N-Propargyl-substituted aromatic polyamides: preparation and thermal crosslinking

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A series of high molecular weight aromatic polyamide copolymers derived from 4,4'-bis(methylamino)-diphenylmethane, 4,4'-bis(propargylamino)diphenylmethane and isophthaloyl dichloride was prepared as potential candidates for use as matrix resins in Kevlar[(R)] fibre composites. These polyamides, which contain pendant propargyl groups, underwent facile crosslinking at 280°C as evidenced by dramatic increases in their glass transition temperatures (T_g) and accompanying loss of solubility. Other attempts to effect crosslinking by exposure to ultraviolet light, electron beam or gamma radiation were unsuccessful.

Keywords Synthesis; copolymers; crosslinking; *N*-propargyl aromatic polyamides; 4,4'-bis(methylamino)diphenylmethane; 4,4'-bis(propargylamino)diphenylmethane

INTRODUCTION

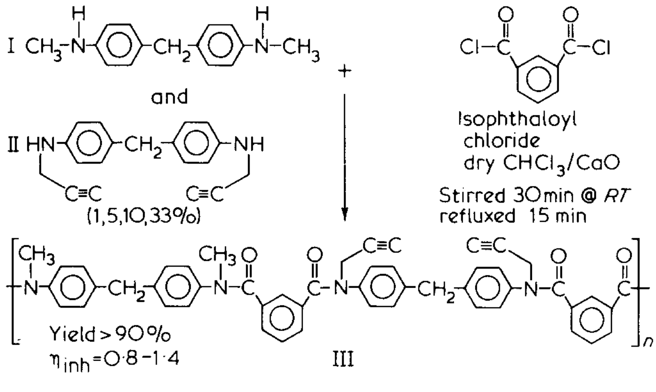
The application of conventional aromatic polyamides as matrix resins for composite or laminate fabrication with organic fibres has not been successful since they fail to meet certain stringent property requirements. To insure adequate rigidity in the composite, a suitable resin must have a softening temperature at least 50°C above the maximum end-use temperature of the composite. Furthermore, the reinforcing organic fibre has a characteristic temperature above which it begins to irreversibly lose its stiffness properties due to a relaxation phenomenon which occurs in a highly oriented fibre.

Attractive organic fibres for structural composite applications are of the aromatic polyamide type such as Kevlar®, which has a relaxation slightly below 300°C. Consequently, in order to preserve fibre stiffness, a processing temperature of 280°C should not be exceeded during fabrication of a structural laminate with this fibre reinforcement. This thermal restriction must now in turn be imposed on the matrix resin in that it should be processable at a temperature which does not infringe upon this upper limit.

Wholly aromatic polyamides derived from primary aromatic diamines are characterized by very high softening temperatures (>250°C) prohibiting their use as matrix resins with organic fibres such as Kevlar®. The high T_g's of these polyamides are associated with intermolecular hydrogen bonding through amide hydrogen and resultant orderly packing of the polymer chains[2]. Therefore, our initial approach at lowering the T_g of aromatic polyamides of this type was to prepare a series of *N*-methyl-substituted aromatic polyamides which lack amide hydrogen[3]. As expected, this structural modification resulted in a significant lowering of the T_g and thus much improved processability. Furthermore, the *N*-methylated polyamides exhibited better thermal stability, reduced crystallinity and greater solubility in organic solvents. The lower T_g values (153°–185°C) of the *N*-methylated polyamides, however, introduced a new problem. Composite materials fabricated from such matrix resins would almost certainly show signs of softening at or near the T_g of the matrix component and thus the full thermal potential of the fibre could not be utilized.

In the current study, the approach used to overcome this problem involved the incorporation of propargyl groups into the *N*-methylated polyamide backbone, with the hope that they would undergo thermal crosslinking. This was accomplished by copolymerization of 4,4'-bis(methylamino)diphenylmethane (I) and 4,4'-bis(propargylamino)diphenylmethane (IIa) with isophthaloyl dichloride to yield copolyamides of type III as illustrated in Scheme I. The copolymers, like the *N*-methyl-substituted homopolymers should have the

Scheme I



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advantage of processability at lower temperatures in addition to the possibility of thermal crosslinking through interaction of pendant propargyl groups. Such crosslinking should lend a degree of rigidity and thermal stability to the resulting composite otherwise unobtainable with normal polyamide matrix materials.

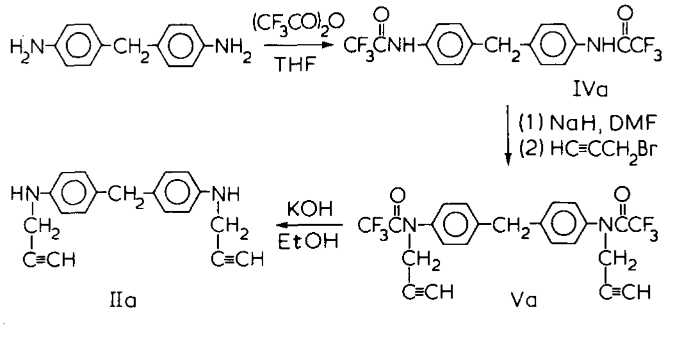
EXPERIMENTAL

Monomers

Commercial isophthaloyl dichloride was doubly distilled and then recrystallized from hexane, m.p. 43–44°C. 4,4'-Bis(methylamino)diphenylmethane (I) which was prepared from the condensation of *N*-methylaniline and formaldehyde was purified by vacuum distillation[4].

4,4'-Bis(propargylamino)diphenylmethane (IIa) was prepared starting with 4,4'-diaminodiphenylmethane as outlined in Scheme II.

Scheme II



4,4'-Bis(trifluoroacetamido)diphenylmethane (IVa)

Trifluoroacetic anhydride (105.0 g, 0.50 mol) was slowly added to 40.0 g (0.20 mol) of 4,4'-diaminodiphenylmethane in 300 ml of tetrahydrofuran (THF). The reaction mixture was then refluxed for 1.5 h, cooled to room temperature and concentrated on a rotary evaporator. The resulting tan solid was recrystallized from chloroform/methanol to yield 77.32 g (99%) of IVa as nearly colourless crystals, m.p. 229–230°C. ^1H n.m.r. (DMSO-d_6): 11.60δ (2H, broad, *s*, amide), 7.57δ (4H, *d*, phenyl), 7.19δ (4H, *d*, phenyl), and 3.88δ (2H, *s*, methylene). Anal. Calcd. for $C_{17}H_{12}N_2O_2F_6$: C, 52.31%; H, 3.10%; N, 7.17%. Found: C, 52.07%; H, 2.88%; N, 7.36%

4,4'-Bis(N-propargyltrifluoroacetamido)diphenylmethane (Va)

To a slurry of sodium hydride (3.7 g, 0.154 mol) in 20 ml of *N,N*-dimethylformamide (DMF) was added dropwise with stirring a saturated solution of trifluoroacetamide (IVa) (20.0 g, 0.0513 mol) in DMF. After quantitative formation of the dianion had occured as determined by hydrogen evolution, the yellow solution was filtered *in vacuo* through a glass frit into another reaction flask. A solution of propargyl bromide (24.41 g, 0.205 mol) in 20 ml of DMF was then added and the reaction mixture was stirred at room temperature for 8 h. The mixture was then poured into ice-cold dilute hydrochloric acid and the precipitated solid was dissolved in chloroform. The solution was dried over anhydrous magnesium sulphate, and concentrated to a yellow solid. Flash chromatography of the crude product using 70:30 chloroform–hexane followed by recrystallization from 95% ethanol gave Va as a white solid, m.p. 154°–155°C. ^1H n.m.r. ($CDCl_3$): 7.26δ (8H, *m*, phenyl), 4.50δ (4H, *d*, propargyl methylene), 4.09δ (2H, *s*, methylene), and 2.29δ (2H, *t*, alkyne).

Table 1 Elemental analyses and physical properties of compounds II, IV and V[a]

Compound no.	Yield (%)	M.p. (°C)	Elemental analyses			
				C	H	N
IV b	99	175–175.5	Calcd	52.31	3.10	7.17
			Found	52.71	2.93	7.38
IV c	99	178–179	Calcd	50.51	2.49	6.93
			Found	50.24	2.38	6.82
IV d	92	244–245	Calcd	50.51	2.49	6.93
			Found	50.27	2.15	6.91
V b	70	85–86	Calcd	59.23	3.46	6.01
			Found	59.02	3.32	5.92
V c	77	93–95	Calcd	57.50	2.94	5.83
			Found	57.56	2.80	5.89
V d	64	126–128	Calcd	57.50	2.94	5.83
			Found	57.33	2.66	5.81
II b	97	56–58	Calcd	83.17	6.61	10.21
			Found	83.28	6.44	10.10
II c	92	87–89	Calcd	79.14	5.59	9.72
			Found	78.85	5.57	9.51
II d	95	117–120	Calcd	79.14	5.59	9.72
			Found	78.94	5.51	9.81

[a] ^1H n.m.r. spectra of all compounds listed were consistent with the assigned structures

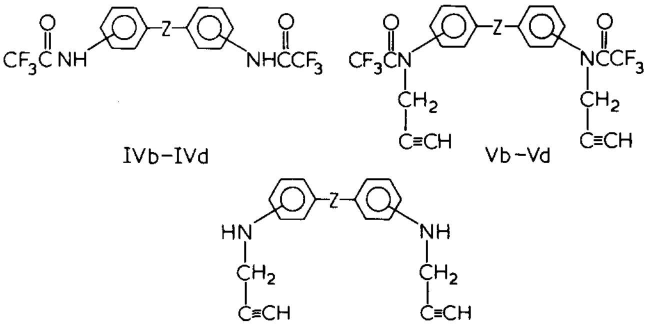
Anal. Calcd. for $C_{23}H_{16}N_2O_2F_6$: C, 59.23%; H, 3.46%; N, 6.01%. Found: C, 59.03%; H, 3.40%; N, 5.99%.

4,4'-Bis(propargylamino)diphenylmethane (IIa)

Powdered potassium hydroxide (0.93 g, 16.63 mmol) was added all at once to a slurry of bis-*N*-propargyltrifluoroacetamide Va (1.94 g, 4.16 mmol) in 100 ml of 95% ethanol. The mixture immediately turned yellow and was stirred at room temperature for 1 h. After this time, the reaction mixture was poured into an ice–water mixture and the product precipitated as a white solid. The crude diamine was then filtered, dried and recrystallized from 95% ethanol to give 1.05 g (92%) of IIa as colourless needles, m.p. 107°–108°C.

^1H n.m.r. (DMSO-d_6): 6.91δ (4H, *d*, phenyl), 6.53δ (4H, *d*, phenyl), 5.70δ (2H, *t*, amine), 3.79δ (4H, *d* of *d*, propargyl methylene), 3.61δ (2H, *s*, methylene) and 2.98δ (2H, *t*, alkyne). Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.17%; H, 6.61%; N, 10.20%. Found: C, 83.41%; H, 6.55%; N, 9.89%.

During the course of this study bis-*N*-propargyl diamines (IIb–IId) were prepared by the same route as diamine IIa in overall yields of 56–70%. As shown in *Table 1*, elemental analysis of these diamines and intermediates were consistent with the assigned structures. Only diamine IIa, however, was employed in the syntheses of polyamides reported in this paper.



IIb, Z=CH_2; $NHCH_2C{\equiv}CH \rightarrow 3,3'$
IIc, Z=CO; $NHCH_2C{\equiv}CH \rightarrow 3,3'$
IId, Z=CO; $NHCH_2C{\equiv}CH \rightarrow 4,4'$

Table 2 Effect of thermal crosslinking on T_g of propargyl copolymers

% Propargyl diamine	$[\eta_{inh}]$	Initial T_g^a (°C)	T_g after 0.25 h @ 280°C^a	T_g after heating to 400°C^b
0	1.21	165	165	154
1	1.01	151	171	–
5	1.08	165	193	–
10	1.42	160	200	–
33	0.79	150	206	228

^{a} Determined on powder by d.s.c. @ 20°C min^{-1} in air
^{b} Determined on t.b.a. braids by cooling 3°C min^{-1} in N_2

METHODS AND RESULTS

Polymers

The solution polymerization of diamine I and isophthaloyl dichloride in *s*-tetrachloroethane has been previously described. The following is an improved general procedure for that polymerization and for the preparation of the propargyl-containing copolymers (III).

Copolyamide III from 4,4′-bis(methylamino)diphenylmethane (I) and bis(propargylamino)diphenylmethane (IIa) (90:10) with isophthaloyl dichloride

A mixture of diamine I (4.07 g, 18.0 mmol) and diamine IIa (0.548 g, 2.00 mmol) contained in a 50 ml resin kettle was dissolved in 20 ml of dried, ethanol-free chloroform. Powdered, vacuum-dried calcium oxide was then added followed by the dropwise addition of a solution of isophthaloyl dichloride (4.06 g, 20.0 mmol) in 10 ml of chloroform. During the addition, the flask was cooled in a water bath. After the addition was complete, the addition funnel was rinsed with an additional 10 ml of chloroform. The viscous mixture was stirred at room temperature for 0.5 h, heated at 60°C for 0.5 h, cooled and diluted with chloroform to a volume of 125 ml. Most of the calcium salts were then removed by filtering through a coarse fritted disc funnel. The resulting opaque solution was shaken with dilute hydrochloric acid, water, dried (magnesium sulphate) and filtered. The polymer was then precipitated by pouring slowly into hexane in a blender. The white, fibrous polymer was then dried *in vacuo* at 100°C for 12 h. The yield of polymer was 6.78 g (94%).

Film preparation

Colourless films of the *N*-propargylated polyamides were cast from 10% (w/w) $CHCl_3$ solutions onto glass plates and cured *in vacuo* at elevated temperatures. Infrared analysis of films cured *in vacuo* at 120°C for 1 h revealed that a significant amount of solvent was still present. The difficulties associated with the complete removal of chlorinated solvents from certain high temperature polymers has been previously reported[3,5]. To remove all traces of $CHCl_3$, the films were heated several days *in vacuo* at 135°C. Curing at higher temperatures (200°C) for shorter periods of time caused yellowing of the films and possible premature crosslinking.

Polymer characterization

Inherent viscosities were measured on 0.5% polyamide solutions in chloroform at 35°C (*Table 2*). Infra-red spectra of polyamide films were obtained on a Digital FTS-15 IR.

Glass transition temperatures (T_g) of polyamide films or powders were determined by differential scanning calorimetry (d.s.c.) on a DuPont model 990 thermal analyser with the standard d.s.c. cell attachments. Torsional braid analyses (t.b.a.) were performed under nitrogen at a heating rate of 3°C min^{-1} on glass fibre braids coated with 10% chloroform polymer solutions and preheated for 1 h at 200°C in nitrogen. Dynamic thermogravimetric analyses (t.g.a.) of polyamide films were performed in static air with a Perkin-Elmer TGS-2 thermogravimetric system using a heating rate of 2.5°C min^{-1}.

Polymer synthesis

High molecular weight polyamide copolymers were prepared by solution polymerization in $CHCl_3$ at concentrations of 10–15% solids (w/w). The proportion of bis-propargyl diamine (IIa) used in the preparation was varied from 1 to 33% in order to evaluate the effect of propargyl group concentration on the T_g of the cured polymer. The homopolymer from diamine (I) and isophthaloyl dichloride was also prepared for comparison. Attempts to polymerize diamine (IIa) with isophthaloyl dichloride yielded only low molecular weight polymer presumably due to premature precipitation of oligomeric polymer chains.

Thermal properties

The T_g's of the polyamide powders were determined by d.s.c. in air before and after thermal crosslinking of the latent propargyl groups at 280°C. These results which are summarized in *Table 2* indicate the increase in T_g after crosslinking to be proportional to the percentage of propargyl diamine incorporated into the polyamide. *Figure 1* shows graphically the increase in T_g with heating time at 280°C.

The d.s.c. scan for the polyamide containing 33% propargyl diamine is shown in *Figure 2*. In addition to a sharp T_g at 150°C, this polymer exhibits a broad exotherm centred at 320°C, thus providing further evidence of crosslinking.

The effect of thermal crosslinking on T_g was also observed by t.b.a. as demonstrated in *Figure 3* for the 33% propargyl copolymer. The initial T_g value (152°C) of this polymer obtained by t.b.a. is in excellent agreement with that determined by d.s.c. (150°C, *Table 2*). However, the T_g

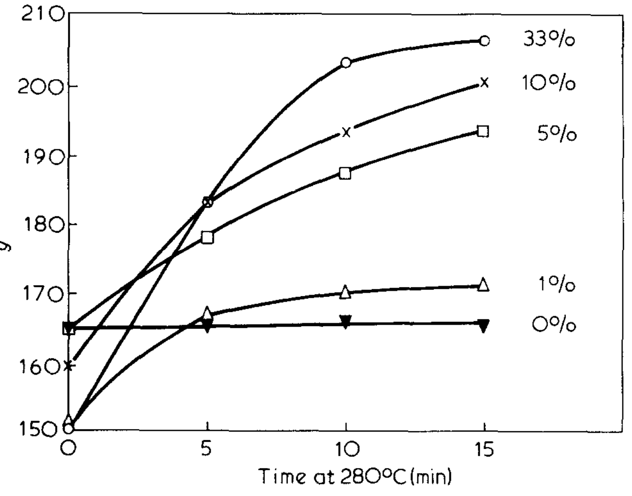
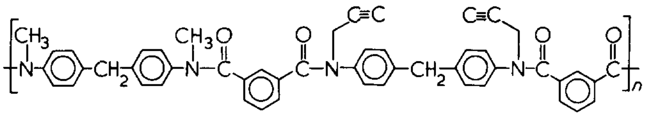


Figure 1 Glass transition temperature as a function of time at 280°C for varying percentages of propargyl content



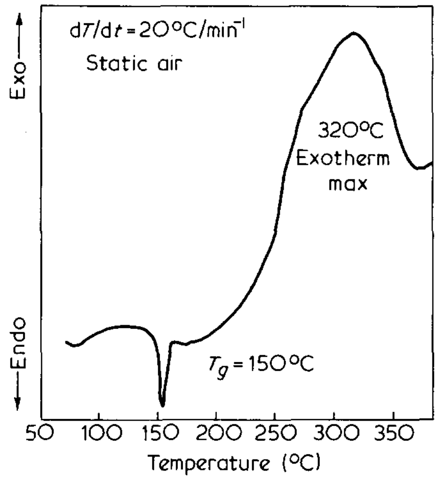


Figure 2 D.s.c. scan of polyamide containing 33% propargyl diamine

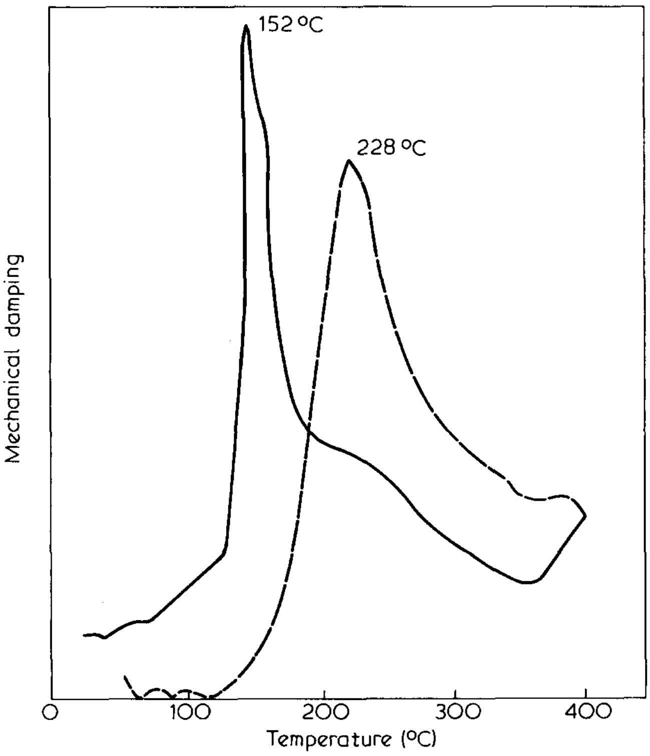


Figure 3 Torsional braid analysis of polyamide containing 33% propargyl diamine. (———) Heat; (— — — —) cool; braids preheated in N_2 1 h @ 200°C

(228°C) following heat-up to 400°C by t.b.a. is somewhat higher than that obtained from d.s.c. (T_g = 206°C) after heating at 280°C. This may be an indication of more effective crosslinking at the higher temperature.

Thermal stability

The dynamic t.g.a.'s of some polyamides are presented in *Figure 4a*. The graph illustrates the superior thermal stability of the methyl-substituted polyamides compared to their unsubstituted analogues, as was mentioned previously. This enhanced thermal stability, however, appears to be diminished upon incorporation of propargyl functionality into the polymer structure. In fact, the t.g.a. curve of the polymer containing 33% propargyl diamine is nearly identical to that of the original unsubstituted polyamide.

Isothermal t.g.a.'s were performed at 300°C in stable air on polyamide films of varying propargyl content (*Figure 4b*). After exposure at 300°C for 200 h, the weight loss of polymer films was found to increase with increasing propargyl content. Although 300°C ageing is considered a harsh treatment for polyamides, it should provide an accelerated view of the long-term ageing properties of these polymers.

Radiation exposure

In an attempt to crosslink latent propargyl groups, polyamide films containing 1–33% propargyl diamine were exposed to ultraviolet, electron beam, and cobalt-60 gamma radiation. The T_g's of the polyamide films were monitored by thermomechanical analysis before and after irradiation. These results are summarized in *Table 3*. Exposure to a 40W u.v. lamp for 300 h in air caused a reduction in the T_g's of all the polyamide films, especially those with the greater propargyl content. The exposed films, which were yellow and extremely brittle[10], were

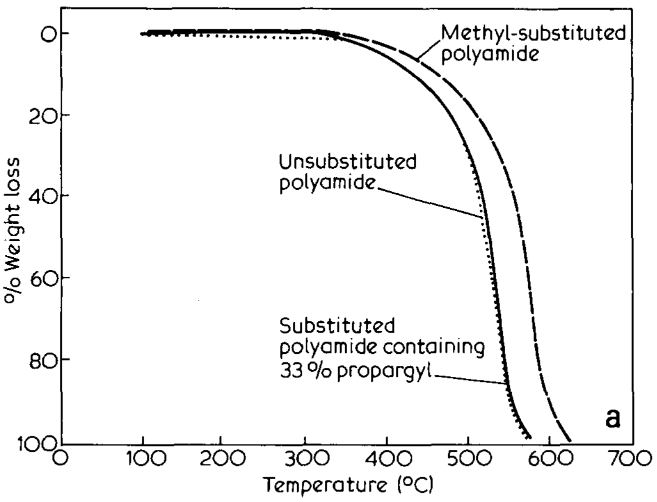


Figure 4a T.g.a.'s comparing thermal stabilities of substituted polyamides

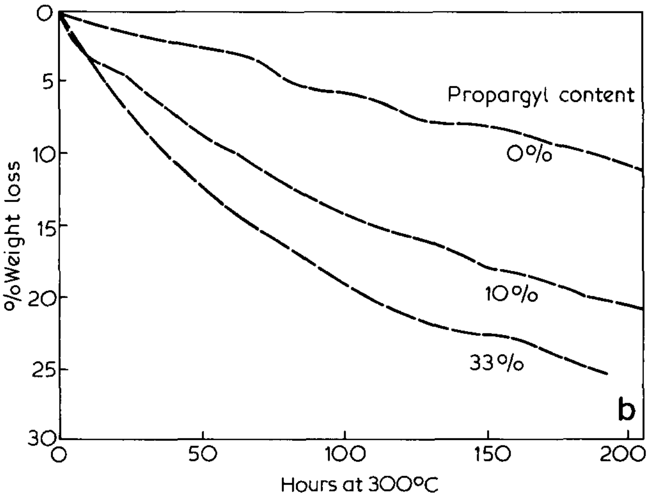


Figure 4b Isothermal weight loss at 300°C/air of propargyl-containing polyamides

Table 3 Radiation exposure to propargyl-containing polyamides

% Propargyl diamine	Initial T_g of film (°C)	U.v.[a] 300 h/air T_g (°C)	Electron beam[b] 25 Mrad T_g (°C)	51 Mrad T_g (°C)	Cobalt-60[b] 51 Mrad T_g (°C)
0	163	158	160	162	161
1	157	153	147	–	–
5	158	154	161	–	–
10	160	145	160	–	–
33	154	127	155	153	156

[a] Films yellowed and became brittle

[b] Films remained essentially colourless and soluble

obviously degraded by the combination of u.v. and humid air. T.g.a. of u.v. irradiated polyamide film containing 33% propargyl diamine showed early weight loss at temperatures below 200°C. However, exposure to radiation from an electron beam (2 MeV electrons from Van de Graaf accelerator) and cobalt-60 (1.2 MeV gamma rays) had relatively no affect on the T_g's. After irradiation by electron beam and cobalt-60, the films were still colourless and soluble indicating that no crosslinking had occurred.

Infra-red analysis of films

The polyamide films were analysed by infra-red spectroscopy (i.r.) before and after thermal crosslinking and irradiation. The i.r. spectrum of the untreated film containing 33% propargyl diamine displayed distinct absorbance peaks at 3290 cm^{-1} ($\equiv$C–H) and 2120 cm^{-1} (C$\equiv$C). Thermal crosslinking of the film in air at 300°C caused a diminishing of the 3290^{-1} absorbance, the complete disappearance of the 2120 cm^{-1} peak and the appearance of a carbonyl shoulder at 1725 cm^{-1} (oxidation of –CH$_2$– hydrogens)[6]. U.v. irradiation caused a weakening of the propargyl triple bond-related bands and the appearance of a broad hydroxyl peak at 3500 cm^{-1} (carboxylic acid –OH) and the same 1725 cm^{-1} peak observed after thermal treatment. No changes in the i.r. spectrum of this polymer were observed subsequent to electron beam or cobalt-60 irradiation.

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