Preparation and Properties of Polyimide Fibers

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Synopsis

Polyimides were synthesized from 4,4'-diamino diphenyl methane and pyromellitic dianhydride using low-temperature solution polycondensation. Solutions of these polyamic acids in dimethylformamide (DMF) were spun into fibers by the wet spinning technique using a mixture of DMF and water as coagulants. Various spinning parameters such as dope concentration, bath composition, and jet stretch were standardized to get polyimide fibers with optimum properties. It was observed that fibers spun at higher jet stretch did not cyclize satisfactorily. Higher dope concentrations gave fibers with better properties. Cyclodehydrated fibers were hot-drawn at 300°C. Fibers with a tenacity of 380 mN/tex, an extension at break of 10%, and initial modulus of 4060 mN/tex were obtained. Mechanical properties of fibers at elevated temperatures, i.e., 100 and 200°C were also measured. Heat aging at 100, 200, and 300°C was carried out for 10 hr. This resulted in an increase in the initial modulus of fibers. However, a 28% decrease in tenacity was observed when the fibers were heat-aged at 300°C. The dynamic thermogravimetry in air showed that fibers were stable up to 400°C. The activation energy of decomposition, calculated from these thermograms in the temperature range 540–610°C was 101 kJ/mole.

INTRODUCTION

Widespread research has been carried out in the last decade toward the development of high-temperature resistant fibers and fibrous materials for both industrial and military applications. Aromatic polyimides have been found to have excellent thermal and chemical stability. They also possess outstanding dielectric properies. The films and fibers prepared from some of these polymers have been reported to have good mechanical properties.
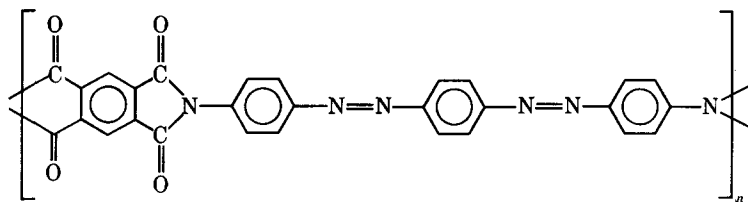
The polyimide fibers and films, e.g., Kapton H,[1] PRD-14,[2] and Arimid PM[3-7] appear to be based on the following polymer[8]:
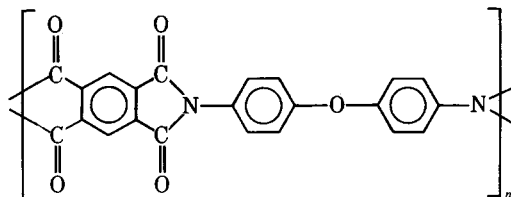
Fibers from poly(amide-imide) and polyazoimide have also been prepared.
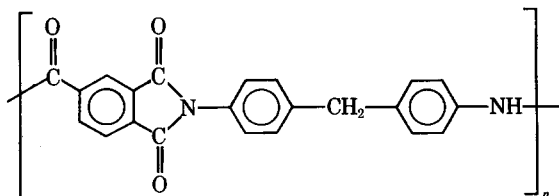

Kermel (polyamide inside)

Black azopolyimide

It would be of interest to study the spinning of polyimide having a structure which is similar to Kapton except that ether linkage is replaced by the —CH_2— group. Spinning of this polymer into fibers has been reported recently by Koton et al.[9] who have investigated a series of polyimides with different backbone structures. The fiber properties can be influenced to a great extent by varying the conditions of spinning. The effect of the conditions of spinning on fiber properties has not been reported by these authors. These authors have also not reported the effect of heating on the properties of fibers. Therefore it was decided to study the spinning of this polymer into fibers and investigate the fiber properties.

EXPERIMENTAL

The polymer was prepared by a two-step condensation method.[10] Polyamic acid precursor was initially prepared in dimethylformamide (DMF) at 0°C. This was spun into fibers by wet spinning and then chemically cyclodehydrated to yield a polyimide fiber with the following structure:
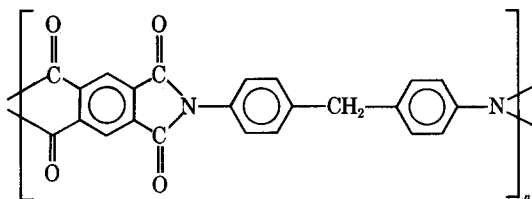
Viscosity of the polyamic acid was measured in DMF using Ubbelhode suspension level viscometer at 30°C. Polymers were characterized by taking IR in film form in both the amic acid and imide state using Hilger-Watt H-800 IR spectrophotometer. The film was prepared from a DMF solution by casting it on a glass plate. The cyclodehydration of films was done by immersing them in acetic anhydride–pyridine solution for 24 hr.

Spinning of Polymers into Fibers

Spinning was done with the help of a bench scale wet spinning equipment which was fabricated for this purpose. A schematic diagram of the wet spinning setup is shown in Figure 1. It consisted of (a) a polymer solution extrusion system, (b) a glass spinneret, (c) coagulation bath, (d) washing bath, (e) a hot plate for drying the fiber, and (f) a final take-up unit with a traverse guide. A
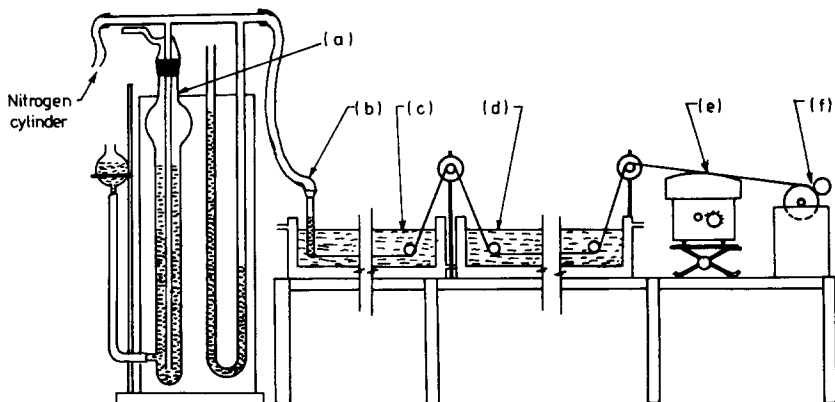
Fig. 1. Schematic diagram of the wet spinning setup.

constant rate of extrusion of the polymer solution was achieved by applying a constant pressure with the help of a manometer and a nitrogen cylinder. The pressure was varied from 0.5 to 2.0 kg/cm^2. The polymer was extruded at a constant linear speed of 50 cm/min in the coagulation bath.

The spinneret consisted of a Pyrex glass tube with a 0.2-mm capillary fused at its bottom at right angles to it.

The coagulation bath consisted of a double jacketed stainless-steel bath (60 × 15 × 14 cm). A steady rate of coagulation was achieved by varying the bath composition. With the help of a roller attached to a variable-speed motor, a known jet stretch could be given. The washing bath was also a double jacketed stainless-steel bath (98 × 15 × 14 cm). The drying unit consisted of a curved plate whose temperature could be controlled with the help of a sunvic energy regulator. The wet fiber could be dried during its traverse over the hot plate. The final winding of the fibers was done with the help of a take-up roller fitted with a traverse guide and variable-speed motor.

Immediately after spinning, the fibers were vacuum dried at 50°C and then kept in a cyclization solution consisting of acetic anhydride:pyridine (1:1) for 36 hr at room temperature. After completion of cyclodehydration (color of the fibers changed from dull white to yellow), the fibers were dipped in dioxane to remove the cyclization solution and then dried in a vacuum oven at 100°C. The fibers so obtained were hot-drawn at 300°C at various draw ratios. Hot drawing resulted in a yellow lustrous filament.

Mechanical properties testing of the fibers was done on Instron. A gauge length of 3 cm with a crosshead speed of 5 cm/min was used. Fibers were tested at 20, 100, and 200°C.

Heat-aging of the fibers for 10 hr was done by keeping them in a furnace maintained at 100, 200, 300°C in air atmosphere. Mechanical properties of the fibers were tested after heat-aging to assess the deterioration in tensile properties. Dynamic thermogravimetry of the fibers was carried out by using Stanton thermogravimetric balance (Model HT-D); 15 ± 2 mg of the fiber was used. The rate of heating in air atmosphere was 6°C/min.

RESULTS AND DISCUSSION

Preparation and Characterization of Polymers

Polyamic acid samples with different intrinsic viscosities were prepared by changing the reaction conditions. Three samples were prepared having [η] 84, 122, 140 cm³/g at 30°C in DMF solution (Fig. 2).

Figure 3 shows the IR spectra of polyamic acid and polyimide. Imide absorption bands were observed at 1775 cm⁻¹ and 1725 cm⁻¹ (imide I), 1375 cm⁻¹ (imide II), 1120 cm⁻¹ (imide III), and 720 cm⁻¹ (imide IV) in the cyclodehydrated samples. All these bands were very strong and were absent in the amic acid spectra. The imide I band is attributed to the stretching vibrations of weakly coupled carbonyl groups. The imide II, III, and IV bands have been assigned to axial, transverse, and out-of-plane vibrations of the cyclic imide structures.[11]

In the spectra of polyamic acid, bands at 3260 cm, 1411, and 1320 cm⁻¹ (due to N—H stretch, O—H in plane deformation, and C—O stretch, respectively) were present. These disappeared after cyclodehydration thus confirming that in polyimides, the amido-acid groups were absent.
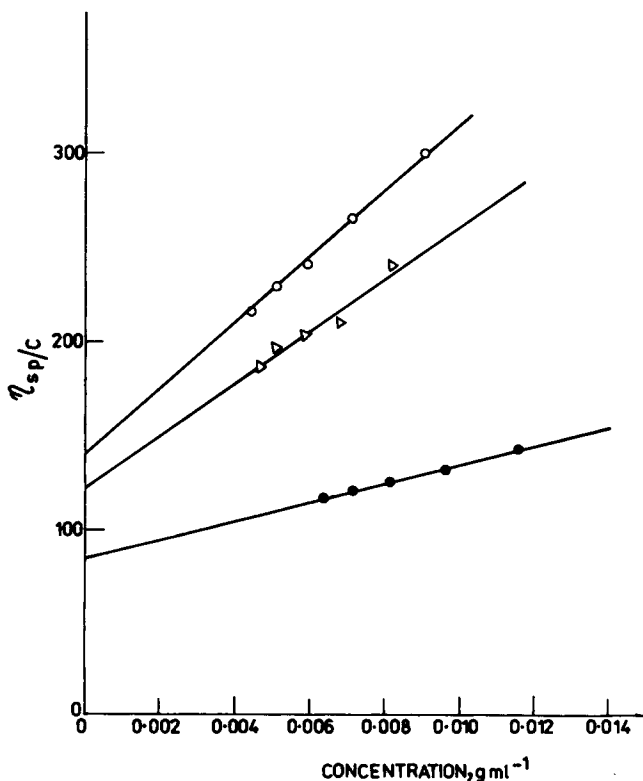

Fig. 2. Intrinsic viscosity plots of polyamic acids in DMF at 30°C.
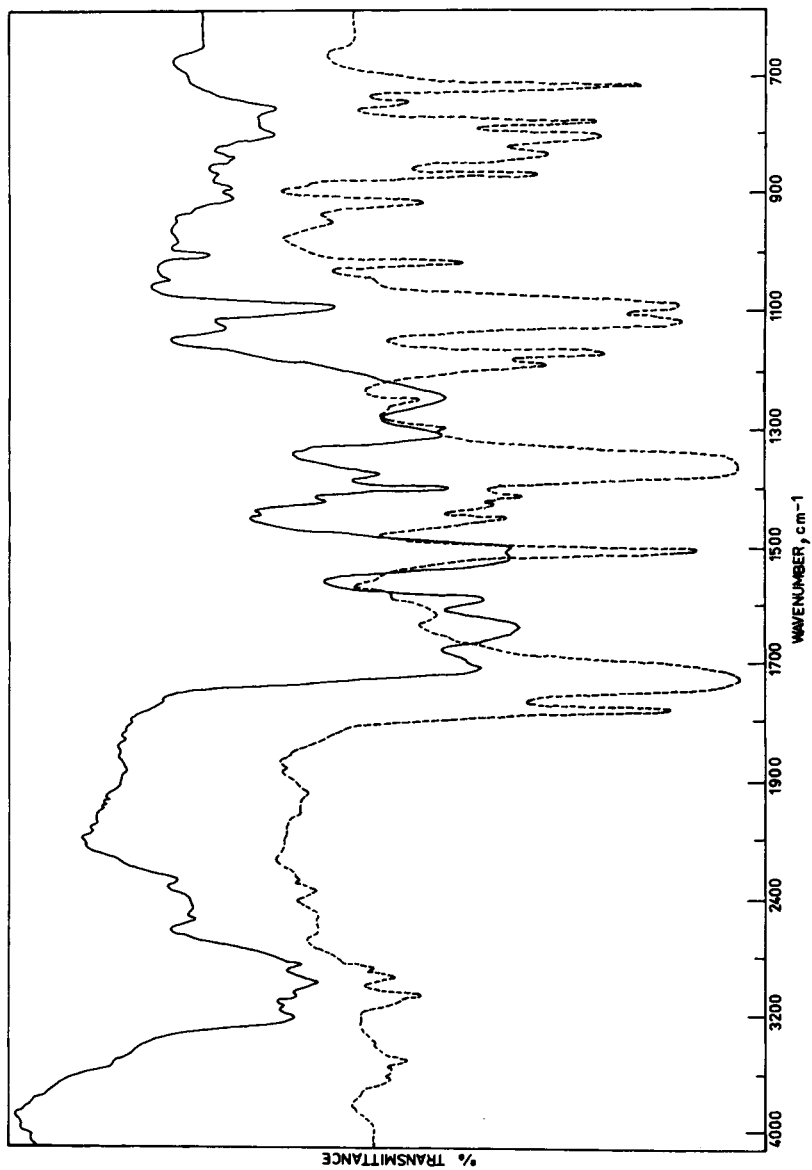
Fig. 3. Infrared spectra of polyamic acid (——) and polyimide (- - -).

Spinning of Polymers into Fibers

Some of the parameters which can influence the ultimate properties of the fibers in wet spinning are (a) intrinsic viscosity of the polymer, (b) polymer concentration in dope, (c) composition of the coagulation bath, (d) jet stretch, and (e) drawing. The conditions for the spinning of fibers were optimized by taking the polymer with $[\eta] = 122$ cm^3/g and a polymer concentration of 10% in the spinning solution.

Effect of Coagulant Composition

Water:DMF mixtures in different ratios (80:20, 70:30, 60:40) were tried as coagulants. Higher concentration of water in the coagulation bath caused a very fast precipitation on the surface of the thread line. A skin was thus formed and the interior of the fiber had entrapped solvent in it. Bath composition of 60:40 and 70:30 were found to give fibers with better properties.

Effect of Stretch During Spinning

Keeping the concentration of dope and composition of coagulation bath at 70:30, stretch during coagulation was varied from 20 to 4. (Stretch is defined as the ratio of take-up speed and extrusion speed of the polymer.) The polyamic acid fibers thus prepared were cyclodehydrated in pyridine–acetic anhydride for 36 hr. Embrittlement of fibers during cyclodehydration was observed in the fibers with higher stretch during spinning. The cyclodehydration was found to be satisfactory in fibers spun at a stretch ratio of 4. It is quite likely that fibers with higher stretch have a high orientation of molecules along the fiber axis and such an orientation may facilitate some interchain cyclodehydration (interchain ring formation) which might result in embrittlement of fibers.

Solvent penetration may also be difficult if the orientation of molecules along the fiber axis is more extensive. This may cause cyclodehydration on the surface only, causing greater shrinkage on the surface than in the bulk. This may lead to the development of cracks and fiber embrittlement.

The mechanical properties of the fibers in the polyamic acid state were evaluated to see the effect of stretching. The results are given in Table I. Reduction in stretch ratio resulted in a decrease in tenacity but an increase in denier and percent extension. This behavior is quite expected because the oriented fiber will have better tensile properties. However, due to the difficulties associated with the subsequent cyclodehydration reaction, it was decided to keep the stretch

TABLE I
Effect of Jet Stretch on the Mechanical Properties of Polyamic Acid Fibers: Dope
Concentration 10%; Bath Composition (Water:DMF), 70:30; $[\eta]$, 122 cm^3/g

Sample	Jet stretch	Denier	Mechanical Properties		
			Tenacity, mN/tex	% Elongation	Initial modulus, mN/tex
A	20	18	115	27	3710
B	15	26	97	37	2560
C	10	43	62	74	2210
D	4	75	53	96	1770

at 4 in all subsequent experiments. The polyimide fiber thus obtained had a tenacity of 88 mN/tex.

Effect of Drawing at 300°C

Polyimide fibers were hot-drawn to draw ratios of 2 and 2.5 at 300°C. Higher draw ratios could not be used because of the fiber breakage. The hot-drawing increased the tenacity of the fibers to 256 nM/tex. Results of hot-drawing are given in Table II.

Effect of Dope Concentration

By keeping coagulation bath composition at 70:30 and jet stretch at 4 the concentration of dope was increased up to 20%. The cyclodehydrated undrawn fibers had higher percentage extensions at break and could be hot-drawn up to a draw ratio of 3.5. The higher draw ratios possible under these conditions yielded polyimide fibers with better mechanical properties (tenacity = 344 mN/tex).

Effect of Intrinsic Viscosity of the Polymers on the Fiber Properties

Polyamic acid with $[\eta]$ = 84 cm^3/g was spun into fibers using a bath composition of 70:30 (H$_2$O:DMF), jet stretch of 4, and 20% dope concentration. A comparison of fiber E_1 and D_4 (Tables III and IV) indicates that tenacity as well as initial modulus of fibers prepared under identical conditions depended on the $[\eta]$ of the polymers. Higher tenacity and initial modulus fibers were obtained with the polymer of higher intrinsic viscosity.

A higher dope concentration could be prepared with this polymer sample of low molecular weight. Spinning was therefore carried out at a dope concentration of 32% using a coagulation bath of composition 70:30 (fiber E_2) and 60:40

TABLE II
Effect of Hot-Drawing on the Mechanical Properties of Polyimide Fibers Based on Sample D

Sample	Draw ratio	Denier	Mechanical Properties		
			Tenacity, mN/tex	% Elongation	Initial modulus, mN/tex
D_1	0	60	88	56	1940
D_2	2.0	37	150	10	3440
D_3	2.5	24	256	9	3620

TABLE III
Mechanical Properties of Polyimide Fibers Prepared under the Following Spinning Conditions: Dope Concentration, 20%; Bath Composition (Water:DMF); 70:30, Jet Stretch, 4

Samples	Draw ratio	Denier	Mechanical Properties		
			Tenacity, mN/tex	% Elongation	Initial modulus, mN/tex
D_4	0	150	71	127	1500
D_5	3.0	48	336	14	4240
D_6	3.5	37	344	11	5300

TABLE IV

Mechanical Properties of Polyimide Fibers.   Intrinsic Viscosity of Polyamic Acid is 84 cm³/g and Jet Stretch is 4

| | | Bath | | | Mechanical properties | | |
| | Dope | composition | Draw ratio | | Tenacity, | % Elonga- | Initial modulus, |
Sample	concentration	water:DMF	(hot-drawn)	Denier	mN/tex	tion	mN/tex
E_1	20%	70:30	0	120	53	106	1150
			2.5	49	203	12	4860
E_2	32%	70:30	0	96	53	71	1590
			2.5	35	221	8	4860
E_3	32%	60:40	0	81	80	123	1240
			2.0	34	256	14	3270
			2.5	32	291	12	3530

(fiber E_3).   The jet stretch was maintained at 4.   Tenacity of the resulting undrawn polyimide fibers did not change with the dope concentration (fibers E_1 and E_2).   An increase in tenacity was observed by changing the bath composition to 60:40 (Table IV).   The drawing of the fibers resulted in an improvement of mechanical properties (E_1,E_2,E_3).

Fibers from a polyamic acid sample with [η] 140 cm³/g were spun using a 20% dope concentration.   Higher concentrations were not tried because of difficulty in dissolution.   A bath composition of 60:40 and jet stretch of 4 was used.   The as-spun fibers were cyclodehydrated and hot-drawn to various draw ratios (Table V).   Figure 4 gives the stress–strain behavior of these fibers in the amic acid and imide (drawn and undrawn) states.   Curves of polyamic acid and polyimide (undrawn) are the characteristic stress–strain curves for amorphous polymers. These have % extensions as high as 180% at the point of break.   In the case of polyamic acid, the curve shows a local yielding maxima between 5% and 10% strain.   After this yielding maxima, the fiber begins to undergo a permanent deformation.   The hot-drawn fibers have high breaking stress at relatively small elongations.

It was observed that tenacity and initial modulus increased with the cyclodehydration of polyamic acid to polyimide.   In fact, after cyclodehydration, a considerable rearrangement in the internal structure of the fiber takes place resulting in a more compact packing of chains to give higher tenacity.   The increase in % extension may be due to the absence of intermolecular hydrogen

TABLE V

Mechanical Properties of the Fiber Spun from the Polymer with the Following Conditions: [η], 140 cm³/g; Dope Concentration 20%; Bath Composition (Water:DMF), 60:40; Jet Stretch, 4

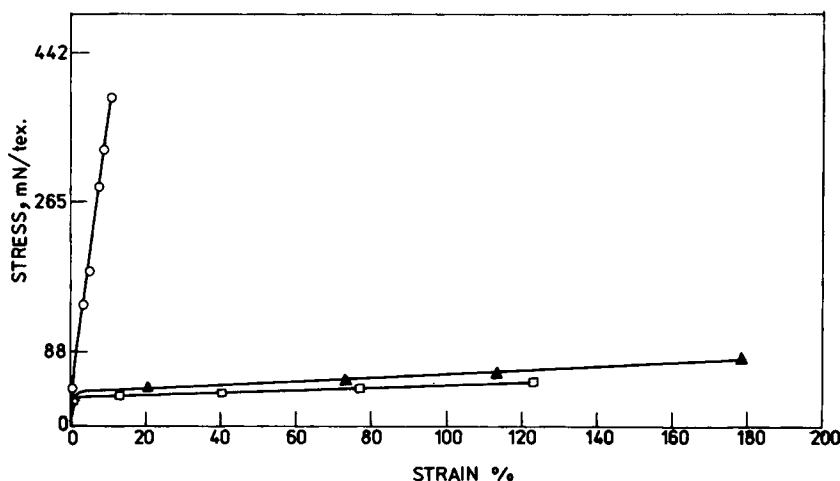| Sample | Draw | | Mechanical properties | | |
No.	ratio	Denier	Tenacity, mN/tex	% Extension	Initial modulus, mN/tex
F[a]	0.0	167	53	119	1410
F_1	0.0	143	80	182	2560
F_2	2.5	64	212	12	3620
F_3	3.0	52	283	11	3970
F_4	3.5	38	380	10	4060

[a] Polyamic acid fiber.

Fig. 4. Stress–strain curves of polyamic and polyimide fibers: (□) amic acid, (▲) undrawn imide, and (○) hot-drawn imide.

TABLE VI
Mechanical Properties of Fibers after Chemical Treatment

Sample No.	Fiber sample	Denier	Mechanical properties		
			Tenacity, mN/tex	% Exten- sion	Initial modulus, mN/tex
1	Original hot-drawn fiber	41	380	17	4060
2	After treatment in boiling water for 2 hr	41	238	9	4970
3	After treatment in 10% H_2SO_4 at 100°C for 2 hr	48	230	9	5020

TABLE VII
Integral Procedural Decomposition Temperatures (IPDT) of 25%, 50%, and 75% Decomposition, Temperature of Maximum Decomposition (T_{max}) and Activation Energies of Decomposition (E^*) of D_6, E_3 and F_4 Hot-Drawn Fibers

Sample	Decomposition Temperature			T_{max}, °C	IPDT, °C	E^*, kJ/ mole	Temperature range for E^* calculation, °C
	25%	50%	75%				
D_6	550	570	600	595	602	101	540–600
E_3	585	600	615	595	565	96	580–610
F_4	565	585	595	595	564	101	560–610

bonding which is present in the polyamic acids. The as-spun imide fibers were hot-drawn at various draw ratios (2.5, 3.0, 3.5). Increase of draw ratio above 3.5 resulted in breakage of fibers. Fibers (F_4) with a tenacity of 380 mN/tex could be obtained at a draw ratio of 3.5.

Mechanical properties of fiber E_4 were also measured at elevated temperature, i.e., at 100 and 200°C. The tenacity and initial modulus of the fibers decreased (194 mN/tex at 100 and 177 mN/tex at 200°C). In Figure 5, the variation in
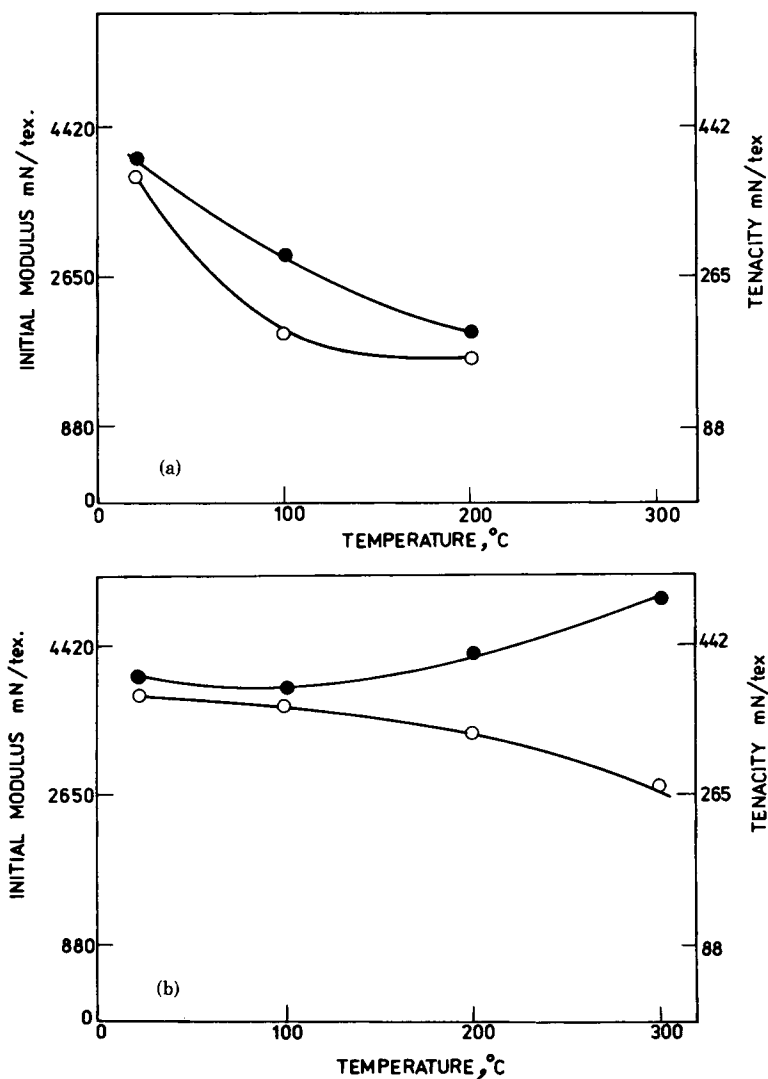
Fig. 5. (a) Initial modulus (●) and tenacity (○) of polyimide fibers at different temperatures of measurement. (b) Initial modulus (●) and tenacity (○) of polyimide fibers after heat aging at various temperatures for 10 hr.

tenacity and initial modulus as a function of temperature is shown. As the temperature of measurement of mechanical properties is raised from 20 to 200°C, the polymer which is initially in the glassy state tends to approach the rubbery state. The mobility of the chains is thus increased resulting in a decrease in initial modulus. The mechanical energy required to break the fiber is also being supplemented by the thermal energy. This may account for a decrease in tenacity of the fibers at elevated temperatures. A reduction in the % extension of the fibers was observed.

The effect of heat aging of fibers at 100, 200, and 300°C for 10 hr in air was also investigated [Fig. 5(b)]. The mechanical properties were measured at 20°C. Heat aging at elevated temperatures increased the initial modulus of the fibers.
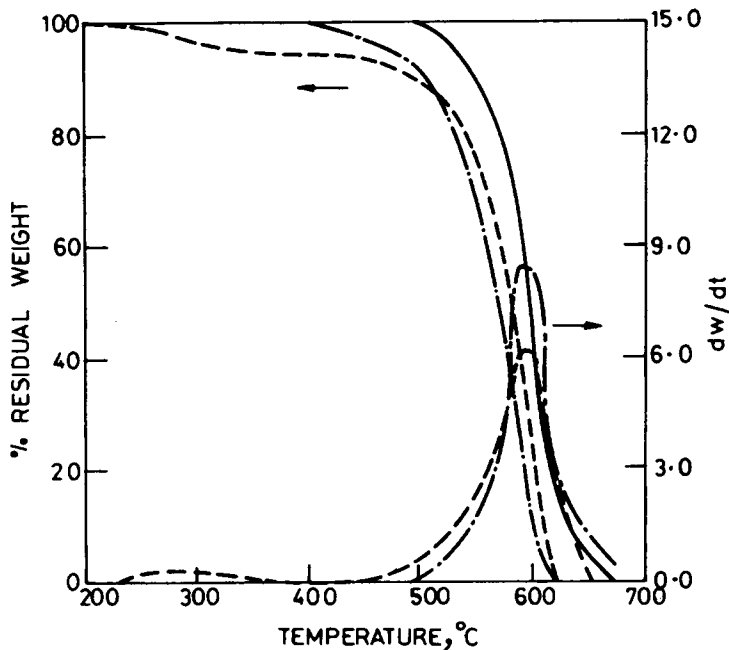
Fig. 6. Primary thermograms and rate of weight loss vs temperature curves of polyimide fibers F_4 (- - -), E_3 (—), and D_6(- -·- -).

Slow crystallization may take place on keeping the fibers at high temperature. This will increase the rigidity and initial modulus. However, a 28% decrease in tenacity was observed. The decrease in tenacity may be due to the degradation of polymer in air.

Table VI gives the mechanical properties of the fiber after it was treated in 10% sulfuric acid at 100°C for 2 hr and in boiling water for 2 hr. A decrease in tenacity occurred in both cases, which might be due to the acid catalyzed hydrolysis of imide linkages in the polymer, hence giving inferior mechanical properties to the fiber. To evaluate the thermal stability of fibers, dynamic thermogravimetry in air was used. In Figure 6, the primary thermograms and rate of weight loss versus temperature curves for hot-drawn fibers D_6, E_3, and F_4 are given. The fibers were stable up to 400°C and only above this temperature was loss in weight observed. Integral procedural decomposition temperatures (IPDT) were calculated according to the method of Doyle[12] (Table VII). IPDT values for E_3 and F_4 were almost the same, whereas D_6 had a higher value. From the primary thermograms, activation energies of decomposition of these fibers were calculated according to the method of Dharwadkar and Karkhanawala.[13] The trend of activation energies suggest that molecular weight had no pronounced effect on the thermal stability of polymers.

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