High-Performance Polymer Films. III. Preparation and Characterization

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ABSTRACT: A series of polyimide and copolyimide films were prepared by film casting, drying, and thermal imidization from the respective precursor poly(amic acid) (PAA) and copoly(amic acid) solutions derived from two dianhydrides, pyromellitic dianhydride (PMDA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), and two diamines, 4,4′-oxydianiline (ODA) and a proprietary aromatic diamine (PD) as monomers. Depending on the solution's inherent viscosity value (molecular weight) and the nature of the polymer chains (derived from rigid or flexible monomers), precursor poly(amic acid) and copoly(amic acid) solution concentrations of 8–12% (w/w) were found to be suitable for the preparation of good quality polyimide/copolyimide films. The recovery of film toughness and creasability from the brittleness at the intermediate temperature of the cure cycle depended not only on the molecular weight of the precursor poly(amic acids)/copoly(amic acids) but also on their chain flexibility. The poly(amic acid) derived from both rigid dianhydride and diamine practically gave rise to a brittle film of polyimide even after curing to 360°C. The resulting polyimide and copolyimide films were compared with Du Pont's Kapton H film. The density of the films was in the range 1.39–1.42 g/cm^3. The thickness of most of the films was in the range 20–30 μm. The HPF 3 film, based on PMDA–PD, appeared to be highly colored (reddish brown), and the HPF 2 film, based on BTDA–ODA, had the lightest yellow coloring among the films in this investigation, including Kapton H film. HPF 2, HPF 6, and HPF 8 films were more amorphous than the other films. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 976–988, 2001

Key words: polyimide/copolyimide films; film casting; poly(amic acids)/copoly(amic acids); inherent viscosity; thermal imidization; cure cycle

INTRODUCTION

Poly(amic acid) solution, the product of the first step in the two-step method of the synthesis of
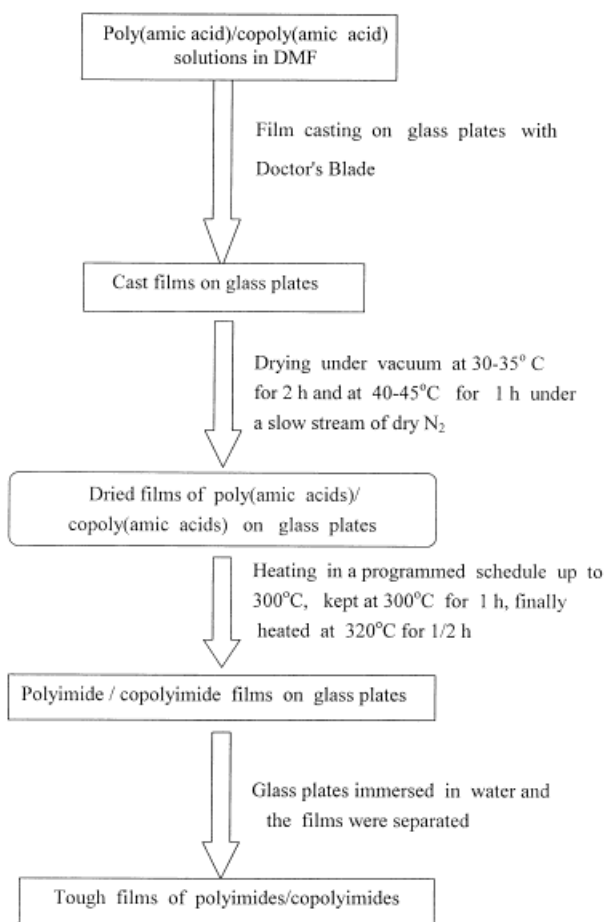
polyimide, is the processing form for the preparation of the finished products of polyimide such as films, fibers, coatings, and so on. The most widely used second step involves the heating of the processed form of poly(amic acid) in the solid state over 300°C to convert it into polyimide.[1–6] Because polyimide is often insoluble and infusible, its precursor, poly(amic acid), is very important as far as its processability is concerned. Characteristic properties of polyimide are its high glass-transition temperature (T_g) and difficulties in

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┌─────────────────────────────────────┐
│  Poly(amic acid)/copoly(amic acid)   │
│          solutions in DMF            │
└─────────────────────────────────────┘
                 │
                 │  Film casting on glass plates with
                 ▽  Doctor's Blade
┌─────────────────────────────────────┐
│      Cast films on glass plates      │
└─────────────────────────────────────┘
                 │
                 │  Drying under vacuum at 30-35° C
                 │  for 2 h and at 40-45°C for 1 h under
                 ▽  a slow stream of dry N₂
┌─────────────────────────────────────┐
│    Dried films of poly(amic acids)/  │
│   copoly(amic acids) on glass plates │
└─────────────────────────────────────┘
                 │
                 │  Heating in a programmed schedule up to
                 │  300°C, kept at 300°C for 1 h, finally
                 ▽  heated at 320°C for 1/2 h
┌─────────────────────────────────────┐
│ Polyimide / copolyimide films on glass plates │
└─────────────────────────────────────┘
                 │
                 │  Glass plates immersed in water and
                 ▽  the films were separated
┌─────────────────────────────────────┐
│  Tough films of polyimides/copolyimides │
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Figure 1   Flow diagram of the preparation of polyimide/copolyimide films.

processability. Through copolymerization, reduction of T_g and processability is expected because copolymerization, in general, results in enhanced processability through a reduction of the interchain interaction and a reduction of crystallinity. Also, it results in flexibility of the rigid polyimide chain, which is measured by creasability.

The preparation of copolyimide films via a two-step method from pyromellitic dianhydride (PMDA) and a mixture of the diamines 4,4′-oxydianiline (ODA) and 3,3′-dimethylbenzidine has been reported.[7] Copolyimide films based on two dianhydrides, 3,3′,4,4′-oxydiphthalic anhydride and 4,4′,5,5′-dioxydiphthalic anhydride, have also been reported.[8] Thus, for the preparation of polyimide/copolyimide films by the two-step method, the respective precursor poly(amic acid)/copoly(amic acid) solutions are cast onto suitable substrates, a major amount of solvent is removed

from the solutions at a low temperature, and then the dried films on the substrates are heated in a programmed schedule to complete the imidization reaction in the second step.[9–11]

Proper precautions and care are most essential during film casting, drying of the cast solutions, and subsequent curing of the dry poly(amic acid) films at high temperatures; otherwise, good quality polyimide films will not be developed, even when the reaction starts with a precursor poly(amic acid) solution with a high inherent viscosity (η_{inh}). Critical concentrations of the casting solutions also have to be maintained for favorable film processing operations. Thickness adjustment during film casting is another crucial point to be taken into consideration.

Because poly(amic acid) solution is very sensitive to moisture, exposure to atmospheric air should be minimized as much as is practical during the film processing operation. In this article, we report in detail the film casting procedure from the precursor poly(amic acid) and copoly(amic acid) solutions in N,N-dimethylformamide (DMF), the drying of the cast films, and the conversion of the solid poly(amic acid) and copoly(amic acid) films to the respective polyimide and copolyimide films by thermal treatment. The physical characteristics such as density, thickness, color, and so on; IR spectroscopic study; and X-ray diffraction analysis of the resulting polyimide and copolyimide films are discussed, along with the characteristics of the reference Kapton H film.

EXPERIMENTAL

Preparation of Polyimide/Copolyimide Films

Film Casting and Drying

A typical procedure for synthesis of poly(amic acid)/copoly(amic acid) was reported elsewhere.[10] The films of precursor poly(amic acid)/copoly(amic acid) solutions were cast onto clean and dry glass plates by a doctor's blade, with thickness maintained at 0.25–0.30 mm. The films were dried under vacuum at 30–35°C for 2 h and finally at 40–45°C for 1 h with passage of a slow stream of dry N₂.

Curing of Films

After vacuum drying up to 40–45°C, the films on glass plates were placed in a curing oven and

Table I   Concentration and η_{inh} of Precursor Polymer Solutions During Film Casting

Batch Number	Monomer Composition (%)	Designation of Precursor Polymers	Concentration of Casting Solutions (% w/w)	η_{inh} (dL/g)	Designation of Polyimide/Copolyimide Film
1	BTDA 100 PD 100	PAA 1	12	1.016	HPF 1
2	BTDA 100 ODA 100	PAA 2	10	1.227	HPF 2
3	PMDA 100 PD 100	PAA 3	10	1.150	HPF 3
4	PMDA 100 ODA 100	PAA 4	8	1.830	HPF 4
5	PMDA 80 BTDA 20 PD 100	PAA 5	13.18[a]	0.760	HPF 5
6	PMDA 20 BTDA 80 PD 100	PAA 6	12	1.720	HPF 6
7	PMDA 80 BTDA 20 ODA 100	PAA 7	10	0.490	HPF 7
8	PMDA 80 BTDA 20 PD 10 ODA 90	PAA 8	10	1.990	HPF 8
9	BTDA 100 PD 20 ODA 80	PAA 9	10	0.939	HPF 9

[a] The casting solution of this concentration was prepared by redissolving the precipitated precursor polymer with an original concentration of 6% (w/w) and an η_{inh} of 2.04 dL/g.

heated in a programmed schedule up to 300°C and kept at that temperature for 1 h. Finally, the films were heated for an additional 0.5 h at 320°C. The resulting films were taken from glass plates by immersion in water. Preparation of the films is schematically presented in Figure 1.

Physical Characteristics

Density Measurement

The density (d) of the film samples was measured by the liquid displacement method in dry toluene at 30°C with a specific gravity bottle and calculated with the following relation:

$$d = \frac{w_1 \times \rho}{w_1 + w_2 - w_3}$$

where w_1 is the weight of the film sample, w_2 is the weight of the specific gravity bottle filled with toluene, w_3 is the weight of the specific gravity bottle filled with toluene and the film sample, and ρ is the density of the toluene at 30°C.

Thickness

The thickness of the film was measured by a thickness gauge (Baker Mercer, India, ISI, IS: 2092).

Color

The colors of different film samples were compared visually.

Elemental Analysis

The elements, namely, carbon, hydrogen, and nitrogen, were analyzed by a Heraeus Carlo Erba (Italy) 1160 elemental analyzer.

IR Spectroscopy

IR spectra of the films were recorded with a Shimadzu (Japan) 470 IR spectrophotometer.

PMDA

BTDA

ODA

Proprietary diamine (PD)

Where Ar is a rigid aromatic moiety
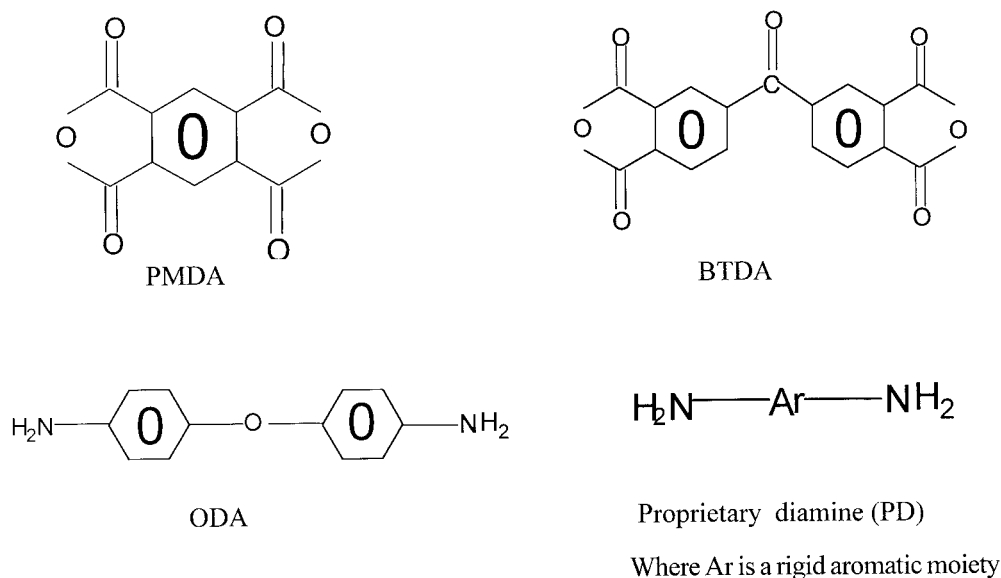
Scheme 1

X-Ray Diffractometry

Wide angle X-ray diffractographs for the film samples were recorded with a JEOL (Japan) X-ray diffractometer with Ni-filtered CuK$_\alpha$ radiation (λ = 1.54 Å) at 20 kV-15 mA and a scanning speed of 4°/min.

RESULTS AND DISCUSSION

Preparation of Polyimide/Copolyimide Films

The conversion of cast films of poly(amic acid) or copoly(amic acid) solutions to the respective polyimide or copolyimide films involved two major transformations. First, the cast films of the precursor polymer solutions were dried at a low temperature under vacuum to drive away most of the solvent, DMF, and to convert the cast film solutions into solid or gelled films of poly(amic acid) or copoly(amic acid).

To control the excessive flow nature of the casting solutions of poly(amic acid) or copoly(amic acid) at the drying stage, a minimum concentration of 8% (w/w) of polymer in the solution was maintained. A casting solution at a concentration far below this limit may create the problem of developing films of uniform thickness because of excessive fluidity during drying. Also, the extent of fluidity of the cast solution got enhanced to
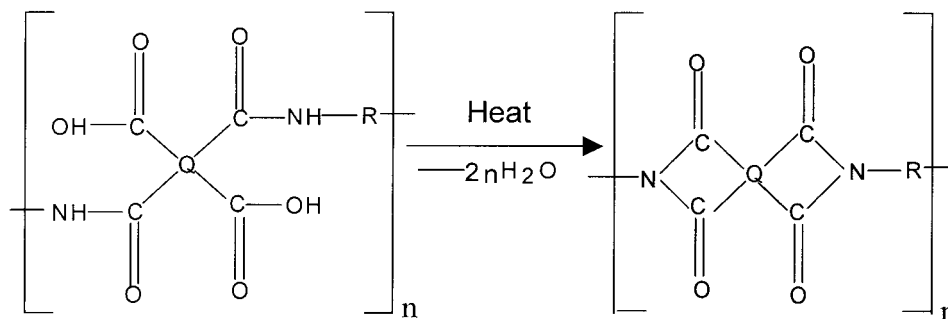
Q : dianhydride moiety   R : aromatic diamine moiety

Scheme 2

Table II   Effect of Chain Structure of Poly(amic acids)/Copoly(amic acids) on Mechanical Properties of Polyimide/Copolyimide Films After Thermal Imidization

Serial Number	Monomer Composition of Poly(amic acids)/ Copoly(amic acids) (%)	η_{inh} (dL/g)	Mechanical Properties of Polyimide/Copolyimide Films After Curing		
			To 300°C	To 320°C	To 360°C
1	BTDA 100 ODA 100	1.227	a	a	—
2	PMDA 100 ODA 100	1.830	a	a	—
3	BTDA 100 PD 100	1.016	—	a	—
4	PMDA 80 BTDA 20 ODA 100	0.490	a	a	—
5	PMDA 20 BTDA 80 PD 100	1.720	—	a	a
6	PMDA 80 BTDA 20 PD 100	0.760	b	b	a
7	PMDA 100 PD 100	1.150	b	b	c

a = Tough and creasable; b = brittle; c = creasable at the thin section of the film, but the thicker section was still brittle when creased by finger pressing, and tear strength was very low.

some extent by raising the temperature by 10–15°C from the ambient temperature during vacuum drying. A casting solution of much lower concentration also required more drying time because of the presence of a comparatively high percentage of solvent. Another problem with a very dilute solution is that the cast solution on the substrate had a tendency to split up (tear) even when properly cleaned glass plates were used as the substrate. All these problems were faced during the casting and drying of films from a copoly(amic acid) solution of 6% (w/w) concentration (batch 5 in Table I). Therefore, a casting solution of a higher concentration was made by isolating the copoly(amic acid) from this 6% solution by a precipitation method with dry acetone as a nonsolvent and by redissolving the precipitated polymer in dry DMF to make an optimumly concentrated casting solution. Films were cast and dried successfully from this solution.

On the other hand, a combined effect of high molecular weight and high concentration of the resulting poly(amic acids)/copoly(amic acids) may have given rise to highly viscous solutions. There may have also been problems with these highly

viscous solutions during film casting. There was the possibility of the entrapment of small air bubbles in the casting solution during mechanical stirring while the polymers were synthesized. These air bubbles may have affected the film quality by reducing mechanical strength, electrical strength, and so on because of the possibility of the appearance of pin holes in the films. For example, the synthesis of poly(amic acid) in batch 4 (Table I) was started with a concentration of 12%. However, the solution became so viscous that the stirring became extremely difficult, and the air bubbles could not come out from the bulk. Then, more solvent was added to lower the polymer concentration from 12 to 10%. However, the solution still appeared to be very viscous for film casting. So, ultimately an 8% solution was made by adding an extra quantity of solvent.

The fluidity of the poly(amic acid) solution derived from flexible dianhydride and flexible diamine were comparatively higher than that of the poly(amic acid) derived from rigid dianhydride and diamine. The influence of dianhydride on the fluidity of poly(amic acid) was more pronounced. Thus, the fluidity of the precursor polymer solu-

Table III   Some Physical Characteristics of the Polyimide/Copolyimide Films

Film Code	Monomer Composition (%)	Density (g/cm^3)	Thickness (mm)	Color
HPF 1	BTDA 100 PD 100	1.415	0.015–0.020	Yellow
HPF 2	BTDA 100 ODA 100	1.405	0.030–0.032	Light yellow
HPF 3	PMDA 100 PD 100	1.390	0.017–0.020	Reddish brown
HPF 4	PMDA 100 ODA 100	1.420	0.028–0.030	Orange
HPF 5	PMDA 80 BTDA 20 PD 100	—	0.028–0.030	Brown
HPF 6	PMDA 20 BTDA 80 PD 100	1.400	0.020–0.030	Orange
HPF 7	PMDA 80 BTDA 20 ODA 100	—	0.020–0.025	Orange
HPF 8	PMDA 80 BTDA 20 PD 10 ODA 90	1.410	0.027–0.030	Orange
HPF 9	BTDA 100 PD 20 ODA 80	—	0.017–0.020	Yellow
Kapton H		1.420	0.025–0.027	Orange

tion poly(amic acid) (PAA) 2, based on benzophe-nonetetracarboxylic dianhydride (BTDA) and ODA, was higher than that of the polymer solution PAA 3, based on PMDA and a proprietary aromatic diamine (PD), with the same concentration for both (10%) and an η_{inh} value even marginally higher for the former (1.227 vs. 1.150 dL/g; Table I). This was observed visually during the pouring of the solutions onto glass plates during film casting. Among the four monomers used in this investigation for the preparation of polyimide and copolyimide films, BTDA and ODA were flexible in nature because of the presence of the linking groups —CO— and —O— in the dianhydride and diamine, respectively. PMDA was the rigid dianhydride, and the PD was also rigid in nature (Scheme 1).

Depending on the η_{inh} value and the chain structure (whether derived from flexible or rigid monomers) of the precursor poly(amic acid) or copoly(amic acid), solutions in the concentration range of 8–13% (w/w) were suitable for the film processing operation to produce good quality polyimide and copolyimide films.

Finally, in the second stage, the solid poly(amic acid) or copoly(amic acid) films were heated in a programmed schedule up to 300°C or higher. The films were transformed into polyimide/copolyimide films on this thermal treatment (Scheme 2). As the process indicates, this imidization reaction was indeed a solid-phase thermal cyclization process.

IR spectroscopy has been used extensively to monitor this reaction by studying the disappearance of the NH stretching vibration at the 3240–3320 cm^{-1} band and the appearance of typical imide-ring bands at 1780cm^{-1} (symmetrical stretching vibration of C=O), 1380 cm^{-1} (stretching C—N vibration), and 725 cm^{-1} (bending vibrations of cyclic C=O).[11–14] For calculating the degree of imidization, the intensities of these imide bands in a sample, preferably in the film form, are compared to those in a sample that has been heated until no changes in the band intensities occurred.[15,16] Heating at 300°C or greater for at least 0.5 h is normally required to obtain the reference sample, which is considered to be 100% imidized.[15–18] In this

Table IV   Elemental Compositions of HPF 1, HPF 4, HPF 8, and Kapton H Films

Film	Calculated (%)			Found (%)		
	C	N	H	C	N	H
HPF 1	74.04	5.95	3.00	75.55	6.06	3.43
HPF 4	69.11	7.33	2.64	66.19	7.76	2.46
HPF 8	69.99	6.97	2.71	67.19	7.39	2.50
Kapton H	—	—	—	66.33	7.81	2.55

investigation, after a programmed heating schedule up to 300°C was followed, an additional heating at 320°C for 0.5 h was performed for each of the polyimide/copolyimide films of different monomer composition.

Poly(amic acid) dried to the solid state still contained a substantial quantity of amide solvents such as DMF (up to 25–30%), which was firmly retained by the polymer in the form of a hydrogen-bonded complex of the type:
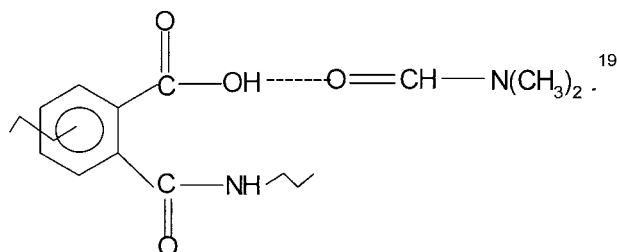
This residual solvent is important for the solid-phase thermal cyclization process. The presence of the solvent makes the imidization rate faster in the initial stage of the solid-phase thermal cyclization. As the process goes on, decomplexation takes place, and the free solvent, diffused into the polymer films, helps imidization occur at a faster rate by allowing the reacting species of polymer chains to attain favorable conformations for cyclization.[15] The residual solvent molecules may also assist in the cyclization process by acting as a proton acceptor–donor system.

As the imidization process continues at elevated temperatures, the residual amide solvent is removed almost simultaneously with water of imidization from the polymer film. At the same time, the T_g of the polymer increases with increased degree of imidization so that the polymer changes from a rubbery to a glassy state. Thus, when the T_g reaches the temperature of the poly-

mer, the cyclization rate becomes slow. This transition to the slow cyclization stage in the glassy state is mainly caused by a decrease in molecular mobility in the polymer backbone when it becomes very difficult for the remaining amic acid groups to attain favorable conformations for cyclization.[16,20–22]

Another phenomenon that occurs during the solid-phase thermal cyclization process of poly(amic acids)/copoly(amic acids) is the remarkable changes that occur in their mechanical properties as the compounds are converted to the corresponding polyimides/copolyimides. It was discovered in a very early study of thermal imidization[23(a)] and was later confirmed by other workers[23(b)] that the magnitude of change that occurs depends on the molecular weight of the starting poly(amic acid). Quantitative studies on the effect of the molecular weight of poly(amic acid) on its mechanical properties during thermal imidization gave similar results.[24]

As shown in the literature,[20,25–27] the variation in the mechanical properties of the film is caused by variation in the molecular weight during the cure cycle. Early work[23(a)] showed that a poly(amic acid) can be finally converted into a tough and creasable polyimide film, when heated above 275°C, when the η_{inh} value of the initial poly(amic acid) is not less than 0.2 dL/g, although a temporary brittle nature of the film may arise at the intermediate temperature of the cure cycle. However, in this investigation, it was observed that the recovery of film toughness and creasability from the brittleness at the intermediate temperature of the cure cycle depended not only on the molecular weight of the poly(amic acids)/copoly(amic acids) but also on their chain flexibility. As the chain flexibility of the poly(amic acid) was reduced with rigid dianhydride and/or diamine, the resulting polyimide film required the final curing temperature to be even more than 320°C for the production of tough and creasable films. Poly(amic acid) of fully rigid chain structure gave rise to a brittle film of polyimide even after curing up to 360°C.

The flexibility of polyimide films is an important property for its commercial success as an insulating material for high-voltage motors. Creasability of polyimide films is a measure of chain flexibility. Chain flexibility depends on chain length and chain structure so far as interchain interaction and crystallinity are concerned. As a copolymer reduces both the interchain interaction and crystallinity, copolyimide films are ex-

pected to be more flexible (and, hence, more creasable) than the homopolyimide films. The effect is more pronounced with comonomers that contain flexible linking groups (e.g., aromatic ether linkages, thio–ether linkages) in the polymer backbone. In this case, flexibility is controlled by the nature of the monomers (flexible or rigid) and whether it is a homopolymer or copolymer.

The qualitative results of the influence of the chain structure of poly(amic acid)/copoly(amic acid) on the ultimate curing temperature for the production of tough and creasable polyimide/copolyimide films are presented in Table II. At the initial stage of the cure cycle, all the polymer films in the form of poly(amic acids)/copoly(amic acids) of different monomer compositions were flexible because of the retention of residual amide solvent, which acted as plasticizer. With the rise of temperature and time, the flexibility of the films deteriorated to an extent, depending on the chain flexibility, because of the combined effects of solvent loss, cyclization to imide structure, and chain cleavage. On further increase of the curing temperature, the molecular weights of the polymer films were increased by recondensation of the amino and anhydride end groups generated from the broken polymer chains. So, ultimately tough and creasable polyimide/copolyimide films were obtained.

A higher curing temperature to produce flexible polyimide films with higher rigidity of the polymer chains may be needed because of a greater restriction of chain mobility during cyclization to imide structure from rigid dianhydride and/or diamine. Therefore, more energy was required to activate the residual reactive groups to attain a favorable conformation that condensed ultimately to imide form and, hence, to recover the molecular weight to produce a tough and creasable film. Thus, the copoly(amic acid) based on PMDA/BTDA (80/20) and ODA (100) gave rise to a tough and creasable film (Serial number 4 in Table II) after curing up to 300°C. On the other hand, the film based on PMDA/BTDA (80/20) and PD (100; Serial number 6 in Table II), which was considered to be more rigid than the previously mentioned film (rigid diamine vs. flexible one), was found to be brittle and not very tear resistant, even after curing up to 320°C, although the η_{inh} of the precursor polymer of the latter film was much higher than that of the former (0.76 vs. 0.49 dL/g; Table II). This film became tough and creasable after curing up to 360°C. The polyimide film

based on PMDA and PD (Serial number 7 in Table II), which was considered to be a product of a fully rigid rod-like polymer, suffered from brittleness and very weak tear strength even after curing up to 360°C. Only the thin sections of the film showed creasability.

Physical Characteristics

The density, thickness, and color of each of the polyimide/copolyimide films are presented in Table III.

The density of different films was in the range 1.39–1.42 g/cm^3. The thickness of the films was in the range 0.015–0.032 mm but mostly in the range 0.025–0.030 mm. This variation in thickness was caused by a change in the concentration of the casting solutions of poly(amic acids)/copoly-(amic acids) in different batches, the variation in fluidity of the casting solutions of different batches, and the variation of the gap adjustment of the doctor's blade.

The color in polyimides may have many origins, including presence of chromophoric units, colored impurities from starting materials (dianhydrides and diamines), and side reactions that form isoimides and charge-transfer complexes.

In this investigation, the dianhydrides and diamines were purified so rigorously that they appeared almost colorless. Therefore, possibility of the contribution of color in polyimides caused by impurities from starting materials was practically absent. Many polyimide researchers have suggested that the color in polyimides is caused by the presence of small amounts of isoimide that form during cyclodehydration of poly(amic acids) to polyimides.[28] It has also been reported that cyclization by chemical treatment favors the formation of isoimides.[29–32] However, on subsequent thermal treatment, these isoimides were converted to imide structures.[24,29] In fact, it has been suggested that in all the methods of conversion, a final brief heating at a temperature near 300°C is essential to remove the last traces of amic acid and isoimide.[33] Therefore, the formation of color caused by presence of isoimides in the polyimide/copolyimide films of the study appeared to be remote.

The interchain electronic interaction in aromatic polyimides via the charge-transfer or electronic polarization mechanism[34] may cause color in polyimide/copolyimide films by the spectral absorption in the ultraviolet–visible range. This in-

(a)

(b)
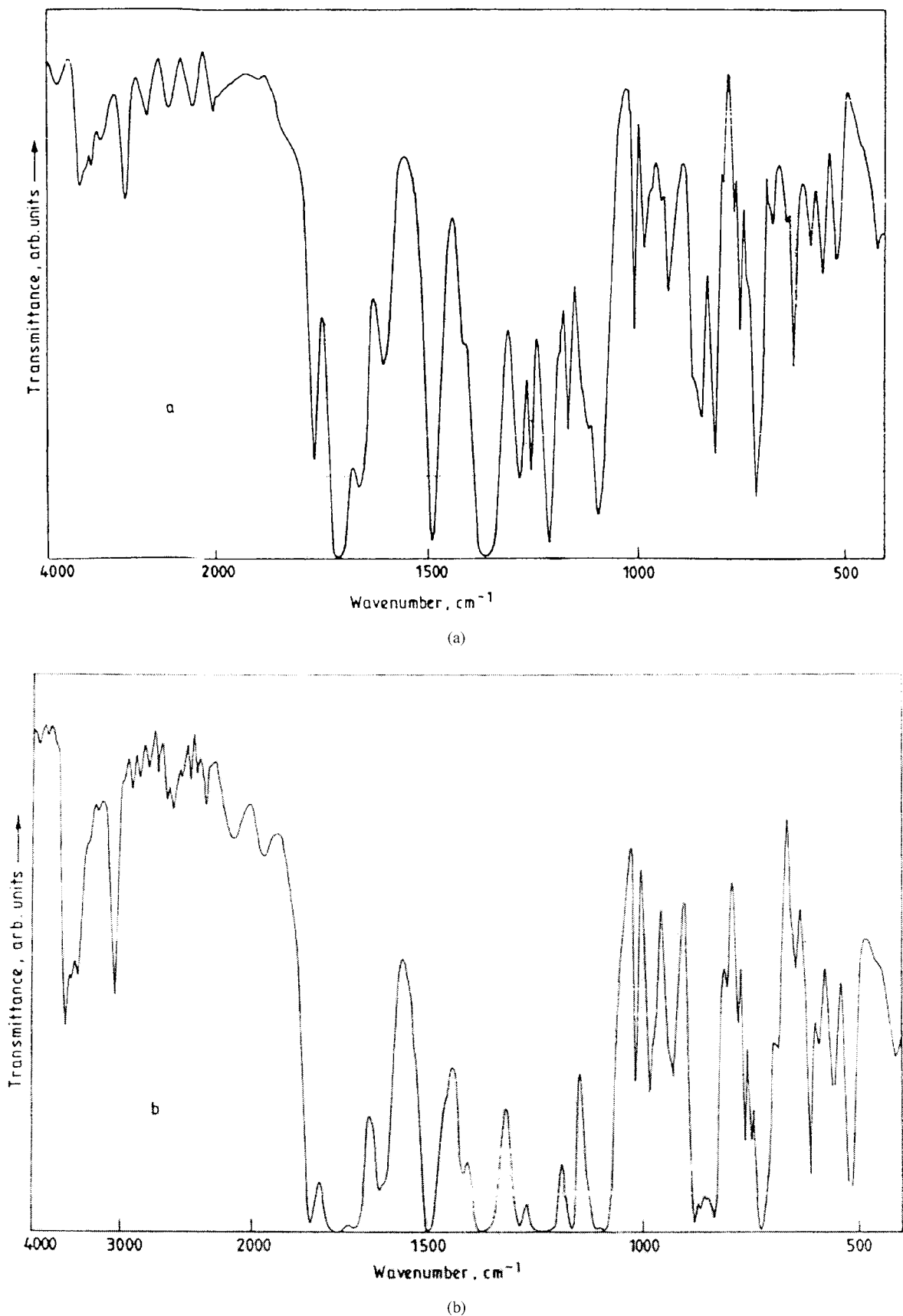
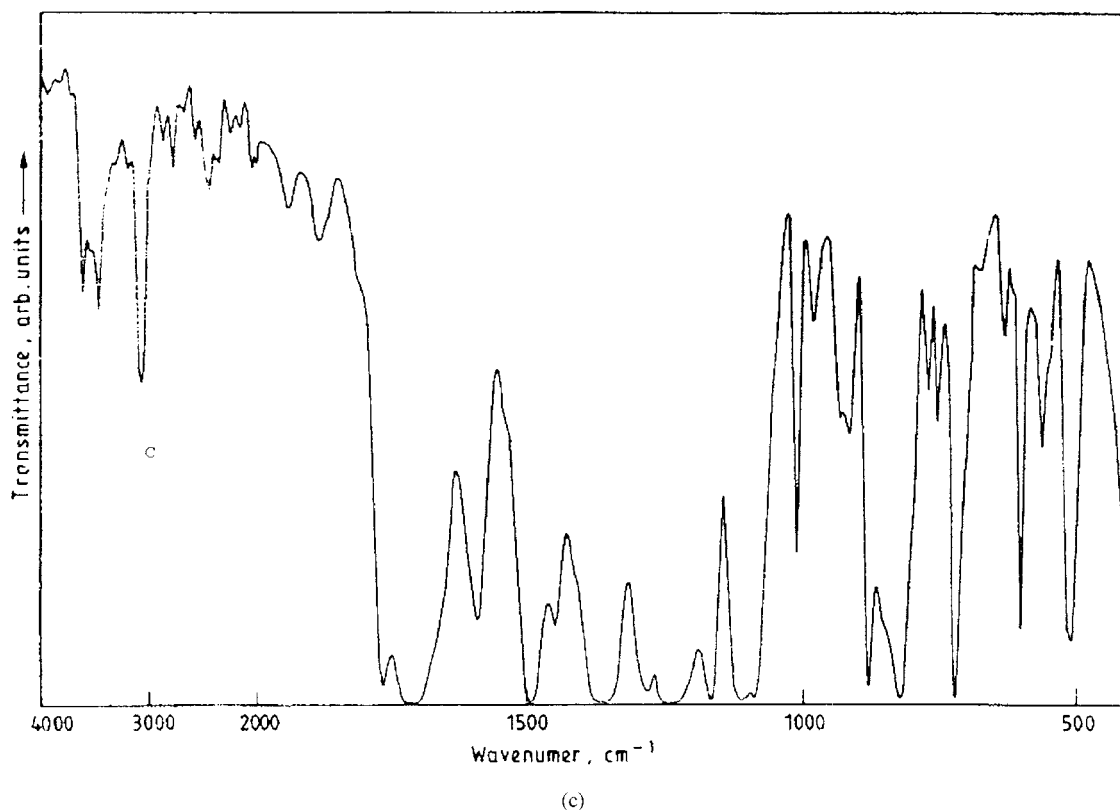**Figure 2**   IR spectra of polyimide/copolyimide films: (a) HPF 1, (b) HPF 2, and (c) HPF 8.

(c)

Figure 2   (*Continued from the previous page*)

teraction is obviously dependent on the electron affinity (Ea) of the dianhydride-derived moiety and the electron availability (ionization potential, IP) of the diamine-derived moiety. Thus, a dianhydride moiety of higher electron affinity will interact more strongly with the diamine moiety than a dianhydride of lower electron affinity. Similar arguments hold good for a diamine with a

Table V   Important Characteristic IR Peaks of Imide Groups of the Films (ν; cm^{-1})

Film Code	C=O Stretching Vibrations	C—N Stretching Vibrations	C=O Deformation Vibrations
HPF 1	1767 (s)	1362 (s)	719 (m)
HPF 2	1767 (s)	1373 (s)	720 (s)
HPF 5	1765 (s)	1375 (s)	725 (m)
HPF 7	1765 (s)	1370 (s)	725 (m)
HPF 8	1765 (s)	1362 (s)	721 (s)
Kapton H	1750 (s)	1375 (s)	720 (m)

s and m indicate strong and medium intensity of the peaks, respectively.

higher electron availability (lower IP). Among the two dianhydrides and the two diamines used, the electron affinity of PMDA was greater than that of BTDA (1.90 and 1.55, respectively), and the ionization potential of ODA was greater than that of PD.[35,36] Therefore, this type of interchain electronic interaction was expected to be at a maximum in the PMDA–PD-derived moiety and at a minimum in the BTDA–ODA-derived moiety among the various possible combinations of dianhydride and diamine centers. Thus, the PMDA–PD-based polyimide film (HPF 3) appeared highly colored, and the film derived from BTDA–ODA (HPF 2) was lightly colored (Table III). Color intensity and its variation in other polyimide/copolyimide films were found to be intermediate of these two extreme varieties of films according to the degree of interchain electronic polarization between electron donor and acceptor moieties of the polymers.
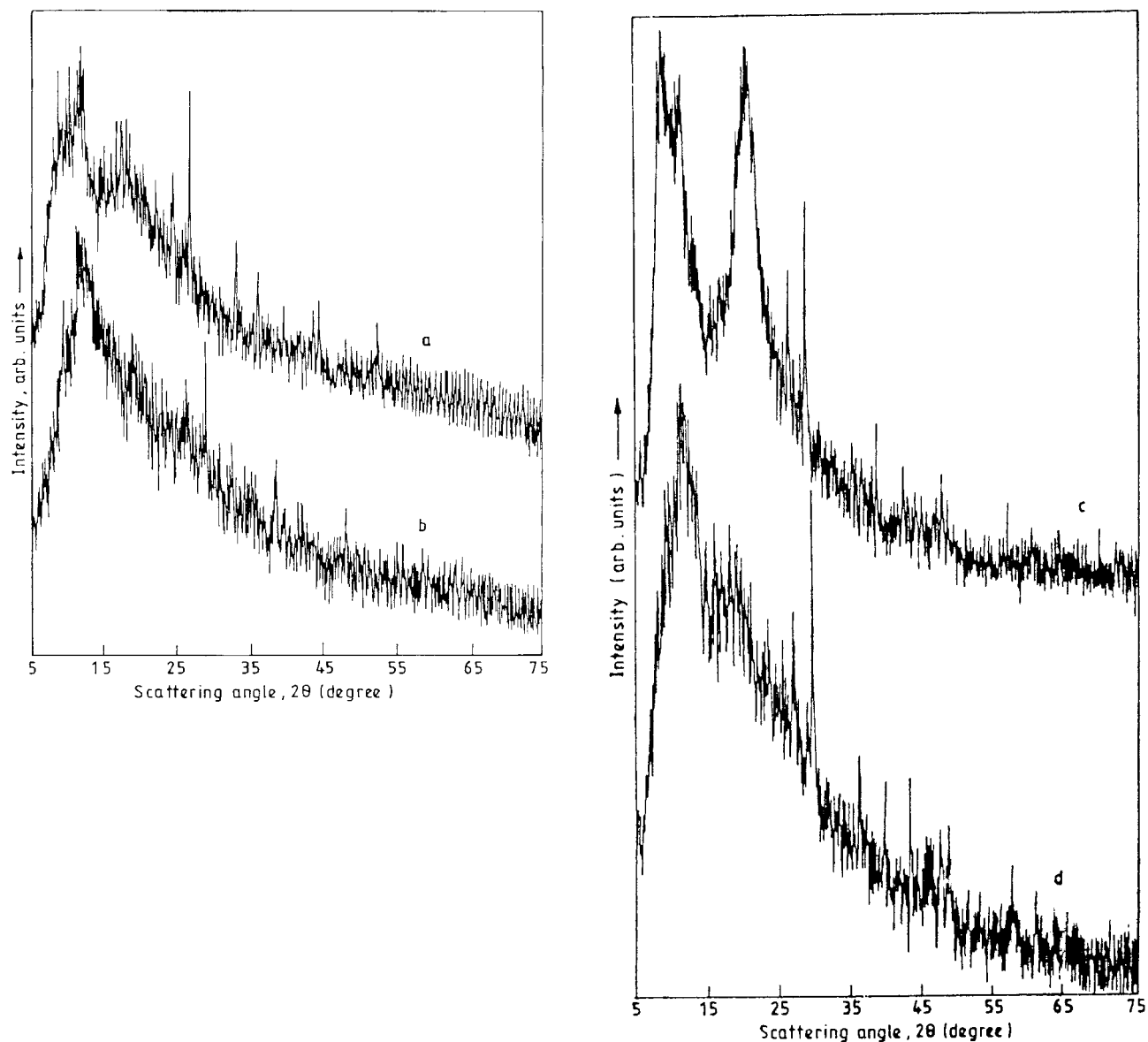
Elemental Analysis

The results of elemental analysis of three films, HPF 1, HPF 4, and HPF 8, and the reference

Figure 3 X-ray diffractographs of polyimide/copolyimide films: (a) HPF 1, (b) HPF 2, (c) HPF 3, (d) HPF 4, (e) HPF 9, and (f) Kapton H.

Kapton H film are presented in Table IV. With quantitative imidization assumed, the elemental compositions of the polymer films were calculated on the basis of the weights of their repeat units. Except a little deviation in carbon percent in HPF 4 and HPF 8 films, the experimental results agreed well with the calculated values.

IR Spectroscopy

IR spectra of polyimide/copolyimide films are shown in Figure 2, and some characteristic ab-

sorption bands of imide groups are presented in Table V. The absorption peaks of the films in the regions 1765–1767 cm^{-1}, 1362–1375 cm^{-1}, and 719–725 cm^{-1} are caused by symmetrical $C\!=\!O$ stretching, symmetrical C—N stretching, and $C\!=\!O$ bending vibrations, respectively, of the imide group. The peak values caused by carbonyl bending vibrations agreed well with the literature values. However, some deviation was observed in absorption peaks arising from $C\!=\!O$ and C—N stretching vibrations. The reported imide absorp-
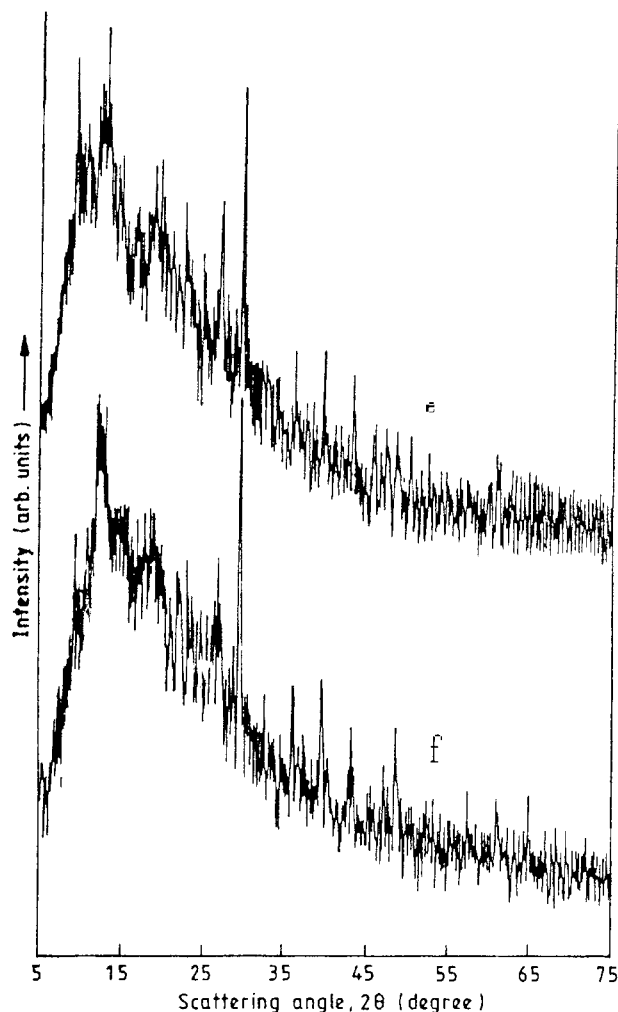
Figure 3 (*Continued from the previous page*)

tion bands were near 1780 cm^{-1} (symmetrical stretching of C=O), 1380 cm^{-1} (C—N stretching), and 725 cm^{-1} (bending of C=O),[12–14,37] assigned basically from the IR spectra of polyimide films derived from PMDA and ODA.

X-Ray Diffractometry

The X-ray diffractographs of the films are shown in Figure 3. All the polymer films possessed some degree of crystallinity. In principle, because of their highly regular, planar ring structure, which possessed strong interchain electronic interaction in aromatic polyimides, the polymer chains should have been closely packed. As a result, aromatic polyimides should have been highly crystalline in nature. However, under conventional conditions of the preparation of polyimide, that is,

on thermal cyclization of isotropic poly(amic acids) films as discussed earlier, polyimides were obtained with low degree of crystallization. The main cause of this was the slow rate of crystallization caused by disorderliness of the polymer chains in the poly(amic acid) stage, by steric hindrance, and by high viscosity of the polymers during thermal cyclization, which led to insufficient molecular mobility.

A comparative study of the crystallinity from the crystalline peak intensity (Fig. 3) of polyimide/copolyimide films under investigation showed that except HPF 2, HPF 6, and HPF 8 films, other films, including Kapton H, showed almost the same degree of crystallinity. HPF 2, HPF 6, and HPF 8 were more amorphous than the other films. Kapton H film and HPF 4, both of which are based on PMDA and ODA, gave almost identical X-ray spectra, with a sharp, intense crystalline peak at an angle of 30°.

CONCLUSIONS

The film processing technique from the precursor poly(amic acids) and copoly(amic acids) was discussed in detail. Conversion of poly(amic acid) and copoly(amic acid) solutions to the respective polyimide or copolyimide films involves two major processing operations. First, films are cast from the precursor polymer solutions and dried at a low temperature (35 to 40°C) under vacuum to get solid or gelled films of poly(amic acid) or copoly(amic acid). Finally, in the second stage, these solid films are heated in a programmed schedule up to 300°C or higher to convert them into polyimide/copolyimide films. Concentration of the casting solutions in the range 8–12 % (w/w) was suitable for the preparation of good quality polyimide/copolyimide films. The recovery of film toughness and creasability from the brittleness at the intermediate temperature of the cure cycle depended not only on the molecular weight (η_{inh} value) of the precursor poly(amic acids)/copoly(amic acids) but also on their chain flexibility. As the chain flexibility of the precursor polymer was reduced with rigid dianhydride and/or diamine, the resulting polyimide/copolyimide films required the final curing temperature to be even higher than 320°C for the production of tough and creasable films. Poly(amic acid) derived from both rigid dianhydride and diamine gave rise to a brittle film of polyimide even after curing up to 360°C.

The films were characterized by density and thickness measurements, color observation, elemental analyses, IR spectroscopy, and X-ray diffractometry. The densities of different films were in the range 1.39–1.42 g/cm. The thicknesses of most of the films were in the range 25–30 μm. The origin of color in the polyimide/copolyimide films was the interchain electronic interaction via a charge-transfer mechanism. The HPF 3 film, based on PMDA–PD, was highly colored (reddish brown), and the HPF 2 film, based on BTDA–ODA, had the lightest yellow color among the films in this investigation, including the Kapton H film. This was because of the fact that the interchain electronic interaction was at a maximum in the PMDA–PD-derived moiety of the HPF 3 film and at a minimum in the BTDA–ODA-derived moiety of the HPF 2 film among the various possible combinations of dianhydridediamine centers present in the other polyimide/copolyimide films. HPF 2, HPF 6, and HPF 8 films were more amorphous than the other films as observed from the X-ray diffractometry study.

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