

# Polyimides with pendent ethynyl groups

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(Received 2 April 1992)

Three novel diamines containing pendent ethynyl, hexynyl and phenylethynyl groups were synthesized and used to prepare polymers and copolymers. When heated to 250–350°C, the ethynyl groups react to form crosslinks. After curing, the homopolymers were brittle owing to the high crosslink density. Copolymers prepared using 10 mol% ethynyl-containing diamine and 90 mol% of diamines with no ethynyl groups were relatively tough, forming creasible films. After a thermal cure, the copolymers became insoluble and exhibited high  $T_g$  values and good thin film properties.

(Keywords: polyimide; diamine; pendent groups; synthesis; ethynyl groups; crosslinking; copolymers; characterization; films)

## INTRODUCTION

Polyimides have received a significant amount of attention over the last 30 years and many polyimides are now commercially available in the form of adhesives, coatings, composite matrices, films, fibres, foams, membranes and mouldings. Polyimides offer an attractive combination of high thermal stability and high mechanical properties. The market for polyimides in 1988 was estimated to be ~550 million dollars<sup>1</sup>. The chemistry, properties and uses for polyimides have recently been summarized in a single source<sup>2</sup>.

As part of the vast amount of work on polyimides, ethynyl (acetylenic) groups have been placed on the ends of imide oligomers<sup>3,4</sup> and pendent along the polymer backbone<sup>5</sup>. Upon thermal curing, the acetylenic groups react to provide chain extension, branching and crosslinking. A series of acetylene-terminated imide oligomers designated Thermid™ are commercially available<sup>6</sup>. Acetylene-containing prepolymers were recently reviewed<sup>7</sup>. The work reported herein concerns the use of novel ethynyl-containing diamines to prepare a series of polyimides containing pendent ethynyl groups. This work was done as part of a study on chemical structure–property relationships to provide information to help design better materials for a variety of aerospace applications.

## EXPERIMENTAL

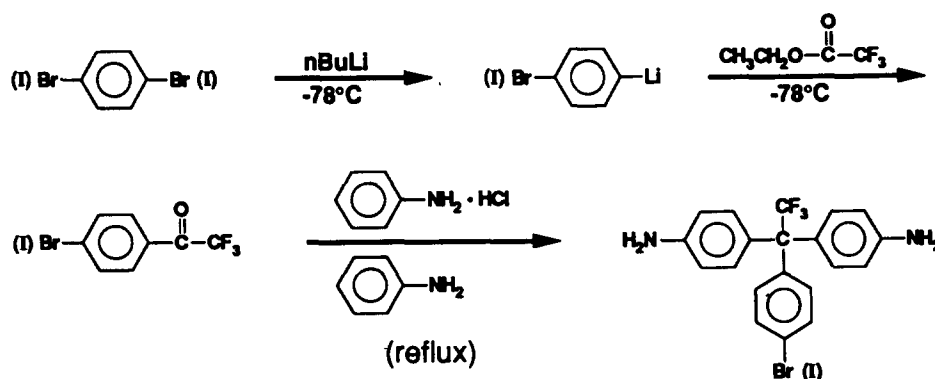
### Monomer syntheses

The monomers containing pendent ethynyl and substituted ethynyl groups were synthesized as shown in Schemes 1 and 2. The synthetic procedure for each reactant and monomer is described.

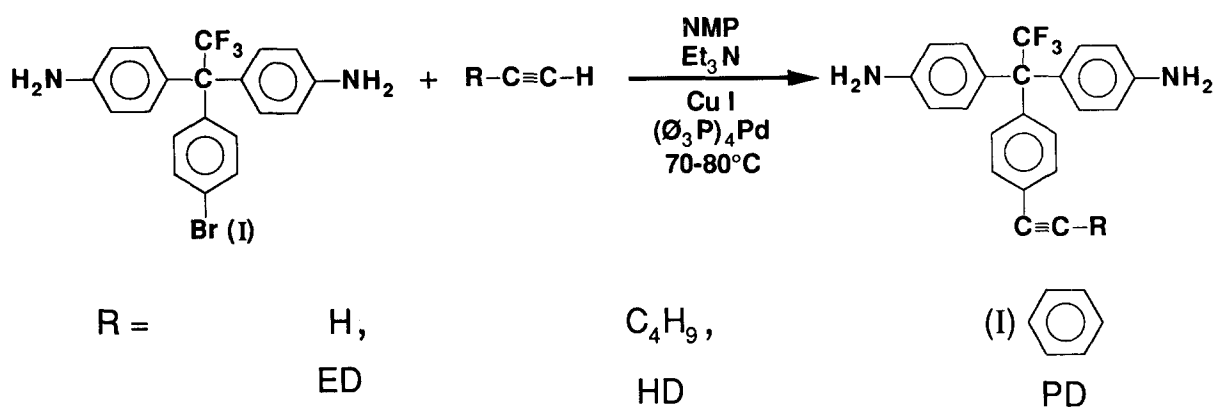
*4-Bromotrifluoroacetophenone.* Into a flame-dried three-necked round-bottomed flask, fitted with a pressure-equalizing addition funnel and under nitrogen, was added 1,4-dibromobenzene (20.04 g, 85.00 mmol). Using a syringe, 150 ml of anhydrous ether was added into the flask. Some of the 1,4-dibromobenzene precipitated when the solution was cooled to  $-78^\circ\text{C}$  in a dry-ice/acetone bath. *n*-Butyllithium (*n*-BuLi) (1.6 M in hexane, 55 ml, 88 mmol) was introduced into the addition funnel with a syringe and the funnel was adjusted for dropwise addition of the *n*-BuLi solution into the reaction flask. The addition was completed in 30 min and the resulting white suspension was stirred at  $-78^\circ\text{C}$  for 2 h. After 2 h, the reaction vessel was removed from the bath and allowed to warm to  $0^\circ\text{C}$  to ensure complete metal–halogen exchange, changing from a suspension to a solution on warming. On recooling to  $-78^\circ\text{C}$ , the suspension reappeared. To this white suspension ethyl trifluoroacetate (13.47 g, 95.00 mmol) was added dropwise. The suspension became a solution before complete addition of the ester, and the solution was left to warm to room temperature in about 12 h.

To quench the reaction, the solution was cooled between  $-30$  and  $-20^\circ\text{C}$ , and 40 ml of aqueous saturated ammonium chloride ( $\text{NH}_4\text{Cl}$ ) was added dropwise. To ensure complete hydrolysis, 40 ml of 1 N hydrochloric acid (HCl) was added and the mixture was allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel and the aqueous layer was removed. The ether solution was washed carefully with saturated aqueous sodium bicarbonate ( $\text{NaHCO}_3$ ) until all the acid was neutralized. The ether solution was transferred to a flask and dried over anhydrous magnesium sulfate ( $\text{MgSO}_4$ ). Suction filtration, followed by rotary evaporation of the solvent, left a yellow-coloured, slightly lachrymatory liquid, which was vacuum-distilled (0.2 Torr,  $80^\circ\text{C}$ ) to obtain 19.75 g (88%) of 4-bromotrifluoroacetophenone as a

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Scheme 1



Scheme 2

dense, colourless liquid. The liquid solidified on storing in the refrigerator.  $^1\text{H}$  n.m.r.: an AB quartet centred at 7.66 ppm.

**4-Iodotrifluoroacetophenone.** This was prepared by a similar procedure in 81% yield from *p*-diiodobenzene.  $^1\text{H}$  n.m.r.: an AB quartet centred at 7.65 ppm.

**1,1-Bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane.** 4-Bromotrifluoroacetophenone (33.53 g, 132 mmol) and purified aniline hydrochloride (23 g, 178 mmol) were placed in a 500 ml single-necked round-bottomed flask. After freshly distilled aniline (93 ml) was added, the reaction mixture was heated under nitrogen to reflux and maintained at reflux for 24 h. On cooling to room temperature, solid  $\text{NaHCO}_3$  (30 g, 357 mmol) was carefully added in portions to neutralize aniline hydrochloride and the reaction mixture was steam-distilled until the distillate was clear. A dark solid mass and water were left in the flask after it cooled to room temperature. Water was decanted off, the solid was dissolved in chloroform and the solution was dried over anhydrous  $\text{MgSO}_4$ . After suction filtration, the dark purple solution was concentrated on a rotary evaporator. The resulting dark purple solid was subjected to column chromatography on silica gel using benzene as eluant. (Carbon tetrachloride ( $\text{CCl}_4$ ) elution, followed by 20% ether in  $\text{CCl}_4$ , also worked but benzene gave better separation.) A total of 43.18 g (77%) of product was collected as a light purple solid. Analytical samples were prepared by multiple recrystallizations from benzene: m.p. 194–196°C.  $^1\text{H}$  n.m.r.: d 3.60 (br s, 4H); 6.35–7.30 (two AB quartets, 12H). Mass spectrum, *m/e* (relative

intensity): 422 ( $\text{M}^+$ , 20), 420 ( $\text{M}^+$ , 20), 353 (100), 351 (100). Elemental analysis calculated for  $\text{C}_{20}\text{H}_{16}\text{BrF}_3\text{N}_2$ : C, 57.02%; H, 3.83%; found: C, 57.40%; H, 3.86%.

**1,1-Bis(4-aminophenyl)-1-(4-iodophenyl)-2,2,2-trifluoroethane.** This was prepared in a similar manner in 59% yield from 4-iodotrifluoroacetophenone: m.p. 171–172°C (after vacuum heat-drying).  $^1\text{H}$  n.m.r.: d 3.50 (br s, 4H), 6.44 (d, 4H), 6.80 (d, 6H), 7.46 (d, 2H). Mass spectrum, *m/e* (relative intensity): 468 ( $\text{M}^+$ , 40), 399 (100), 272 (20). Calculated for  $\text{C}_{20}\text{H}_{16}\text{IF}_3\text{N}_2$ : C, 51.30%; H, 3.44%; N, 5.98%; found: C, 51.40%; H, 3.36%; N, 5.97%.

**1,1-Bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane (ED).** 1,1-Bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane (15.17 g, 35.95 mmol) was dissolved in a mixture of 60 ml of triethylamine and 20 ml of *N*-methylpyrrolidinone (NMP). Copper(I) iodide (CuI, 0.16 g, 0.84 mmol, 2.3 mol%), tetrakis(triphenyl phosphine)palladium(0) (1.00 g, 0.86 mmol, 2.4 mol%) and trimethylsilylacetylene (7.00 g, 71.43 mmol) were then added. The solution was sealed in the flask with a rubber septum and the magnetically stirred mixture was heated at 80°C for 24 h.

After the reaction, the solvent mixture was removed on a rotary evaporator, the residue was extracted with ether and the suspension was suction-filtered. The ether extract was washed with water and then dried over anhydrous  $\text{MgSO}_4$ . Suction filtration followed by rotary evaporation of the solvent left 20.87 g of crude 1,1-bis(4-aminophenyl)-1-(4-trimethylsilylethynylphenyl)-2,2,2-trifluoroethane. This crude material was dissolved in 100 ml of methanol, and  $\text{Na}_2\text{CO}_3$  (6.06 g, 57.0 mmol)

was added for desilylation. The flask was stoppered and stirred at room temperature for 24 h. After filtering off the solids, methanol was removed by rotary evaporation. The residue was extracted with ether to remove any inorganic substances that might have dissolved in methanol. Aqueous washing of the ether solution, followed by drying with anhydrous  $\text{MgSO}_4$ , suction filtration and rotary evaporation, left 16.12 g of crude monomer. Purification was effected by column chromatography with silica gel. Initial slow elution with benzene removed faster eluting impurities. The solvent was then changed to a 50/50 (v/v) mixture of ether and benzene to elute the product. Rotary evaporation of the eluant left a brown viscous oil, which upon vacuum drying for 3 days formed a yellow foamy solid.  $^1\text{H}$  n.m.r. of this solid showed that some benzene was still occluded in the product. To remove the benzene, the product was vacuum dried at  $80^\circ\text{C}$  for about 30 min. On cooling to room temperature, a brittle orange glass was left, which was ground to provide the monomer as a yellow powder weighing 10.37 g (78%). Analytical samples were prepared by recrystallization from deuterated chloroform ( $\text{CDCl}_3$ ): m.p.  $161\text{--}163^\circ\text{C}$ .  $^1\text{H}$  n.m.r.:  $\delta$  2.88 (s, 1H), 3.42 (br s, 4H), 6.20–7.08 (m, 12H). Mass spectrum,  $m/e$  (relative intensity): 366 ( $\text{M}^+$ , 25), 297 (100). Calculated for  $\text{C}_{22}\text{H}_{17}\text{F}_3\text{N}_2$ : C, 72.12%; H, 4.68%; N, 7.65%; found: C, 72.34%; H, 4.79%; N, 7.45%.

*1,1-Bis(4-aminophenyl)-1-(4-phenylethynylphenyl)-2,2,2-trifluoroethane (PED)*. Into a single-necked round-bottomed flask were added 1,1-bis(4-aminophenyl)-1-(4-iodophenyl)-2,2,2-trifluoroethane (6.27 g, 13.39 mmol), tetrakis(triphenylphosphine)palladium(0) (0.52 g, 0.45 mmol, 3.36 mol%) and CuI (0.11 g, 0.58 mmol, 4.3 mol%). After the addition of triethylamine (24 ml) and of NMP (8 ml), phenylacetylene (2.80 g, 27.45 mmol) was introduced into the flask. A reflux condenser, connected to a nitrogen line, was attached to the flask and the stirred mixture was maintained at  $70^\circ\text{C}$  for 3 days. The solvent mixture was removed on a rotary evaporator and the dark-red oily residue was extracted with ether continuously until further extraction with fresh ether gave a colourless organic layer. All the ether extracts were collected, washed with water and dried over anhydrous  $\text{MgSO}_4$ . Suction filtration and solution concentration on the rotary evaporator gave a dark-red oil, which solidified to a fluffy yellow solid.

The crude product was applied onto a column of silica gel and eluted initially with benzene. After the faster moving components of the crude mixture had eluted (this fraction was a dark-red oil), elution was continued with a 9:1 (v/v) mixture of benzene and ether respectively. The product obtained from this fraction on rotary evaporation was a bright yellow foamy solid weighing 3.45 g (58%). The  $^1\text{H}$  n.m.r. spectrum of this product indicated that some occluded benzene was still left in the solid. The product was therefore subjected to vacuum drying at  $80^\circ\text{C}$  for 30 min. The resulting orange glass was ground into a yellow powder. M.p.: the compound started to shrink at  $85^\circ\text{C}$ , became a glassy ball at  $90\text{--}92^\circ\text{C}$  and melted into an orange liquid at  $100\text{--}102^\circ\text{C}$ .  $^1\text{H}$  n.m.r.:  $\delta$  3.66 (br s, 4H), 6.36–7.36 (m, 17H). Mass spectrum,  $m/e$  (relative intensity): 442 ( $\text{M}^+$ , 30), 373 (100). Calculated for  $\text{C}_{28}\text{H}_{21}\text{F}_3\text{N}_2$ : C, 76.00%; H, 4.78%; N, 6.33%; found: C, 75.63%; H, 4.95%; N, 6.15%.

*1,1-Bis(4-aminophenyl)-1-(4-hexynylphenyl)-2,2,2-trifluoroethane (HD)*. This compound was prepared in 76% yield from 1,1-bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane and 1-hexyne by the same procedure as for the phenylethynylphenyl analogue. M.p.: the compound started to soften and shrink at  $53^\circ\text{C}$ , became a transparent mass at  $62^\circ\text{C}$  and melted at  $93^\circ\text{C}$ .  $^1\text{H}$  n.m.r.:  $\delta$  0.90 (unresolved, 3H), 1.50 (unresolved, 4H), 2.32 (unresolved, 2H), 3.42 (br s, 4H), 6.55 (AB q, 8H), 7.02 (AB q, 4H). Mass spectrum,  $m/e$  (relative intensity): 422 ( $\text{M}^+$ , 20), 353 (100). Calculated for  $\text{C}_{26}\text{H}_{25}\text{F}_3\text{N}_2$ : C, 73.92%; H, 5.96%; N, 6.63%; found: C, 74.29%; H, 6.13%; N, 6.63%.

*Other monomers.* The other monomers used in this study, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF), were obtained from commercial sources and were sublimed or recrystallized prior to use. The 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDAM) was an experimental material obtained from Mr Harvey Grubbs, Chemistry Department of Virginia Polytechnic Institute and State University.

#### Polymer synthesis

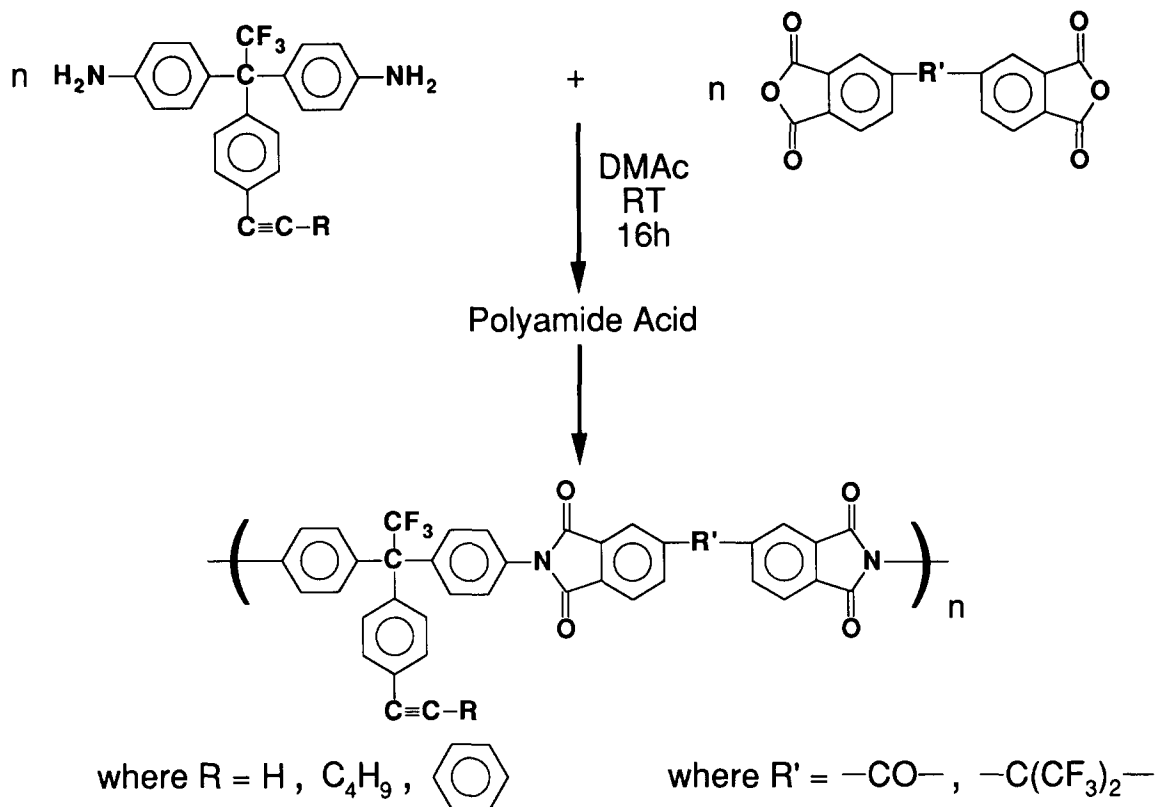
The polyamide acids were prepared by adding the dianhydride to a solution of the diamine in *N,N*-dimethylacetamide (DMAc) followed by stirring for  $\sim 16$  h at room temperature (RT) under nitrogen as shown in *Scheme 3*. The polyamide acids were either thermally imidized (1 h each at 100, 200,  $300^\circ\text{C}$ ) or chemically imidized by adding acetic anhydride and triethylamine to the polyamide acid solution and stirring overnight. Copolymers were prepared under the same reaction conditions using 10 mol% of the ethynyl-containing diamine and 90 mol% of either 3FDAM or BDAF.

The following example illustrates the synthesis of polyimides with pendent phenylethynyl groups. PED (2.2124 g, 0.005 mol), BTDA (1.6112 g, 0.005 mol) and DMAc (21.7 g) were added to a three-necked flask equipped with a stirring motor and nitrogen purge. The reaction mixture was stirred for 8 h at RT to form a polyamide acid with  $\eta_{\text{inh}} = 0.56 \text{ dl g}^{-1}$ . This solution was cast onto plate glass and cured in air for 1 h each at 100, 200 and  $350^\circ\text{C}$  to form a crosslinked yellow polyimide film with no  $T_g$  detected by differential scanning calorimetry (d.s.c.) at a heating rate of  $20^\circ\text{C min}^{-1}$ . This film was completely insoluble in either DMAc or chloroform.

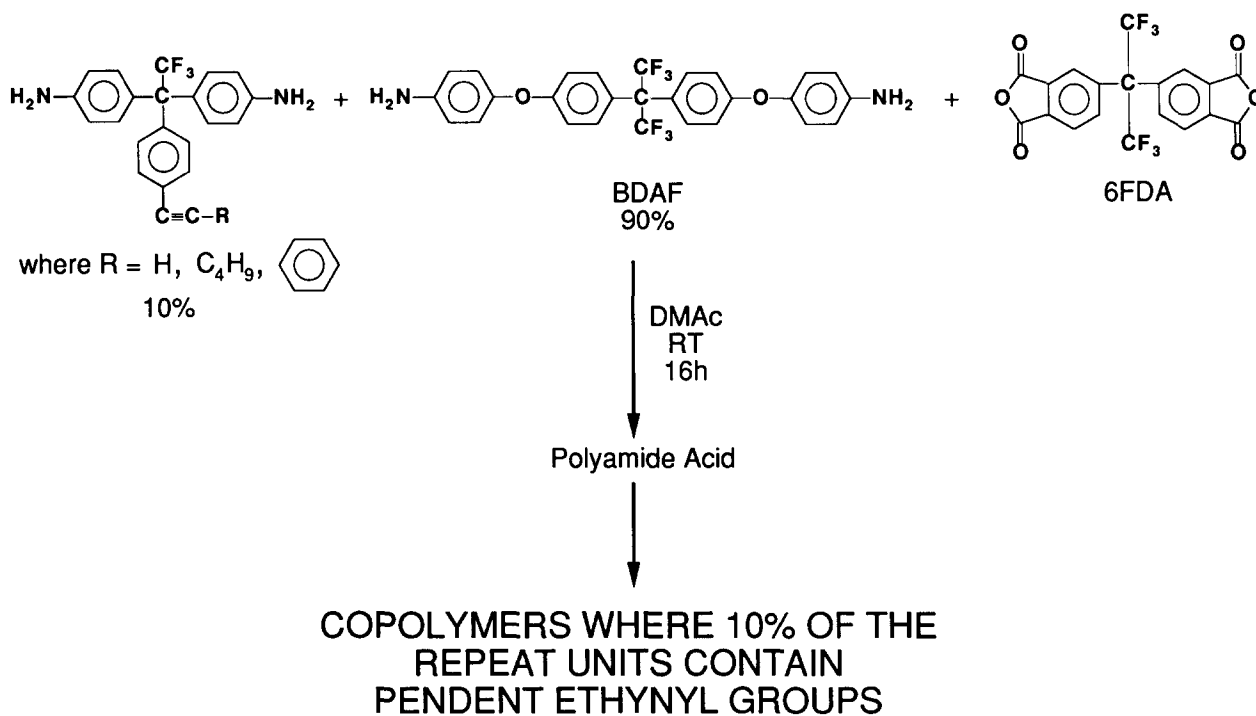
The same procedure was used with ED and HD in place of PED to provide polyamide acids with  $\eta_{\text{inh}}$  values of 0.80 and  $0.40 \text{ dl g}^{-1}$ , respectively (*Table 1*). After curing for 1 h at  $300^\circ\text{C}$ , the resulting polyimides failed to exhibit  $T_g$  values and were insoluble in DMAc and chloroform. Some of the polyamide acids were chemically converted to the polyimides by adding acetic anhydride and triethylamine and stirring overnight. The soluble polyimides were then recovered by precipitation in water and washing in methanol.

#### Copolymer synthesis

The synthesis of imide copolymers containing pendent ethynyl or substituted ethynyl groups is depicted in *Scheme 4*. These copolymers were prepared using 10 mol% of the diamine containing a pendent ethynyl



Scheme 3



Scheme 4

group and 90% of a diamine without a pendent ethynyl group, although any ratio of these diamines could be used. Table 2 gives the  $\eta_{inh}$  values of the amide acid copolymers and the original and final  $T_g$  values of the imide copolymers when 90 mol% of the diamine is 3FDAM. Table 3 gives similar data when using 90 mol% BDAF as the complementary diamine.

The following example illustrates the synthesis of an imide copolymer where one out of ten repeat units

contains a pendent phenylethynyl group. PED (0.4425 g, 0.001 mol), BDAF (4.6662 g, 0.009 mol), 6FDA (4.4425 g, 0.01 mol) and DMAc (54.1 g) were added to a three-necked flask equipped with a stirring motor and nitrogen purge. The reaction was stirred for 8 h at RT to form a polyamide acid with  $\eta_{inh} = 1.47 \text{ dl g}^{-1}$ . This solution was cast onto plate glass and cured in air for 1 h each at 100, 200 and 350°C to form a creasible, lightly crosslinked yellow imide copolymer film with  $T_g = 273^\circ\text{C}$  by d.s.c.

This film was completely insoluble in DMAc or chloroform but did swell somewhat.

The same procedure was used to prepare copolymers with ED and HD in place of PED to provide polyamide acids with  $\eta_{inh}$  values of 1.54 and 1.08 dl g<sup>-1</sup>, respectively. After curing for 1 h at 300°C, the resulting lightly cross-linked polyimides had  $T_g$  values of 275 and 269°C, respectively, and were insoluble in DMAc and chloroform but did swell somewhat.

#### Characterization

Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected. Inherent viscosities ( $\eta_{inh}$ ) were obtained on 0.5% solutions in DMAc at 25°C. Differential scanning calorimetry (d.s.c.) was performed at a heating rate of 20°C min<sup>-1</sup> with the apparent  $T_g$  taken at the inflection point of the  $\Delta T$  versus temperature curve. Thermogravimetric analysis (t.g.a.) was conducted on film specimens at a heating rate of 2.5°C min<sup>-1</sup> in flowing air or nitrogen.

#### Films

DMAc solutions (15% solids) of the polymers and copolymers were centrifuged, and the decanted solution was spread onto plate glass and dried at RT to a tack-free form in a low-humidity chamber. The films on glass were dried for 1 h each at 100, 200 and 300°C (polymers containing phenylethynyl groups were dried to 350°C instead of 300°C) in air. Mechanical tests were performed according to ASTM D882 on four or more specimens per test condition.

## RESULTS AND DISCUSSION

The ethynyl- and substituted ethynyl diamines were prepared in relatively high crude yields, but purification by simple recrystallization was difficult. Column chromatography proved more successful and afforded diamines whose elemental analyses agreed well with the theoretical values. The ethynyl diamines visually melted over a broad range and sintered and softened prior to melting, indicative of impure material. However, by d.s.c. at a heating rate of 20°C min<sup>-1</sup>, ED and HD exhibited relatively sharp melting endotherms at 176 and 141°C, respectively. PED exhibited a broad endotherm peaking at 76°C. The exothermic peaks in the d.s.c. curves due to reaction of the ethynyl groups occurred at 261°C for ED, 300°C for HD and 370°C for PED, showing that the substituent on the ethynyl group influenced the curing reaction. The chemical structure and purity of all the ethynyl-containing diamines were further verified by mass spectroscopy and <sup>1</sup>H n.m.r.

All polyamide acids were prepared in the conventional manner using exact stoichiometry in DMAc at 15% solids content (weight to weight) by adding the dianhydride to a stirred solution of the diamine(s) under nitrogen at ambient temperature. A mild exotherm occurred initially and the resulting viscous solutions were stirred under nitrogen overnight at ambient temperature. The polyamide acids were subsequently converted to the polyimides chemically by adding acetic anhydride and triethylamine and stirring overnight under nitrogen or by casting a polyamide acid film onto plate glass and heating in air for 1 h each at 100, 200, 300°C (350°C for the phenylethynyl materials).

The polyamide acid from the reaction of 3FDAM and 6FDA exhibited an  $\eta_{inh}$  of 0.81 dl g<sup>-1</sup> and upon thermal conversion yielded a polyimide with a  $\eta_{inh}$  of 0.67 dl g<sup>-1</sup>, a  $T_g$  of 329°C (after heating to 400°C in the d.s.c.) and high solubility in DMAc and chloroform. This polyimide was prepared solely for comparative purposes and had been initially reported in 1985<sup>8</sup>.

In addition, another homopolymer was prepared for comparative purposes from the reaction of BDAF and 6FDA. The polyimide exhibited an  $\eta_{inh}$  of 0.80 dl g<sup>-1</sup> and a  $T_g$  of 263°C (after heating to 400°C in the d.s.c.). This polymer was also previously reported<sup>9</sup>.

Low inherent viscosities (as shown in Table 1) and presumably low molecular weights were obtained for the polyamide acids from the reaction of HD with BTDA or 6FDA. This has been tentatively attributed to the purity of HD even though the d.s.c. melting endotherm, elemental analysis and <sup>1</sup>H n.m.r. suggested relatively high purity. High  $\eta_{inh}$  values were obtained for polyamide acids from the reaction of ED and PED with BTDA and 6FDA. As a reminder, the d.s.c. melting endotherm of PED was broad and not characteristic of a high-purity material. When the polyamide acid solutions were cast as thin films on plate glass and subsequently dried in air for 1 h at 300°C (350°C for the PED polymers only), no  $T_g$  by d.s.c. could be detected and the films were very brittle as expected because of the high crosslink density. Chemically imidized polymers based on 6FDA displayed exothermic peaks indicative of the ethynyl curing reaction at 298°C for the ED, 321°C for the HD and 427°C for the PED polymers. These are 20–50°C higher than the exothermic peaks of the monomers alone. No further work was done with these polymers because of their limited utility.

The focus shifted to the preparation of copolymers that would yield more usable materials with a lower crosslink density. Copolymers were prepared from the reaction of 90 mol% of either 3FDAM or BDAF and 10 mol% of the ethynyl-containing diamines with 6FDA. Characterization of the copolymers is presented in Tables 2 and 3. The 3FDAM copolymers formed brittle films even though the  $\eta_{inh}$  values were relatively high (>0.67 dl g<sup>-1</sup>). When chemically imidized, the copolymers remain soluble in DMAc. Upon heating to 400°C in a hermeti-

Table 1 Inherent viscosity of polyamide acids

Diamine	Dianhydride	Polyamide acid, $\eta_{inh}$ (dl g <sup>-1</sup> )
ED	BTDA	0.94
ED	6FDA	0.80
HD	BTDA	0.40
HD	6FDA	0.26
PED	BTDA	0.77
PED	6FDA	0.68

Table 2 Characterization of 3FDAM/6FDA-based copolymers

Diamine with 90% 3FDAM	$\eta_{inh}$ (dl g <sup>-1</sup> )		D.s.c. $T_g$ (°C) <sup>a</sup>	
	Polyamide acid	Polyimide <sup>a</sup>	Initial	Final <sup>b</sup>
10% ED	0.83	0.69	ND	342
10% PED	0.82	0.67	ND	341

<sup>a</sup> Chemically imidized, acetic anhydride and triethylamine

<sup>b</sup> After heating to 400°C

**Table 3** Characterization of BDAF/6FDA-based copolymers

Diamine with 90% BDAF	$\eta_{inh}$ (dl g <sup>-1</sup> )		D.s.c. $T_g$ (°C) <sup>a</sup>	
	Polyamide acid	Polyimide <sup>a</sup>	Initial	Final <sup>b</sup>
10% ED	1.54	1.34	265	275
10% HD	1.08	0.89	264	269
10% PED	1.47	1.25	265	273

<sup>a</sup> Chemically imidized, acetic anhydride and triethylamine<sup>b</sup> After heating to 400°C

cally sealed d.s.c. pan, the 3FDAM-based ethynyl-containing copolymers displayed an exothermic peak with maximum at 365 to 370°C. No apparent  $T_g$  values were detected during the initial heatings. After heating to 400°C, quenching and rerunning the same samples,  $T_g$  values of 342 and 341°C were recorded. The  $T_g$  of the homopolymer from the reaction of 3FDAM and 6FDA (no ethynyl groups) was 329°C after the same thermal history as the 3FDAM-based copolymer. In addition to an increase of ~12°C in the  $T_g$  due to the thermal reaction of the ethynyl groups, these polymers became insoluble but swelled appreciably in DMAc and chloroform.

The BDAF polymers had significantly higher  $\eta_{inh}$  as shown in Table 3 than the corresponding 3FDAM polymers. These polyamide acids were also chemically converted to the polyimides, which were readily soluble in chloroform and DMAc. The three polyimides exhibited the same initial  $T_g$  values as expected since the difference in chemical structure is minor (the pendent ethynyl group substituent) and all the polyimides were of high molecular weight as suggested by the  $\eta_{inh}$  values. Upon heating to 400°C in hermetically sealed d.s.c. pans, the ethynyl groups pendent on the polyimides reacted, resulting in an increase in the polymer  $T_g$  of 5 to 10°C, and causing the polymer to become insoluble but swell in DMAc and chloroform.

Thin films were cast from the polyamide acid solution and subsequently converted to the polyimide by curing for 1 h at 300°C. The polyimide film containing pendent phenylethynyl groups was cured for 1 h at 350°C instead of 300°C to effect reaction of the phenylethynyl groups. The curing process removes the solvent, cyclodehydrates the polyamide acid to polyimide and induces reaction of the pendent ethynyl group. The film tensile properties of the polyimides containing 10 mol% of the pendent ethynyl groups and a homopolymer containing no ethynyl groups are reported in Table 4. Room-temperature tensile strengths, moduli and elongations of the lightly cross-linked polyimide were in the ranges 14.8–17.7 ksi, 416–534 ksi and 5.9–6.7% at RT and 9.6–10.4 ksi, 280–317 ksi and 7.5–111% at 177°C, respectively. These values were similar to those of the BDAF/3FDAM homopolymer except for the higher elongation of the homopolymer. When tested at 177°C, the films retained 60–65% of their strengths and moduli while elongations increased significantly.

Also presented in Table 4 is the temperature of 5% weight loss by t.g.a. for the BDAF copolymers. The HD-derived polymer exhibited the poorest thermal stability by t.g.a. in air with 5% weight loss occurring at 401°C. In nitrogen, the temperature of 5% weight loss was the same for the three copolymers. To obtain more meaningful data on thermal stability, isothermal stability was measured at 316°C (600°F) for the homopolymers

**Table 4** Thermal stability and thin-film properties of 6FDA-based copolymers

Diamine components	Temperature of 5% wt loss by t.g.a. (°C)		Tensile strength (ksi) <sup>a</sup>	Tensile modulus (ksi) <sup>a</sup>	Elongation (%)
	Air	N <sub>2</sub>			
10% ED, 90% BDAF	468	493	14.8 (9.9) <sup>b</sup>	416 (312)	6.7 (7.5)
10% HD, 90% BDAF	401	493	17.8 (9.7)	534 (317)	5.9 (12.1)
10% PED, 90% BDAF	450	493	17.7 (9.6)	518 (301)	6.1 (47)
100% BDAF	—	—	15.6 (10.4)	433 (280)	26.7 (111)

<sup>a</sup> 1 ksi ≈ 6.895 MPa<sup>b</sup> ( ) indicates values when tested at 177°C

and copolymers for 6FDA. The copolymers made with 10% ED or PED and 3FDAM had equivalent stability as the homopolymer, showing a retention of 97% of original weight after 300 h at 316°C. The copolymers made with 10% ED or PED and BDAF also had equivalent stability as the homopolymer, showing a retention of 94% of the original weight after 300 h at 316°C; while the 10% HD copolymer was considerably less stable with 82% weight retention. This result was not surprising considering the aliphatic content of the copolymer.

## CONCLUSIONS

Diamines containing pendent ethynyl and substituted ethynyl groups were prepared and purified. Polymers and copolymers prepared from these diamines and commercially available dianhydrides form films that could be crosslinked thermally to improve solvent resistance. The toughness and solubility of the copolymers could be systematically controlled by varying the amount of ethynyl-containing diamine used in the synthesis, which controls the final crosslink density. Thermal stability for the ethynyl- and phenylethynyl-containing copolymers was equivalent to the homopolymers.

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