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Novel perfluorononenyloxy group containing aromatic polyamides

Chun-Shan Wang* and Rong-Wen Yang
Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China
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A series of novel perfluorononenyloxy group containing aromatic polyamides were synthesized by direct polycondensation of 5-(perfluorononenyloxy)isophthalic acid (I) with various aromatic diamines in N-methyl-2-pyrrolidone (NMP) containing lithium chloride. In this process, triphenyl phosphite and pyridine were used as condensing agents. All the aromatic polyamides were amorphous and readily soluble in various polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide, and N-methyl-2-pyrrolidone. Transparent and flexible films of these polymers could be cast from the DMAc solutions. The polymers having inherent viscosity of 0.81–1.42 dl g^{-1} were obtained in quantitative yields. These polymers were thermally quite stable. The glass transition temperatures of these aromatic polyamides were in the range of 275–308°C by d.s.c. and 282–319°C by d.m.a., and the 10% weight loss temperatures in nitrogen and air were above 498 and 488°C, respectively. Moreover, these polymers maintained good mechanical properties ($G' \sim 10^8$ Pa) up to 280°C and had lower moisture absorption than common polyamides. © 1997 Elsevier Science Ltd.

(Keywords: 5-(perfluorononenyloxy)isothalic acid; direct polycondensation; polyamides)

INTRODUCTION

Wholly aromatic polyamides (aramids) are one of the families of high performance speciality thermoplastics because of their good thermal stability, chemical resistance, and excellent mechanical properties. However, the poor solubility and high melting temperature caused by the high crystallinity and stiffness of the polymer backbones lead to processing difficulty. Therefore, many studies have focused on the dissolution of this problem[1–9]. These studies include: (1) introducing flexible segments into the polymer chain, (2) replacing symmetrical aromatic rings by the unsymmetrical ones, which leads to a reduction in crystallinity, (3) introducing bulky pendant groups to minimize crystallization, (4) forming a non-coplanar structure, thereby making crystallization impossible.

Most aramids have been synthesized by the low-temperature solution polycondensation of aromatic diacid chloride with aromatic diamine in polar aprotic solvents. In another method, diamine–diacid chloride monomer pairs have also been used to prepare polyamides by interfacial condensation. The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids using triphenyl phosphite (TPP) and pyridine as condensing agents has been known to be a convenient method for the preparation of aromatic polyamides[10,11]. According to this procedure a high molecular weight polymer could be produced in a high yield and the preparation of diacid chlorides would be omitted.

Much attention has been focused recently on the preparation of fluorine-containing aromatic condensation polymers because of their unique properties and high performance[12,16]. The incorporation of fluorine atoms into polymer structures has been intensively explored in the past decade with the hope of fine-tuning several properties of particular interest. It is known that the increase in solubility, processability, transparency and the decrease in moisture absorption can be achieved by the incorporation of fluorine atoms in the polymers.

Although some work has been reported on the fluorine-containing aromatic polyamides[17–21], they were not as extensively investigated as the well-known fluorinated polyimides[22–32]. In this study, a synthesis of 5-(perfluorononenyloxy)isophthalic acid (I) was performed. From I and various aromatic diamines, a series of novel perfluorononenyloxy group containing aromatic polyamides were synthesized by direct polycondensation. The primary aim of this work was to illustrate the effect of perfluorononenyloxy group on the properties of polyamides, such as inherent viscosity, solubility, thermal properties, mechanical properties and moisture absorption. In addition, the effects of reaction conditions such as monomer concentration, reaction temperature, reaction time, the concentration of condensing agents, and the amount of metal salt on the inherent viscosity of the resulting polymers will also be investigated.

EXPERIMENTAL

Materials

5-Hydroxyisophthalic acid (from Aldrich, Milwaukee, WI), hexafluoropropene trimer (from Aldrich), and

* To whom correspondence should be addressed

triethyl amine (from Ferak, Germany) were used as received. Commercially obtained anhydrous lithium chloride was dried under vacuum at 180°C for 8 h. Triphenyl phosphite (TPP, from JANSSEN, UK) was purified by distillation under reduced pressure. 1,4-Phenylenediamine ($\mathbf{II}_a$, from JANSSEN), 1,3-phenylenediamine ($\mathbf{II}_b$, from JANSSEN), 4,4′-methylenedianiline ($\mathbf{II}_c$, from JANSSEN), 4,4′-oxydianiline ($\mathbf{II}_d$, from TCI, Tokyo, Japan), 4,4′-sulfonyldianiline ($\mathbf{II}_e$, from TCI), 4,4′-(hexafluoroisopropylidene)dianiline ($\mathbf{II}_f$, from Aldrich) were purified by vacuum sublimation. N-Methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide, and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

*Synthesis of 5-(perfluorononenyloxy)isophthalic acid (**I**)*

5-Hydroxyisophthalic acid (**I**) was synthesized according to the method reported[33], mp 321–322°C, yield 81.2%. The reaction is shown in *Scheme 1*. The infrared (i.r.) spectrum (KBr) of (**I**) exhibited absorptions at 3300–2500 cm^{-1} (COOH), 1701 cm^{-1} (C=O) and 1239 cm^{-1} (C–O–Ar). ^{19}F n.m.r. (DMSO-d_6) δ (ppm): 6.01 (3F, CF_3, *d*), −9.13 (6F, CF_3, *s*), −10.30 (6F, $CF)_3$, *d*), −105.57 (1F, CF, quart.), −107.80 (1F, CF, quint.). Mass spectrum *EI m/e* intensity (%): 612 (100, M^+). Anal. calcd for $C_{17}H_5F_{17}O_5$: C, 33.33%; H, 0.83%. Found C, 33.28%; H, 0.79%.

Polymerization

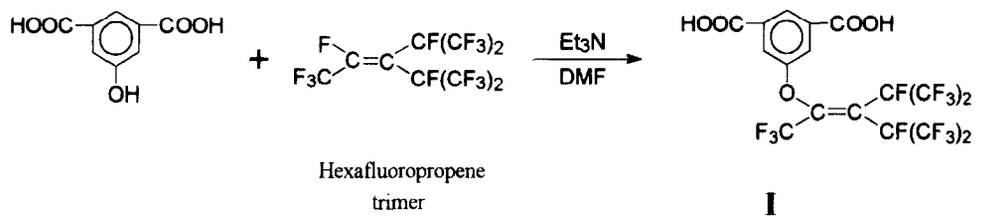
A typical example of the polycondensation is given below and the reaction is shown in *Scheme 2*.

*Polyamide $\mathbf{III}_d$ from **I** and $\mathbf{II}_d$*

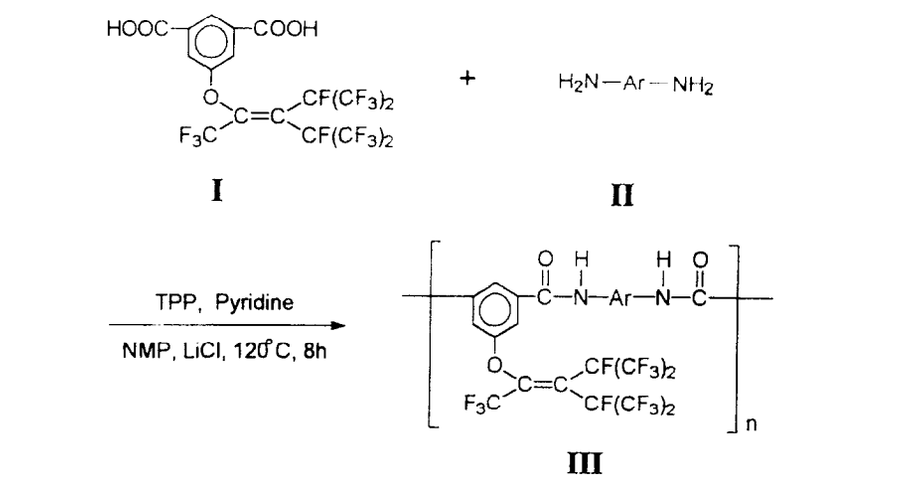
A mixture of 0.612 g (1 mmol) of **I**, 0.192 g (1 mmol) of $\mathbf{II}_d$, 0.4 g of lithium chloride, 0.62 g (2 mmol) of TPP, 2 ml of pyridine, and 8 ml of NMP was heated with stirring at 120°C for 8 h. The reaction mixture was then trickled into 400 ml of stirring methanol, giving rise to a fibrous precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100°C under vacuum. The yield was almost quantitative. The inherent viscosity of the polymer in DMAc was 1.51 dl g^{-1} measured at a concentration of 0.5 g dl^{-1} at 30°C. The i.r. spectrum exhibited absorptions at 3334 cm^{-1} (N–H) and 1656 cm^{-1} (C=O), characteristic of the amide group.

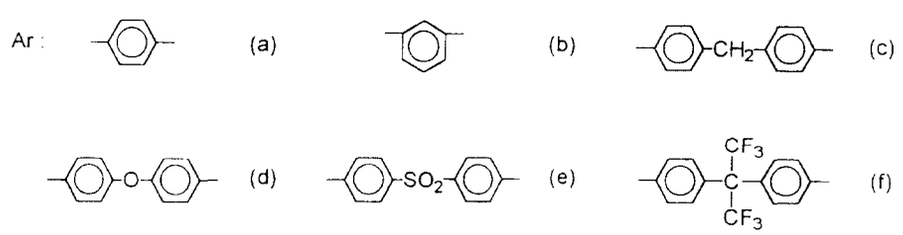
Measurements

The i.r. spectra were measured with a Jasco VALOR III spectrometer. In a typical experiment, an average of



Scheme 1





Scheme 2

20 scans per sample was made. The ^{19}F n.m.r. spectrum was measured with a Bruker AMX-400 n.m.r. spectrometer at 376.43 MHz, using dimethyl-d_6 sulfoxide as a solvent. The ^{19}F chemical shifts were calibrated by using benzotrifluoride as an internal standard. Elemental analyses were carried out with Heraeus CHN-Rapid element analyser. Mass spectrometric analyses were performed on a VG 70–250 S GC/MS spectrometer with a solid inlet. Melting points were obtained on a polarizing microscope (Laboratory Devices MEL-TEMP. II.) melting-point apparatus and were uncorrected. The inherent viscosities were measured with a Ubelohde capillary viscometer (Schott-AVS310). D.s.c. data were obtained from 8–10 mg samples in a nitrogen atmosphere at a flow rate of 30 $cm^3\ min^{-1}$ and a heating rate of 20°C min^{-1} using a DuPont 910 d.s.c. Thermogravimetric analyses (t.g.a.) were performed on a DuPont 951 thermal analyser using a heating rate of 20°C min^{-1} in N_2 at a flow rate of 50 $cm^3\ min^{-1}$. Dynamic mechanical analyses (d.m.a.) were made with a Perkin–Elmer DMA 7e. The storage modulus G' and $\tan\delta$ were studied when the sample was subjected to temperature scan mode at a programmed heating rate of 5°C min^{-1} from ambient to 350°C at a frequency of 1 Hz and an amplitude of 0.2 mm. A sample 10 mm in length, 2 mm in width, and approximately 0.2 mm in thickness was used. The wide-angle X-ray measurements were performed at room temperature with film specimens about 0.2 mm thick on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered Cu K_α radiation (40 kV, 15 mA). The scanning rate was 4° min^{-1}. Qualitative solubility was determined using 0.01 g of polymer in 2 ml of solvent. The amount of moisture absorption was measured at a relative humidity of 70%. Specimens were standing at room temperature, and the weight differences after 3 days were measured.

RESULTS AND DISCUSSION

Monomer synthesis

5-(Perfluorononenyloxy)isophthalic acid (**I**) was synthesized from 5-hydroxyisophthalic acid and hexafluoropropene trimer (*Scheme 1*). The elemental analysis, mass spectrometric analysis, characteristic peaks in the ^{19}F-n.m.r. spectrum, and characteristic bands in the i.r. spectrum correlate sufficiently well with the proposed 5-(perfluorononenyloxy)isophthalic acid (**I**) structure.

Effects of the reaction conditions on the inherent viscosity of $\mathbf{III}_d$

Effect of monomer concentration. Part I in *Table 1* reveals that the inherent viscosity of $\mathbf{III}_d$ increased with increasing monomer concentration initially. This may be attributed to the higher collisions between reactants in a concentrated solution than a diluted one. However, the effect levels off after the concentration of the monomer exceeded 0.10 M.

Effect of reaction time. Part II in *Table 1* indicates that the effect of reaction time on the inherent viscosity of $\mathbf{III}_d$ is rather small after the reaction exceeds 6 h. However, if the reaction is too long, the inherent viscosity does decrease slightly, perhaps as a result of the increase in side reaction. Notably, around 8 h is the optimum reaction time.

Effect of pyridine/NMP ratio. Part III in *Table 1* reveals that inherent viscosity of $\mathbf{III}_d$ increased with the addition of pyridine. Perhaps because of the pyridine, the triphenyl phosphite and the monomer produce a complex form which promoted polycondensation. Experimental results also indicated that the inherent viscosity of $\mathbf{III}_d$ would reach a maximum when the volume ratio of pyridine to NMP was 0.25.

Effect of reaction temperature. Part IV in *Table 1* reveals that if the temperature of reaction was lower than 60°C, the reactants would not dissolve and it would be difficult for the polycondensation reaction to proceed. The inherent viscosity of $\mathbf{III}_d$ increased markedly with increasing reaction temperature. However, when the reaction was carried out at 150°C, a reduction in inherent viscosity was observed. Excessive high temperature may have caused an adverse effect on the complex derived from lithium chloride and phenol and led to an increase in side reaction[11]. Therefore, the inherent viscosity of $\mathbf{III}_d$ was decreased.

Effect of lithium chloride. Part V in *Table 1* indicates that the addition of LiCl may improve the solubility of polyamides $\mathbf{III}_d$ by decreasing the hydrogen bond between the molecules. Moreover, LiCl may form a complex with the generated phenol to reduce the side reaction and thus yield a higher inherent viscosity[11]. However, if the quantity added is excessive, it may have an adverse effect on the solubility of $\mathbf{III}_d$. Experimental results indicate that the most suitable quantity of LiCl to be added is 5% (w/v). When LiCl was added excessively, a highly viscous swollen gel was generated during the reaction, and then the inherent viscosity of $\mathbf{III}_d$ decreased. This result is quite similar to that in previous literature[11].

Effect of TPP/monomer mole ratio. Part VI in *Table 1* indicates that when the mole ratio of TPP to **I** equals 2, the inherent viscosity of $\mathbf{III}_d$ reaches a maximum. Moreover, all of the polymers $\mathbf{III}_d$ had a high inherent viscosity when the mole ratio of TPP to **I** exceeded 2. However, when the ratio of TPP to **I** was less than 2, the inherent viscosity of $\mathbf{III}_d$ was small. This was probably due to a complex formation between **I** and TPP during polycondensation and when the mole ratio of TPP to **I** was 2, it could completely form a complex. This result is similar to that in previous literature[34].

Optimum reaction conditions for $\mathbf{III}_d$. From the above results, the most favourable reaction conditions for polyamide $\mathbf{III}_d$ are summarized: the monomer concentration of 0.10 M, pyridine/NMP ratio of 0.25, TPP/monomer mole ratio at 2, the quantity of LiCl to be added at 5% w/v, the reaction temperature at 120°C, and the reaction time of 8 h.

Synthesis of polymers

Various polyamides were synthesized from **I** with the corresponding aromatic diamines by using the most favourable conditions for the formation of $\mathbf{III}_d$. The reactions are shown in *Scheme 2*. All polyamides were obtained in almost quantitative yields. The inherent viscosities of polyamides are summarized in *Table 2*. The polyamides had inherent viscosities in the range of 0.81–1.42 dl g^{-1}. The inherent viscosities of the polyamides increased with decreasing rigidity of the polymer

Table 1 Effect of reaction conditions on polymerization

	Reaction conditions						Polymer		
Part	Monomer conc. (M)	Reaction time (h)	Pyridine/ NMP (v/v)	Reaction temp (°C)	LiCl (w/v%)	TPP/I (mol/mol)	Yield (%)	η_{inh} [a] (dl g^{-1})	Remark[b]
I	0.02	10	1/4	110	5	2.5	95.7	0.57	S
	0.04	10	1/4	110	5	2.5	96.5	0.73	S
	0.06	10	1/4	110	5	2.5	97.6	0.85	S
	0.08	10	1/4	110	5	2.5	98.1	0.94	S
	0.10	10	1/4	110	5	2.5	98.3	1.21	S
	0.12	10	1/4	110	5	2.5	98.2	1.24	S
	0.14	10	1/4	110	5	2.5	98.4	1.23	S
II	0.10	2	1/4	110	5	2.5	96.7	0.78	S
	0.10	4	1/4	110	5	2.5	97.8	0.95	S
	0.10	6	1/4	110	5	2.5	98.0	1.14	S
	0.10	8	1/4	110	5	2.5	98.3	1.25	S
	0.10	10	1/4	110	5	2.5	98.2	1.21	S
	0.10	12	1/4	110	5	2.5	98.4	1.18	S
III	0.10	8	0	110	5	2.5	95.9	0.69	S
	0.10	8	1/9	110	5	2.5	97.5	1.03	S
	0.10	8	1/4	110	5	2.5	98.3	1.25	S
	0.10	8	3/7	110	5	2.5	98.2	1.21	S
	0.10	8	2/3	110	5	2.5	98.1	1.19	S
	0.10	8	1	110	5	2.5	98.0	1.15	S
	0.10	8	3/2	110	5	2.5	97.9	1.13	
IV	0.10	8	1/4	60	5	2.5	17.2	0.15	S
	0.10	8	1/4	80	5	2.5	31.3	0.39	S
	0.10	8	1/4	100	5	2.5	90.4	1.23	S
	0.10	8	1/4	120	5	2.5	98.5	1.42	S
	0.10	8	1/4	140	5	2.5	98.4	1.33	S
	0.10	8	1/4	150	5	2.5	98.3	1.17	S
V	0.10	8	1/4	120	0	2.5	25.3	0.25	S
	0.10	8	1/4	120	2	2.5	97.3	1.17	S
	0.10	8	1/4	120	5	2.5	98.2	1.31	S
	0.10	8	1/4	120	8	2.5	98.1	1.12	S
	0.10	8	1/4	120	10	2.5	97.4	1.01	G
	0.10	8	1/4	120	15	2.5	96.2	0.83	G
VI	0.10	8	1/4	120	5	1.0	95.3	0.64	S
	0.10	8	1/4	120	5	1.5	97.8	0.97	S
	0.10	8	1/4	120	5	2.0	98.2	1.51	S
	0.10	8	1/4	120	5	2.5	98.3	1.45	S
	0.10	8	1/4	120	5	3.0	98.4	1.41	S
	0.10	8	1/4	120	5	3.5	98.3	1.40	S
	0.10	8	1/4	120	5	4.0	98.2	1.42	S

[a] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C
[b] S, homogeneous solution; G, viscous swollen gel

Table 2 Synthesis of polyamides[a]

Polymer	Yield (%)	η_{inh} [b] (dl g^{-1})
III$_a$	98.2	1.42
III$_b$	98.3	1.25
III$_c$	98.0	1.17
III$_d$	98.5	1.51
III$_e$	98.2	0.93
III$_f$	97.8	0.81

[a] Polymerization was carried out with 1 mmol of each monomer (0.1 M), 0.62 g (2 mmol) of TPP, 2 ml pyridine, and 0.4 g of LiCl in 8 ml NMP at 120°C for 8 h
[b] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C

backbone, depending on the diamines used. Elemental analysis of polyamides are shown in *Table 3*. In all cases, the carbon values were found to be lower than those calculated for the expected structures. The saturated amount of moisture absorption was in the range of 2.0–3.3 wt% at room temperature. The corrected values were in good agreement with the calculated ones after the absorbed moisture was included.

Properties of polymers

The solubility of these polymers was tested in various

Table 3 Elemental analysis of polyamides

Polymer	Formula (MW)		Elemental analysis (%) C	H	N	$H_2O\%$[a]
III_a	$(C_{23}H_9F_{17}N_2O_3)_n$	Calcd:	40.37	1.33	4.09	
	$(684.31)_n$	Found:	39.74	1.66	3.89	2.2
		Corrected[b]:	40.63	1.45	3.98	
III_b	$(C_{23}H_9G_{17}N_2O_3)_n$	Calcd:	40.37	1.33	4.09	
	$(684.31)_n$	Found:	39.28	1.74	3.63	2.8
		Corrected:	40.41	1.47	3.73	
III_c	$(C_{30}H_{15}F_{17}N_2O_3)_n$	Calcd:	46.53	1.95	3.62	
	$(774.43)_n$	Found:	45.02	2.28	3.63	3.0
		Corrected:	46.39	2.01	3.74	
III_d	$(C_{29}H_{13}F_{17}N_2O_4)_n$	Calcd:	44.86	1.69	3.61	
	$(776.41)_n$	Found:	43.08	1.99	3.38	2.6
		Corrected:	44.23	1.75	3.37	
III_e	$(C_{29}H_{13}F_{17}N_2O_5S)_n$	Calcd:	42.25	1.59	3.40	
	$(824.47)_n$	Found:	41.01	2.02	3.14	3.3
		Corrected:	42.41	1.71	3.25	
III_f	$(C_{32}H_{13}F_{23}N_2O_3)_n$	Calcd:	42.22	1.44	3.08	
	$(910.42)_n$	Found:	41.29	1.59	3.11	2.0
		Corrected:	42.13	1.49	3.17	

[a] $H_2O\% = (W - W_0)/W_0 \times 100\%$; W = weight of polymer sample after standing at room temperature for 3 days; W_0 = weight of polymer sample after drying in vacuum at 100°C for 12 h
[b] Corrected value = found value/(1 − $H_2O\%$) for C and N; corrected value = (found value − $H_2O\%$)/(1 − $H_2\%$) for H

Table 4 Solubility of polyamides[a]

Solvent[b]	Polymer III_a	III_b	III_c	III_d	III_e	III_f
NMP	+	+	+	+	+	+
DMF	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
Pyridine	+	+	+	+	+	+
m-Cresol	+	+	+	+	+	+
o-Chlorophenol	+	+	+	+	+	+
THF	−	−	−	+	+	+

[a] (+) Soluble at room temperature, (−) insoluble
[b] NMP: N-methyl-2-pyrrolidone; DMF: N,N-dimethylformamide; DMAc: N,N-dimethylacetamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran

Table 5 Thermal properties of polyamides

Polymer	T_g[a](°C) D.s.c.	D.m.a	Decomposition temperature[b] (°C) In N_2	In air	Char yield[c] (%)
III_a	308	319	526	513	62
III_b	275	282	515	501	67
III_c	287	293	498	488	63
III_d	285	291	506	495	64
III_e	303	311	517	503	66
III_f	301	314	513	499	69

[a] Glass transition temperature (T_g) measured by d.s.c. and d.m.a. at a heating rate of 20 and 5°C min^{-1}, respectively
[b] Temperature at 10% weight loss recorded by T_G at a heating rate of 20°C min^{-1}
[c] Residual weight% at 800°C in nitrogen

solvents at room temperature, and the results are summarized in *Table 4*. Almost all polyamides were readily soluble in polar aprotic solvents such as NMP, DMF, DMAc, DMSO, and even in pyridine, *m*-cresol and *o*-chlorophenol. Their high solubility is attributed to the introduction of bulky perfluorononenyloxy group to

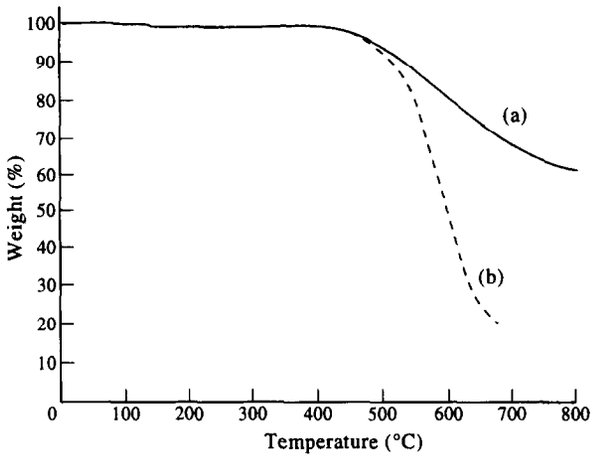


Figure 1 T_g curves for polyamide III_a at a heating rate of 20°C min^{-1} in (a) nitrogen and (b) air

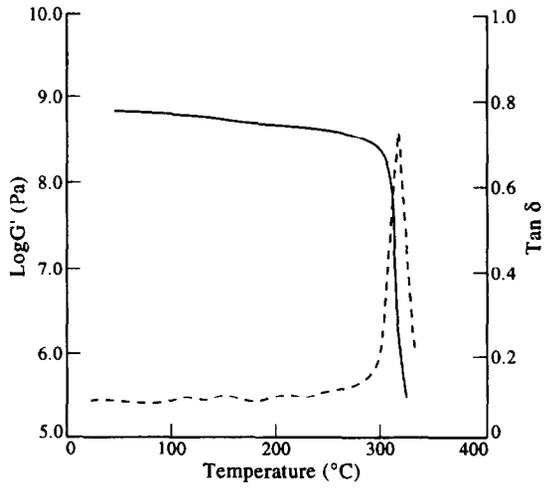


Figure 2 D.m.a. curves for III_e film at a heating rate of 5°C min^{-1}

the polymer backbone. Moreover, that polyamides $\mathbf{III}_d$, $\mathbf{III}_e$ and $\mathbf{III}_f$ are found to have higher solubility in tetrahydrofuran compared with other polyamides of similar structure. The higher solubility may be due to the presence of aryl ether, sulfonyl and hexafluoropropane moieties. However, all polymers were entirely insoluble in chloroform, benzene, and methanol. The X-ray diffraction studies of the polymers show that all polyamides exhibit an amorphous pattern. In general, most of the cardopolymers are amorphous, primarily because of the bulky pendant structure.

The thermal behaviour of these polyamides was evaluated by d.s.c., d.m.a. and t.g.a. The results are summarized in *Table 5*. Representative T_g curves of polyamide $\mathbf{III}_a$ are shown in *Figure 1*. All polyamides showed a similar decomposition behaviour and did not lose weight below 450°C in nitrogen. In nitrogen or air atmosphere, the 10% weight loss temperatures are about 498–526°C or 488–513°C, respectively. The char yield% of perfluorononenyloxy group containing polyamides in nitrogen atmosphere was more than 62 wt% even at 800°C.

Since the residual water or solvent and the history of thermal annealing may sometimes influence the first heating run of d.s.c. samples were at first heated to 250°C and the T_g was determined by the second heating. In the d.m.a. measurement, the peak of tan δ was identified as the glass transition temperature because a large decrease in G' occurred at this point. The polymers have glass transition temperatures of 275–308°C by d.s.c. and 282–319°C by d.m.a. The T_g decreased with decreasing rigidity and symmetry of the polymer backbone. Tough and flexible films of polyamides could be obtained by casting from their DMAc solutions. *Figure 2* shows the d.m.a. curves of polyamide $\mathbf{III}_e$ film at a heating rate of 5°C min^{-1}. All the perfluorononenyloxy group containing aromatic polyamides showed similar d.m.a. curves and maintained good mechanical properties ($G' \sim 10^8$ Pa) up to temperatures close to main transition well above 282°C.

CONCLUSIONS

5-(Perfluorononenyloxy)isophthalic acid (**I**) has been synthesized in 81.2% yield. Novel perfluorononenyloxy group containing aromatic polyamides could easily be obtained by direct polycondensation of **I** with various aromatic diamines by means of triphenyl phosphite in NMP–pyridine solution in the presence of lithium chloride. All polyamides are amorphous and have good solubility in many polar aprotic solvents. The amount of moisture absorption is very low compared to common polyamides. Moreover, perfluorononenyloxy group containing aromatic polyamides possess good thermal properties and excellent mechanical properties.

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