

# Polyimidizations from acylated diamines and dianhydrides

John A. Kreuz

High Performance Films, E.I. DuPont de Nemours & Co. Inc., Circleville Research Laboratory, Circleville, OH 43113, USA

(Received 9 December 1993; revised 11 October 1994)

Imide ring formation upon heat treatment of diacylated diamines and dianhydrides was shown to be highly efficient. Evidence to support this conclusion was obtained from thermal gravimetric analyses, differential scanning calorimetry and infra-red spectroscopy. Equimolar mixtures of diacylated diamines and dianhydrides form eutectic mixtures, which quantitatively eliminate the corresponding acid to form imides. Besides the possibility of polyimidization, the reaction of acylated amino end-groups with anhydride end-groups was demonstrated to be useful for chain extension by post-heating a lower-molecular-weight polyimide based on pyromellitic dianhydride (PMDA) and 4,4'-aminodiphenyl ether (ODA). Advantages gained by this technique are narrower molecular-weight distributions and higher-solids poly(amic acid) solutions with lower solution viscosities, which allow more facile fabrication into useful articles.

(Keywords: polyimides; chain extension; acylated amines)

## INTRODUCTION

The most common way to make high-molecular-weight polyimides is to synthesize high-molecular-weight poly(amic acid) precursors by solution polymerization of diamines with dianhydrides in dipolar aprotic solvents. Viscous poly(amic acid) solutions are then fabricated into fibres, films or some other shaped structures. Finally, the shaped poly(amic acid)s are converted thermally or chemically to polyimides with concurrent drying<sup>1</sup>.

Among the many other considerations for making polyimides has been the general thought of utilizing thermally activated functionalities on diamines, tetraacids, amino end-groups, or *ortho* diacid end-groups. These functionalities would be inert at ambient fabrication temperatures, but would generate imide rings at high temperatures. Such an approach could be extremely useful for solventless polyimidizations in composites manufacture, or it could facilitate formation of high-molecular-weight polyimides by chain extension of lower-molecular-weight precursors. The latter application would allow higher-solids and lower-solution-viscosity poly(amic acid)s to be shaped into articles that would eventually yield very high-molecular-weight polyimide structures.

Much work has been done on thermally reactive end-groups that will polymerize into three-dimensional crosslinked networks. Among those systems are the bismaleimides, oligomeric polyimides end-capped with benzocyclobutane, and oligomeric polyimides end-capped with ethynyl groups. However, the first successful

experimental work aimed at generation of linear polyimides from thermally activated functionalities was initially reported in 1967 by Dixon *et al.*, who used urethane or urea derivatives of diamines with dianhydrides to make polyimides<sup>2</sup>. Portions of this work were patented in 1974<sup>3</sup>. Dine-Hart and Wright extended the work to diacetyl derivatives of diamines and dianhydrides<sup>4</sup>. One composition consisted of 4,4'-diacetamidodiphenylmethane and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), where the resin produced from thermal elimination of acetic acid was designated as Resin 212. Details of the synthesis were not provided, but the properties of the resin were attractive and comparable to those from conventional routes. Additional work in this area were reported in 1982 by Keske *et al.*, who made injection-mouldable poly(amide-imide)s from acylated aromatic and aliphatic diamines with trimellitic anhydride<sup>5</sup>. A variation of the melt polymerization technique, reported in 1984, showed that hexamethylenediamine could be incorporated exclusively in the imide portion of the poly(amide-imide) to provide greater thermal durability to the final poly(amide-imide) than if it were randomly distributed<sup>6</sup>. More recently, in 1988, a Japanese patent application disclosed acetyl end-capping of amino groups in poly(amic-acid)s as a means to provide low solution viscosities at high polymer concentrations<sup>7</sup>.

The success of these previous investigations prompted us to pursue a study of the reaction chemistry of diacylated diamines and dianhydrides to form polyimides, and to apply the knowledge to practical goals of more facile processing of polyimides. This paper is a summary and status report of that work.

\* To whom correspondence should be addressed

## EXPERIMENTAL

## Diacylated diamines

Diacylated diamines were prepared by adding an excess of either the acyl anhydride or acyl chloride to the respective diamines dissolved in *N,N*-dimethylacetamide (DMAc), and allowing the solution to stand at room temperature for several days under nitrogen. The product was subsequently isolated in deionized water, washed with deionized water, and dried under nitrogen and vacuum to constant weight. The products had elemental analyses and infra-red spectra consistent with the structures intended. Melting points by d.s.c. were sharp.

## Poly(amic acid)s

Poly(amic acid)s were prepared using a constant-speed stirrer in a nitrogen-filled glove-box. The diamine was dissolved first in DMAc, which had been dried over 4 Å molecular sieves. The desired amount of acetyl end-capping agent was then added in the form of acetic anhydride. After 20 min stirring, the solid dianhydride was added over a period of 15 min to the stirred solution. Generally, the dianhydride was added to 96–98% equivalence of the initial diamine present. Finally, a 6% solution of pyromellitic dianhydride (PMDA) in DMAc was added to increase the molecular weight and to adjust the stoichiometry to the desired level of equivalence.

## Inherent viscosities and s.e.c. analyses

Viscosities ( $\text{dl g}^{-1}$ ) were measured at 30°C using a Ubbelohde semimicro dilution viscometer. Concentrations were 0.5 g of solids per 100 ml of solution. The solvent for the poly(amic acid)s was DMAc (Burdick & Jackson, 4 Å molecular sieve dried) and for the polyimides it was concentrated sulfuric acid.

The s.e.c. analyses on the poly(amic acid)s were done by the method of Walker<sup>8</sup>. The chromatograph was a DuPont 8800 with a column containing DuPont ZorbaxR PSM (40–1000) bimodal mixed-bed absorbent. The detection wavelength was set at 254 nm.

## Polyimides

Polyimides were prepared by mixing excess acetic anhydride and tertiary amine with the poly(amic acid) solution and then casting the mixture onto a glass plate at 70°C. After the films were self-supporting, they were attached to pin frames and heated for 30 min in vacuum under a  $\text{N}_2$  bleed at 300°C.

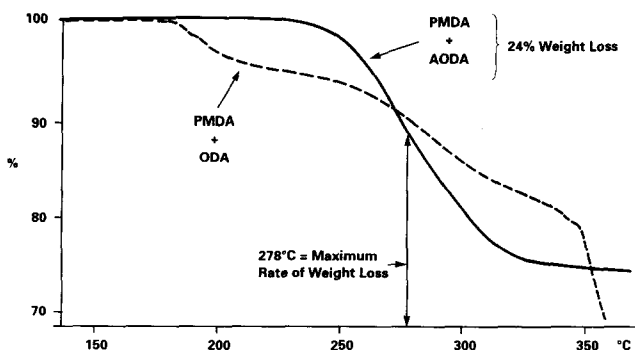
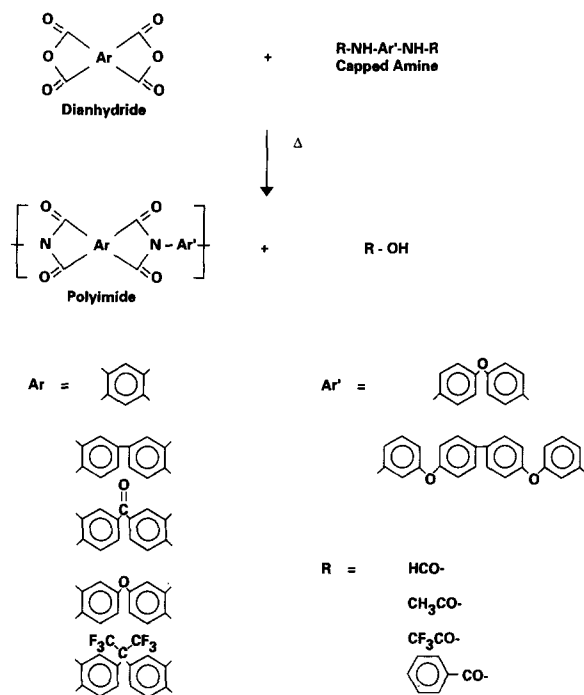


Figure 1 T.g.a. thermograms of a mixture of PMDA and AODA and a mixture of PMDA and ODA



Scheme 1 The chemistry that is being investigated

## Thermal treatment of polyimides

The polyimide films were subjected to further heat treatment for viscosity studies by immersing small samples in a sand bath at the desired temperature and for the required period of time.

Films for property studies were maintained on frames and heated at 415°C for 1 min.

## RESULTS AND DISCUSSION

## Reactions of dianhydrides and diacylated diamines

Diacylated diamines were examined for their tendency to polyimide with dianhydrides under solventless conditions. Preparation of samples for testing consisted of grinding the diacylated compound with the dianhydride in equivalent amounts. These commingled powders were subjected to t.g.a. and d.s.c. analyses. The chemistry that was being investigated is shown in Scheme 1.

The t.g.a. analyses clearly indicated a single weight-loss step that occurred in the region of 270 to 350°C for the combinations examined. This weight loss was equivalent to the calculated weight loss of the corresponding acid of the diacylated amine, suggesting quantitative formation of the polyimide. A typical example of the t.g.a. scans that were obtained is shown in Figure 1. When the starting components were 4,4'-diacetamidodiphenyl ether (AODA) and pyromellitic dianhydride (PMDA), a single weight-loss step occurred, but a control consisting of the free diamine and dianhydride showed multiple weight-loss steps.

Samples for d.s.c. analyses were prepared similarly. The normal melting endotherms of each of the components were replaced by a single, sharp eutectic melting endotherm. Aside from these sharp eutectic endotherms, some smaller endotherms were found, depending on the starting components. These are believed to reflect heat losses during the polyimidization and perhaps glass

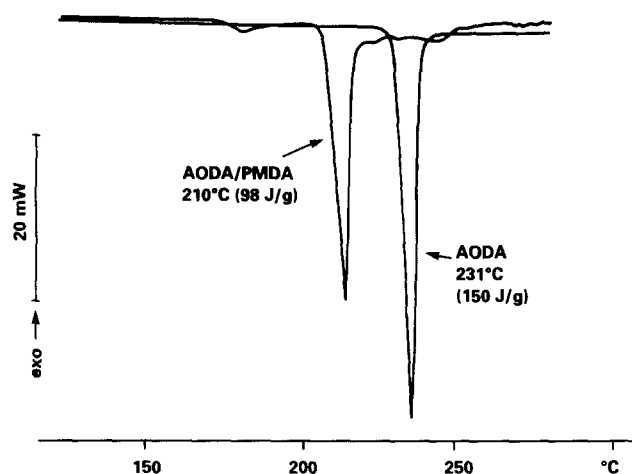


Figure 2 D.s.c. thermograms of a mixture of PMDA and AODA and of AODA alone

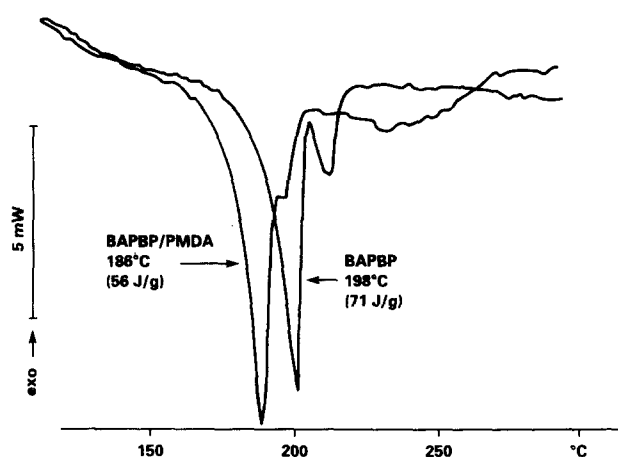


Figure 3 D.s.c. thermograms of a mixture of PMDA and BAPBP and of BAPBP alone

transitions of the formed polyimides. Typical differences between the individual component melting points and the eutectic melting points are illustrated in Figures 2 and 3. Results in Figure 2 are from AODA and PMDA and those in Figure 3 are from 4,4'-bis(3-acetamidophenoxy)biphenyl (BAPBP) and PMDA. The component common to both systems and not shown in the figures is PMDA, the melting endotherm of which is 286°C (126 J g<sup>-1</sup>).

A number of different acylated ODAs were studied besides the acetyl derivative. These included the formyl, trifluoroacetyl and benzoyl derivatives, which were admixed and heated with PMDA to examine their propensities to polyimide. Other dianhydrides tested were 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-(diphenyl ether)tetracarboxylic dianhydride (ODPA) and 4,4'-(2,2-hexafluoroisopropylidene) diphthalic anhydride (6FDA). A summary of the combinations used is given in Table 1. The weight losses for the respective acids were more nearly quantitative for the acetyl derivatives, with the benzoyl derivatives being a close second. Also, the i.r. spectra of the final products were indistinguishable from the spectra of the polyimides prepared by conventional routes. I.r. spectra of a polyimide obtained from

BAPBP and PMDA and of the same polyimide made conventionally from the corresponding diamine and PMDA are compared in Figure 4.

In the case of the formyl and trifluoroacetyl derivatives, the weight losses were not as quantitative. Moreover, the i.r. spectra showed that the imide was contaminated with anhydride residue. Based on these results, it would appear that, under the conditions imposed in these experiments, formyl and trifluoroacetyl are less facile leaving groups than acetyl.

The precise, quantitative nature of this reaction when acetyl is the leaving group, however, requires more examination. With proper choice of reaction conditions and reactants, practical polyimidization may be possible. In support of this contention is that, in the case of AODA

Table 1 Solventless polyimizations

Dianhydride <sup>a</sup> /m.p. (°C)	Diamide <sup>b</sup> /m.p. (°C)	Eutectic m.p. (°C)	Max. slope	
			Wt loss temp. (°C)	PI (%) by t.g.a. <sup>c</sup>
PMDA/286	AODA/231	210	278	98–101
BPDA/298		223	321	99–100
BTDA/225		203	305	99–113*
ODPA/227		206	310	ca. 110*
6FDA/244		220	304	ca. 110*
PMDA/286	TFAODA/239	221	321	<90*
BPDA/298		231	340	<90*
PMDA/286	BODA/265	235	311	ca. 90
BPDA/298		247	347	ca. 97
PMDA/286	FODA/143	139	228–268	109*
PMDA/286	BAPBP/198	186	275	105

<sup>a</sup> PMDA = pyromellitic dianhydride; BPDA = 3,3',4,4'-biphenyltetracarboxylic dianhydride; BTDA = 3,3',4,4'-benzophenonetetracarboxylic dianhydride; ODPA = 3,3',4,4'-(diphenyl ether)tetracarboxylic dianhydride; 6FDA = 4,4'-(2,2-hexafluoroisopropylidene) diphthalic anhydride  
<sup>b</sup> AODA = 4,4'-diacetamidodiphenyl ether; TFAODA = 4,4'-trifluoroacetamidodiphenyl ether; BODA = 4,4'-dibenzamidodiphenyl ether; FODA = 4,4'-diformamidodiphenyl ether; BAPBP = 4,4'-bis(3-acetamidophenoxy)biphenyl

<sup>c</sup> Estimated yields of polyimides (PIs) were made from the t.g.a. thermograms. The i.r. spectra of all products were strongly indicative of the presence of high concentrations of polyimide. The \* designates that the i.r. of the product showed the presence of some cyclic anhydride

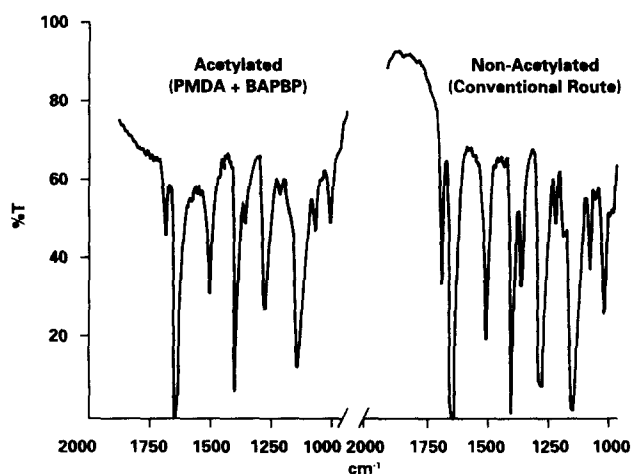


Figure 4 I.r. spectra of polyimides made from PMDA and acetylated and non-acetylated 4,4'-bis(3-aminophenoxy)benzene

and BPDA, a tiny blister film of polyimide, as confirmed by i.r., was observed to bridge the vent holes of the d.s.c. pan after the conclusion of a d.s.c. run. Perhaps, the lower  $T_g$  of this polyimide, which was 265°C when made by conventional methods, allows higher-molecular-weight polyimide to form.

Other observations of the interactions of acylated diamines and dianhydrides are noteworthy and suggest that an acylated amine and anhydride will form a charge-transfer complex due to electron donating/withdrawing natures of the respective components. Quite possibly a preferred close arrangement of the two components aids in the imidization reaction. For example, colourless solutions of AODA and PMDA in tetrahydrofuran (THF), when mixed in equivalent amounts, will instantaneously turn yellow-orange and will remain as such. The colour is reminiscent of the transitory yellow-orange that occurs on the surface of solid PMDA when it is added to a solution of ODA during poly(amic acid) preparations. A similar colour has been reported from vapour phase dianhydride-diamine reactions, and the cause has been ascribed to a charge-transfer complex<sup>9</sup>.

When solutions of the differently amidated ODAs are mixed with PMDA, the intensity of yellow-orange colour decreases in the order acetyl > benzoyl > trifluoroacetyl. Additionally, when the d.s.c. runs of many of the eutectic mixtures were interrupted after the eutectic melting point was reached, many of the solidified melts were yellow-orange in colour.

Our other experiment was done to ascertain the extent of polymerization for the solventless thermal treatments of the diacetylated diamines and dianhydrides. After heating the eutectic of AODA and PMDA to 420°C in the t.g.a. crucible, the resinous product was dissolved in concentrated sulfuric acid over a period of 50 h at room temperature. A portion of this resin (26%) remained undissolved after this period. The soluble portion displayed an inherent viscosity of 0.2 dl g<sup>-1</sup> (30°C). This suggests that the reaction does give polyimide, but the distribution of molecular weight is broad, and cross-linking rendered the product insoluble.

#### End-capped polymerizations with acetylated diamine and pyromellitic dianhydride

The high yield of the thermal imidization between an acylated amine and an anhydride was intriguing because

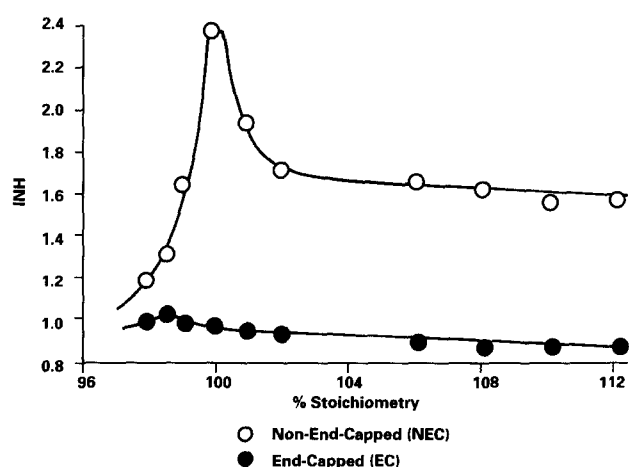


Figure 5 Viscosity behaviour of end-capped vs. non-end-capped poly(amic acid)s

Table 2 Molecular-weight characteristics of end-capped poly(amic acid)s derived from PMDA and ODA

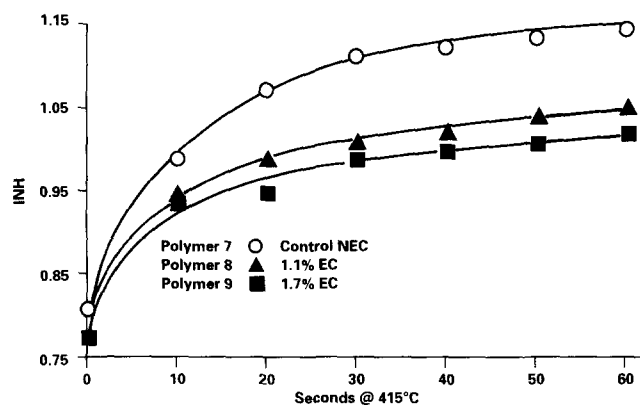
Polymer No.	$M_w$	$M_n$	MWD	Comments <sup>a</sup>
1	160 700	32 200	4.98	No end-cap
2	93 800	23 400	4.00	No end-cap; 112% PMDA
3	41 500	13 200	3.15	1.8% end-cap
4	41 200	12 800	3.22	1.8% end-cap; 112% PMDA
5	150 500	17 100	8.80	No end-cap
5	100 500	15 900	6.32	No end-cap; 18 h/50°C
6	83 900	14 000	5.99	1.0% end-cap
6	68 600	12 800	5.36	1.0% end-cap; 18 h/50°C
7	83 700	17 700	4.73	No end-cap; 2611 poise
7	64 500	16 500	3.91	No end-cap; 1 h/61°C
8	53 000	14 200	3.73	1.1% end-cap; 1741 poise
9	50 300	14 800	3.40	1.7% end-cap; 1300 poise
9	54 400	14 900	3.65	1.7% end-cap; 1 h/61°C

<sup>a</sup> Percentage solids of poly(amic acid)s were: numbers 1, 3, 5, 6 = 19%; numbers 2, 4 = 17%; number 7 = 20; numbers 8, 9 = 25. PMDA content was 100% of stoichiometric equivalence, unless otherwise noted

it suggested the potential of making lower-molecular-weight end-capped poly(amic acid)s, which after post-heating would generate higher-molecular-weight polyimide products. The anticipated advantage was that high-solids poly(amic acid) solutions could be prepared with relatively low solution viscosities. This approach was pursued by first synthesizing the end-capped poly(amic acid)s, and then characterizing some of their molecular-weight parameters. The polyimide examined in this portion of the work was that derived from PMDA and ODA.

Polymerizations were carried out by dissolving the diamine in the polymerization solvent and adding the desired amount of acetic anhydride end-capping agent. The range of end-capping examined was between 1.00 and 1.80% of the total amount of amino end-groups in the diamine. The dianhydride was added last.

Viscosity increases of these end-capped poly(amic acid)s, as the dianhydride approached stoichiometric equivalence and beyond, were not nearly as dramatic as was the very rapid rise experienced with non-end-capped controls. Figure 5 compares the very slight viscosity maximum of an end-capped system to the intense viscosity rise of a non-end-capped polymer. Molecular weights on these poly(amic acid)s, as measured by size exclusion chromatography (s.e.c.)<sup>8</sup>, clearly indicated not only that the molecular weight was limited by the end-capping, but that the molecular-weight distribution was narrowed somewhat (Table 2). Inhibited growth of unusually large chains seems to have occurred. It also appears that end-capped poly(amic acid)s underwent equilibration less than did non-end-capped polymers. This phenomenon of equilibration, manifested by a decrease of weight-average molecular weight primarily to a levelled value<sup>8</sup>, is probably caused by transamidation. Note how ageing at 50°C or at 61°C caused less change in the weight-average molecular weight of the end-capped polymers (numbers 6 and 9) than what occurred with the non-end-capped polymers (numbers 5 and 7). It has not been determined at the present time what the cause is for this apparent molecular-weight stabilization. It might



**Figure 6** Viscosities of polyimides derived from PMDA/ODA as a function of time at 415°C. Viscosities were measured at 0.5% in sulfuric acid at 30°C, after post-heating at 415°C for times shown. See Table 2 for information on the polymers

accrue from the tendency of large chains to amide-interchange and to redistribute more readily than shorter chains. Then again, the measurement might be an artifact of the presence of statistically fewer large chains in the end-capped polymers.

On a practical basis this phenomenon allows the preparation of poly(amic acids) that have good molecular-weight stability at high solids concentrations. For example, the molecular weight of polymer number 9 (25% solids) did not change after 1 h at 61°C (Table 2).

#### Chain extension of end-capped polyimide films

Polyimide films were prepared from the poly(amic acids) by mixing them with acetic anhydride and a tertiary amine and then casting on glass plates at 70°C. After the films became self-supporting, they were clamped on frames and further dried to 300°C under vacuum and nitrogen. The films were then subjected to post-heat-treatment in a sand bath at 415°C for various periods of time with the intent of increasing the molecular weight.

The increases in molecular weights of the polyimide films, as indicated by increases in their inherent viscosities in sulfuric acid, are given in Figure 6. Molecular-weight characterization data for the precursor poly(amic acids) are found in Table 2 (polymers 7, 8 and 9). The effect of the acetyl end-caps is again evident in terms of the lower molecular weights displayed by the poly(amic acids), but it is also very interesting that imidizations resulted in polyimides that had nearly equivalent viscosities to non-end-capped polyimide controls. When post-heating was imposed, both the control polyimide and the end-capped ones increased in molecular weight. The viscosities of the end-capped polyimides rose to almost the same levels as the controls. The data suggest that, even with the control polyimide, chemical imidization resulted in temporary loss of molecular weight, since the poly(amic acid) had an inherent viscosity of  $1.56 \text{ dl g}^{-1}$  (in DMAc), whereas the polyimide cured to only 300°C had an inherent viscosity of  $0.80 \text{ dl g}^{-1}$  (in  $\text{H}_2\text{SO}_4$ ). Although there is some question about the validity of equating inherent viscosities in these two media to about the same molecular-weight levels, the work of Wallach<sup>10</sup> appears to offer substantiation. It is, therefore, suspected that the loss of molecular weight in the control was also the result of end-capping, which occurred during equi-

**Table 3** Polyimide film properties from acetyl end-capping and thermal chain extension

Film properties <sup>a</sup>	Control, no end-cap	Sample, end-capped <sup>b</sup>
Modulus (GPa)	2.87	2.92
Elong. (%)	88	88
Tenacity (MPa)	234	221
Prop. tear ( $\text{g } \mu\text{m}^{-1}$ )	0.43	0.47
Pin hole flex (number)	5709	7515
Density ( $\text{g ml}^{-1}$ )	1.422	1.424
Diel. str. ( $\text{V } \mu\text{m}^{-1}$ )	194	185
Diel. const. (1 kHz)	3.52	3.53
Tan $\delta$ (1 kHz)	0.0014	0.0015

<sup>a</sup> All properties were measured at room temperature. Mechanical properties were averages of two directions that were perpendicular to each other

<sup>b</sup> 1.00 mol% end-capped poly(amic acid)

bration of the poly(amic acid). Available acetic anhydride is believed to have acetylated amino groups, forming capped chains.

Generation of higher-molecular-weight polyimide occurred at 415°C, because this temperature is equivalent to the high  $T_g$  of the polyimide based on PMDA/ODA, which has been reported to be 380°C<sup>11</sup>, 395°C<sup>12</sup> and 420°C<sup>13</sup>. The acetylated amino end-groups were felt to require mobilization in order to find anhydride groups and this is only achieved easily if the temperature to chain-extend is above the  $T_g$ .

The properties of the polyimide films made from the end-capped poly(amic acids) were equivalent to control films made from poly(amic acids) without end-caps (Table 3). These results strongly suggest that reactive end-capping with amide-type groups offers the possibility of applying this intriguing chemical reaction to the practical processing of polyimides.

#### CONCLUSIONS

High-yield imide formation is possible from direct thermal treatment of diacylated diamines and dianhydrides. Polyimides can form if reaction conditions and choices of starting materials are properly chosen, such as BPDA/AODA.

Acyl end-capping can be used to control molecular weights of poly(amic acids). Not only are number-average molecular weights suppressed and excessively high weight-average molecular weights prevented, but molecular-weight distributions are narrowed and poly(amic acid) equilibration is slowed.

Acyl end-capped polyimides can be chain-extended at high temperatures. Processing of end-capped poly(amic acids) can be carried out with high-solids solutions to enhance fabrication steps.

#### ACKNOWLEDGEMENTS

I am very appreciative for the technical advice, suggestions and editorial advice offered by my colleagues, Drs R. J. Angelo, C. E. Sroog and C. C. Walker. Assistance of Tom Lutz was indispensable to the successful development of this work and he also is gratefully acknowledged for many excellent efforts on tedious experiments. Bill Chaffin also assisted diligently on the completion of this work.

## REFERENCES

- 1 Sroog, C. E., Endry, A. L., Abramo, S. V., Berr, C. E., Edwards, W. M. and Olivier, K. L. *J. Polym. Sci. (A)* 1965, **3**, 1373
- 2 Dixon, D. R., Rose, J. B. and Turton, C. N. UK Pat. Appl. 38-220, 1967
- 3 Dixon, D. R., Rose, J. B. and Turton, C. N. US Pat. 3832330, 1974
- 4 Dine-Hart, R. A. and Wright, W. W. RPG Conf., Sept. 1973, Paper 7
- 5 Keske, R. G. and Stephens, J. R. US Pats 4309528, 4321357 and 4323393, 1982
- 6 Keske, R. G., Stephens, J. R. and Dunlap, R. W. *Polym. Prepr.* 1984, **25**(2), 12
- 7 Ohta, T., Yamamuro, T., Takamiya, N. and Kasai, T. Jap. Pat. Appl. 63-68634, 1988
- 8 Walker, C. C. *J. Polym. Sci. (A)* 1988, **26**, 1649
- 9 Ijima, I. and Takahashi, Y. *Macromolecules* 1989, **22**, 2944
- 10 Wallach, M. L. *J. Polym. Sci. (A-2)* 1969, **7**, 1995
- 11 Coulhan, R. E. and Pickering, T. L. *Polym. Prepr.* 1971, **12**(1), 305
- 12 Yoshiyuki, O., Kazuo, I., Masaaki, K. and Yoshio, I. *Kobunshi Ronbunshu* 1990, **47**(4), 353
- 13 Coburn, J. C. and Pottiger, M. T. 'Advances in Polyimide Science and Technology' (Eds. Feger, Khojasteh and Htoo), Technomic, Lancaster, PA, 1993, p. 360