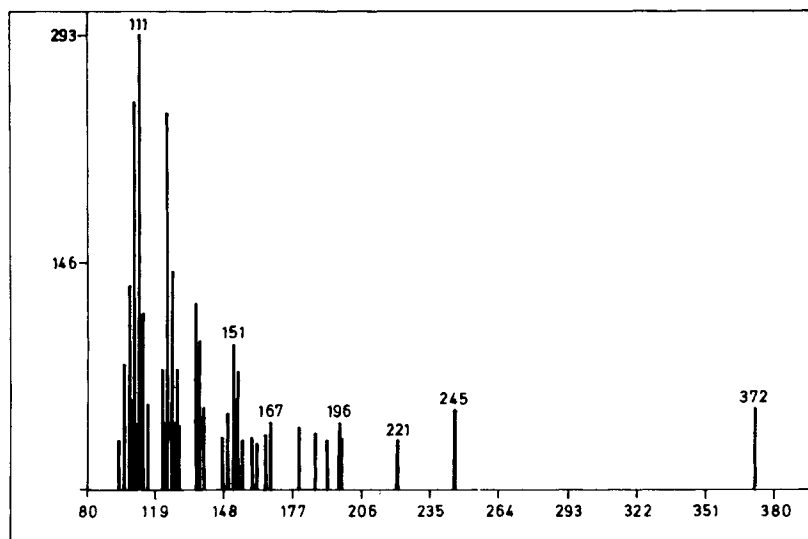
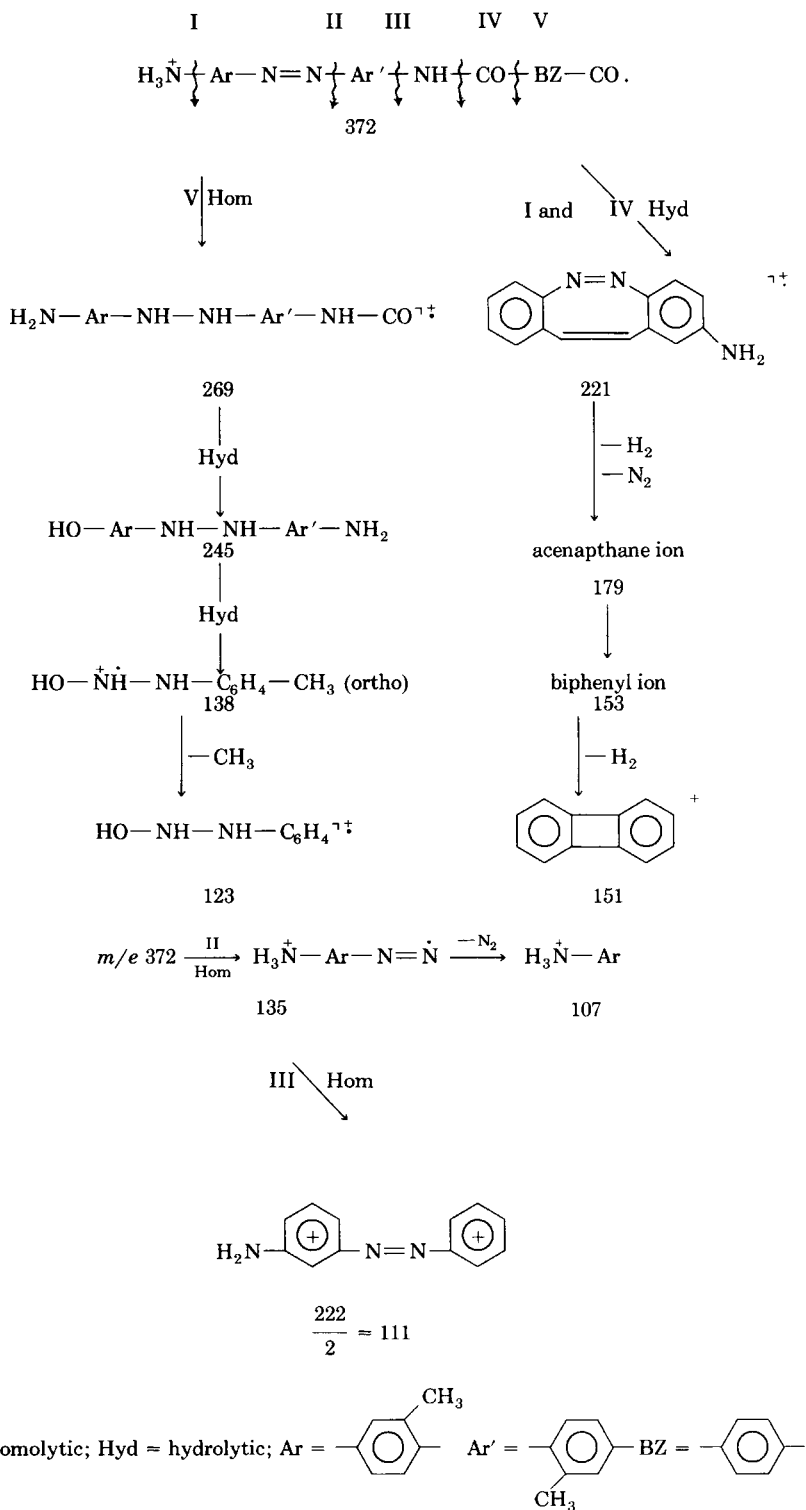


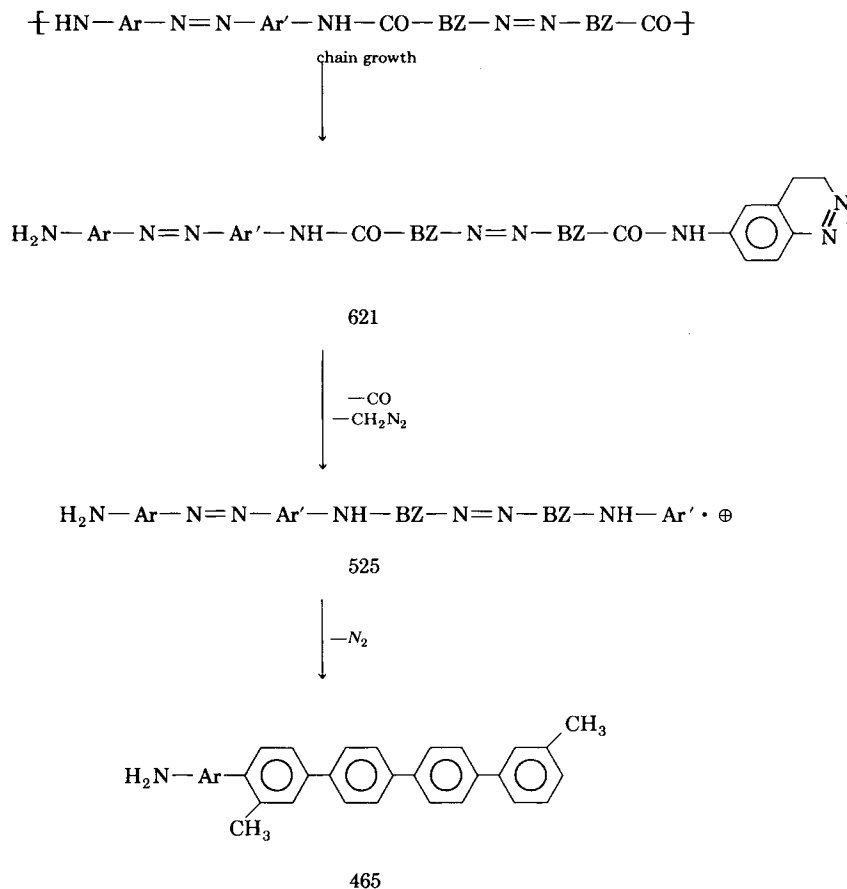
Fig. 2. Pyrolysis-mass spectrum of CH_3 -TA at 200°C .

The base peak of CH_3 -TA at 200 and 355°C corresponds to m/e 111. The possible fragmentation pattern is shown in Scheme 1. The repeating unit of the polymer (m/e 372), the diamine in the hydrazo form (m/e 245), and the diacid component (m/e 167) of the polymer are seen to appear in the mass spectrum recorded. The hydrolytic cleavages at I and IV in the polymer chain followed by the elimination of nitrogen molecule results in m/e 179 which confirms the presence of azo group. In addition to this, the hydrolytic cleavage at IV leads to terephthalic acid moiety. The base peak of CH_3 -AZ corresponds to m/e 124 at 180°C , m/e 121 at 200°C , m/e 109 at 280 and 320°C , and m/e 111 at 360°C . The possible fragmentation pattern is shown in Scheme 2. Though the bonds are vulnerable in the polymer backbone, the fragments with m/e values 621, 525, and 465 are formed by the growth of the polymer chain. This increase in chain length may be due to the increase in temperature of the polymers that are pyrolysed. The parent peak at m/e 474 does not seem to appear in the mass spectrum recorded. This undergoes further fragmentation giving rise to a component with m/e 465. The fragment with m/e 243 corresponds to the diamine component of the polymer formed due to the hydrolytic cleavage of the amide bonds. The diacid component does not seem to appear as such.

Fiber Studies

Analysis of Table II shows that better tensile properties are obtained for the fibers drawn from CH_3 -AZ than those derived from CH_3 -TA. This can be explained on the basis of the structure of the polymer and spinning conditions. Factors such as the extent of orientation of polymer molecules and the concentration of voids formed in the fiber during spinning generally seem to decide the tensile properties.⁶ The extent of orientation in aromatic polyamides

Scheme 1. Fragmentation pattern for CH₃-TA

Scheme 2. Fragmentation pattern for CH₃-AZ

is generally known to depend upon the number of para-linked benzene rings in the repeat unit. The extent of voids formation probably depends on the rate of coagulation. Rapid coagulation may result in high voids concentration.⁷

CH₃-AZ permits better close packing of the chains as the repeating unit of this polymer contains two azo groups per unit structure whereas, in CH₃-TA, there is only one. This close-packed superstructure prevents the penetration of the nonsolvent molecules into the polymer dope, leading to slower coagulation. This results in the formation of low voids content and better tensile properties. This is supported by the observation of low voids that are distributed throughout the cross section of the fiber, as seen from its SEM photographs (Fig. 3). The voids in CH₃-AZ are not only less concentrated than those observed in CH₃-TA, but also a higher volume fraction of these voids is found in the annular than in the core part of the fiber. This is because the amount of nonsolvent that reaches the core of the fiber is less. In other words, the rate of coagulation decreases from the annular to the core. This explains the better tensile properties observed for CH₃-AZ compared to

TABLE II
Tensile Properties of Fibers^a

Polymer	Spin-stretch ratio	Draw ratio	Draw temp (°C)	Denier (g)	Tenacity (g/den)	Elongation (%)	Initial modulus (g/den)
CH ₃ -TA	22.0	1.0	—	18.0	0.93	17.06	8.5
	22.0	1.0	100	16.1	1.18	15.20	11.2
	22.0	1.0	150	13.6	1.35	11.66	18.3
	22.0	1.4	—	19.0	1.20	15.82	11.6
	14.0	1.4	—	19.5	1.12	16.02	10.8
	14.0	1.4	100	18.3	1.24	14.31	12.7
	14.0	1.4	150	15.1	1.40	9.19	22.2
	14.0	1.4	150	15.1	1.40	9.19	22.2
CH ₃ -AZ	5.0	1.0	—	25.3	0.98	15.00	10.5
	5.0	1.0	150	23.4	1.26	11.39	12.5
	5.0	1.0	200	22.6	1.33	9.20	15.2
	5.0	1.2	—	25.0	1.22	13.60	11.6
	5.0	1.2	150	22.4	1.58	9.21	28.6
	5.0	1.2	200	21.5	1.74	6.00	43.5

^aDope composition = 20% concn H₂SO₄; spinnerette used = 100 μm.

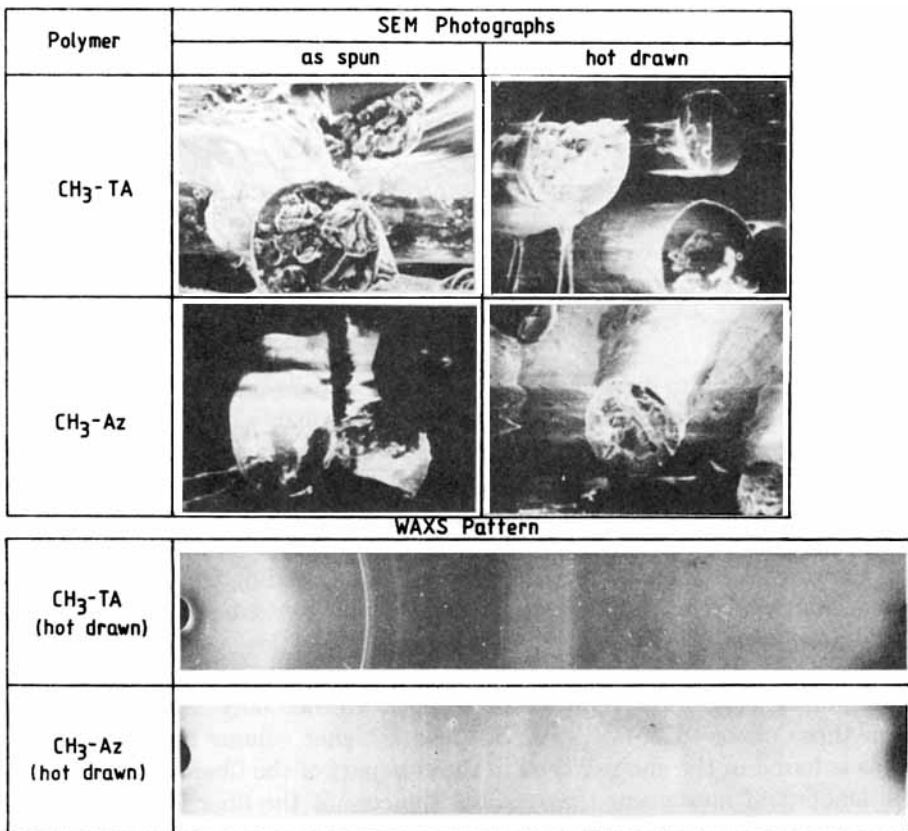


Fig. 3. SEM photographs and WAXS patterns of the fibers.

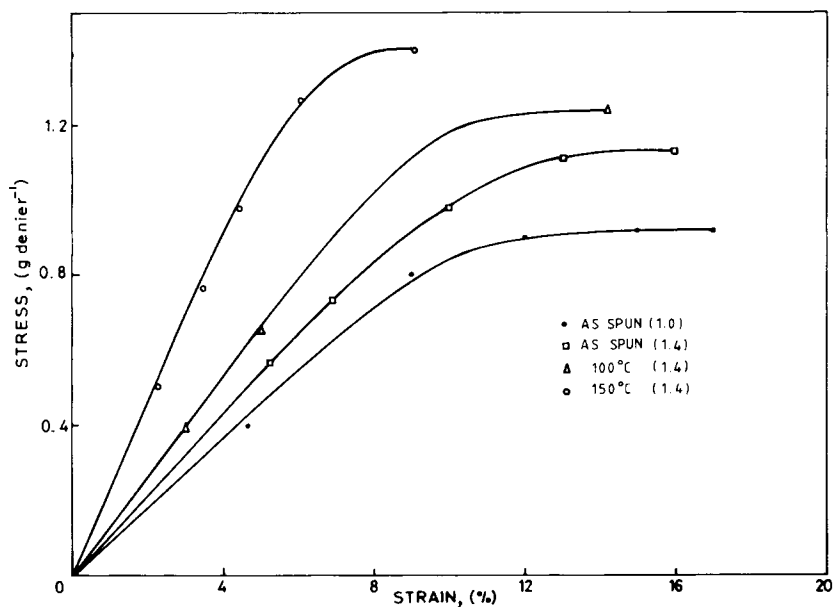


Fig. 4. Typical stress-strain curves of the CH_3 -TA fibers: (●) as-spun (1.0); (□) as-spun (1.4); (Δ) 100°C (1.4); (○) 150°C (1.4).

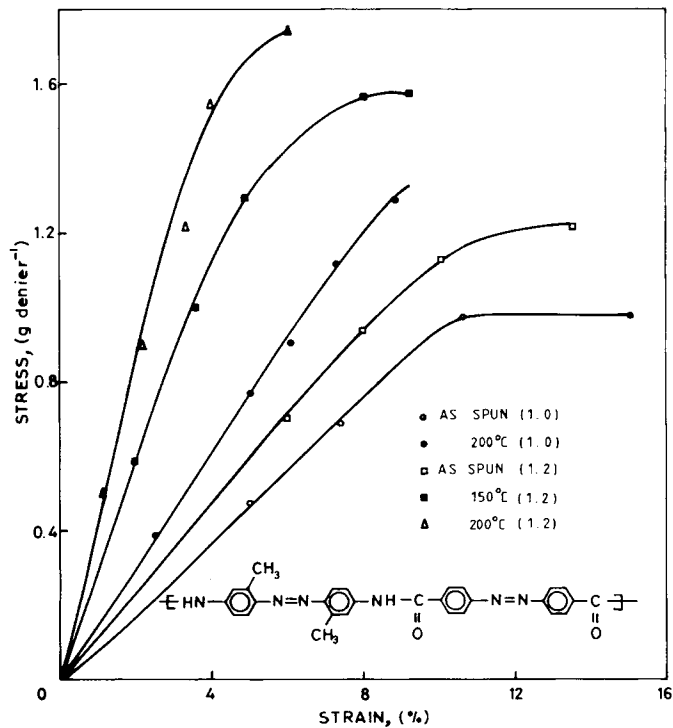


Fig. 5. Typical stress-strain curves of the CH_3 -AZ fibers: (○) as-spun (1.0); (●) 200°C (1.0); (□) as-spun (1.2); (■) 150°C (1.2); (Δ) 200°C (1.2).

CH₃-TA. For fibers of CH₃-TA, a higher stretch ratio seems to result in higher tensile properties. This is due to the retention of orientation imparted by the stretch at the face of the spinnerett during coagulation. Hot drawing of the as-spun fibers increases the tensile properties owing to the increase in orientation (Figs. 4 and 5). Hot drawing increases the tenacity and initial modulus at the expense of percentage of elongation at break. It is seen from SEM photographs that the voids are larger and better defined for hot-drawn than for undrawn fibers. This may be due to the expansion of air and solvent molecules trapped in the fibers.

The WAXS patterns of the fibers can also be correlated with the tensile properties (Fig. 3; Table II). The development of arcs in the equatorial line with a background of diffused halo for the hot-drawn fibers confirms that they have a certain amount of orientation along the fiber axis. The "as-spun" fibers, which have very little orientation, are seen to have only a diffused halo in its WAXS pattern and no arcs.^{8,9}

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