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NEW POLYMER SYNTHESES—41. SYNTHESIS OF THERMOPLASTIC AROMATIC POLY(ETHER–AMIDE)S FROM SILYLATED AMINOPHENOLS

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Abstract—*N,O*-Bistrimethylsilyl 3- or 4-aminophenol were condensed with iso-phthaloyl chloride or terepthaloyl chloride at temperatures ≤110°, so that a highly selective acylation of the amino groups took place. The resulting silylated diphenol amides were either isolated or condensed with 4,4′-difluorodiphenylsulphone in a "one-pot procedure" at temperatures up to 320°. Regardless of stepwise condensation or "one-pot procedure", inherent viscosities >0.45 dl/g were never obtained. However, polycondensation of *O*-trimethylsilyl diphenols prepared from *N*-methyl-4-aminophenol and iso- or terephthaloyl chloride yielded poly(ether–amide)s with inherent viscosities up to 0.8 dl/g. In this way poly(ether–sulphone), poly(ether–ketone)s with alternating sequences of amide ether and sulphone or ketone groups could be prepared. All poly(ether–amide)s are thermoplastic amorphous materials with glass-transition temperatures in the range of 150–210°. Cocondensation of silylated diphenols containing amide groups with other silylated diphenols allows a broad variation of properties including introduction of crystallinity, when oligo(ether–ketone) blocks are formed.

INTRODUCTION

Aromatic polyamides are of great technical interest because they possess a combination of useful properties such as high thermostability, low inflammability and excellent mechanical properties in the form of fibres [1–5]. Polyamides with a regular array of stiff monomer units such as Nomex® or Kevlar® are more or less crystalline materials with high melting points and low solubility in non-aggressive solvents. Incorporation of ether, sulphide or sulphone groups into aromatic polyamides enhances the flexibility of the back-bone, and reduces the crystallinity so that even completely amorphous, transparent materials may be obtained without any loss of thermostability or increase of inflammability. Polyamides containing ether, sulphide and/or sulphone groups may be easier to process from the melt and show better solubilities in various organic and inorganic solvents.

The synthesis of aromatic polyamides is usually based on the condensation of aromatic diamines [1–5] or their bistrimethylsilyl derivatives [6, 7] with dicarboxylic acid chlorides in aprotic, polar solvents such as dimethylformamide, *N,N*-dimethylacetamide or *N*-methylpyrrolidone. Addition of lithium chloride is required to prevent precipitation of the growing oligomers and termination of the chain growth. The present work was aimed at studying a new synthetic approach based on silylated aminophenols. Silylation of aromatic amino groups does not affect their nucleophilicity and acylation is easily feasible at room temperature [8, 9]. In contrast, silylation of OH-groups provides excellent protection against electrophilic attack at least at temperatures ≤150°C and in the presence of catalysts, esterification and etherification of silylated phenols (or alcohols) is feasible [10–13]. Thus, silylated aminophenols were supposed to enable the synthesis of aromatic poly(ether–amide)s in such a way that formation of amide bonds is conducted as a first step at moderate temperatures followed by polycondensation and formation of ether bonds at high temperatures [equations (1) and (2)]. Finally, it is worth noting that silylation in combination with distillation is an excellent means to purify aminophenols, in as much as free aminophenols are sensitive to oxidation and unstable on storage in the presence of air.

EXPERIMENTAL PROCEDURES

Materials

3- and 4-aminophenol,bisphenol-A and 4,4′-dihydroxydiphenylether were gifts of Bayer AG (4150 Krefeld-Uerdingen, B.R.D.), and were silylated with trimethylchlorosilane and triethylamine in boiling toluene without further purification. The silylated phenols were isolated by distillation. Isophthaloyl chloride and terephthaloyl chloride were also gifts of Bayer AG. They were distilled or recrystallized from toluene. *N*-Methylaminophenol sulphate (Aldrich Co., St Louis, Mo., U.S.A.) was converted to free *N*-methylaminophenol by means of 6 N NaOH (for silylation see below). 4,4′-Difluorobenzophenone and 4,4′-difluorodiphenylsulphone (DFDPS) (Aldrich Co., St Louis, Mo., U.S.A.) were used after two recrystallizations.

Silylation of N-methyl-4-aminophenol

Crude *N*-methyl-4-aminophenol (1 mol) was dissolved in 1.2 l. of dry, 1,4-dioxane; triethylamine (1.1 mol) was added at once and trimethylchlorosilane (1.1 mol) was added dropwise under stirring and heating. After complete addition, the reaction mixture was refluxed for 2 hr, cooled with ice and diluted with 400 ml ligroin. The reaction mixture was then filtered with exclusion of moisture and the product was isolated by distillation *in vacuo*.

Table 1. Yields and properties of silylated diphenols

Formula No.	Yield (%)	Melting point (°C)	Elemental formula (Formula weight)	Elemental analyses	C	H	N
4b	65	251–253	$C_{26}H_{32}N_2O_4Si_2$	Calcd	63.37	6.56	5.69
			(492.81)	Found	63.33	6.49	5.68
5a	85	204–206	$C_{26}H_{32}N_2O_4Si_2$	Calcd	63.37	6.56	5.69
			(492.81)	Found	63.29	6.57	5.75
5b	86	256–259	$C_{26}H_{32}N_2O_4Si_2$	Calcd	63.37	6.56	5.69
			(492.81)	Found	63.11	6.58	5.33
6a	78	125–127	$C_{28}H_{36}N_2O_4Si_2$	Calcd	64.58	6.97	5.38
			(520.78)	Found	64.28	7.06	5.36
6b	81	148–150	$C_{28}H_{36}N_2O_4Si_2$	Calcd	64.58	6.97	5.38
			(520.78)	Found	64.25	6.95	5.22

Yield: 87%; b.p. 90–92°/10^{-2} mbar.

Analyses calcd for $C_{10}H_{17}$ NOSi (195.34): C 61.49, H 8.77, N 7.17; found C 61.35, H 8.70, N 6.90.

^{1}H-NMR ($CDCl_3$): $\delta = 0.22$ (s, 9H), 2.78 (s, 3H), 3.45 (s, 1H), 6.62 (m, 4H) ppm. 3- and 4-aminophenol were silylated with trimethylchlorosilane and triethylamine in boiling toluene. Their properties agree with those reported in the literature [14, 15].

*Amide monomers derived from 3- or 4-aminophenol (**4b**, **5a, b**)*

An *N,O*-bistrimethylsilyl aminophenol (0.2 mol) was dissolved in 200 ml of dry toluene and a solution of isophthaloyl chloride or terephthaloyl chloride (0.1 mol) in 200 ml of dry $CHCl_3$ was added dropwise with stirring. The reaction mixture was stirred for 20 hr at 20–25°, then refluxed for 30 min and concentrated *in vacuo*. After portionwise addition of ligroin and cooling with ice, the crystallized products were isolated by filtration and recrystallized from 1,4-dioxane/ligroin. For yields and properties see Table 1.

*Amide monomers from N-methyl-4-aminophenol (**6a,b**)*

O-Trimethylsilyl-*N*-methyl-4-aminophenol (0.4 mol) and triethylamine (0.41 mol) were dissolved in 400 ml of dry 1,4-dioxane and a solution of isophthaloyl chloride terephthaloyl chloride (0.2 mol) in 200 ml of dry dioxane was added dropwise with stirring. The reaction mixture was refluxed for 0.5 hr, cooled with ice and filtered with exclusion of moisture. Hexamethyldisilazane (20 ml) was added and the filtrate was refluxed for 3–4 hr to sublime residual triethylamine hydrochloride into the condenser. Finally the dioxane solution was concentrated *in vacuo*, and the product crystallized by portionwise addition of ligroin with cooling with ice.

Polycondensations

(A) With purified monomers. A silylated amide monomer (40 mmol), DFDPS (40 mmol) and 100 mg cesium fluoride were weighed into a cylindrical glass reactor equipped with stirrer, gas inlet and outlet tubes. The reaction vessel was rapidly heated to 180–190° where the condensation started. The temperature was then gradually raised to 320° (within 2.0–2.5 hr). The liberated fluorotrimethylsilane was removed with a slow stream of N_2. Finally, the condensation was completed at 320° by applying vacuum for 30 min. The condensate was dissolved in a mixture of dichloromethane and trifluoroacetic acid (4:1 by volume) and precipitated into cold methanol.

(B) With crude monomers. An *N,O*-bistrimethylsilyl aminophenol (50 mmol) was added dropwise to a solution of isophthaloyl chloride or terephthaloyl chloride (25 mmol) in 40 ml of dry toluene. The reaction mixture were refluxed for 1 hr and concentrated *in vacuo*. pH DFDPS (25 mmol) and 100 mg KF were added and this mixture was rapidly heated under N_2 to 180–200° and then gradually to 320°. The reaction product was worked up as described above.

(C) "One-pot procedure". An *N,O*-bistrimethylsilyl aminophenol (50 mmol) was added dropwise to a solution of DFDPS ph (25 mmol) and dicarboxylic acid chloride (25 mmol) in 40 ml of dry toluene. The reaction mixture was refluxed for 1 hr and concentrated *in vacuo*. KF (100 mg) was added to the residue which was then heated at 180° and finally to 320°.

(D) Cocondensation. A silylated amide monomer (25 mmol), a silylated diphenol (25 mmol), DFDPS or 4,4′-difluorobenzophenone (50 mmol) and 50 mg cesium fluoride were weighed into a cylindrical glass reactor and condensed as described for (A).

Measurements

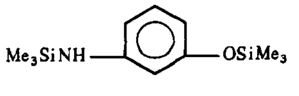
The inherent viscosities were measured with an automated Ubbelohde viscometer at 20°. The i.r.-spectra were measured with KBr discs on a Nicolet 20 SXB FTIR Spectrometer. The DSC-measurements were conducted with a Perkin Elmer DSC-4 in Al pans under N_2 at a heating rate of 20°/min.

RESULTS AND DISCUSSION

(A) Syntheses of monomers containing amide groups

3- and 4-aminophenol were silylated as usual with trimethylchlorosilane and triethylamine in boiling toluene and isolated by distillation. Under the same reaction conditions, only a *O*-monosilylated derivative of *N*-methyl 4-aminophenol (**3**) was obtained. The acylation of **1** and **2** with isophthaloyl chloride or terephthaloyl chloride in dry toluene or dioxane was an exothermic reaction which was completed by brief refluxing of the reaction mixture. The acylation of **3** with isophthaloyl chloride or terephthaloyl chloride was conducted in the presence of triethylamine in boiling 1,4-dioxane. Yields and properties of the silylated diphenols **4b**, **5a**, **b** and **6a**, **b** are listed in Table 1.

The silylated diphenol **4a** was never isolated and purified. Because of its good solubility in organic solvents such as toluene or dioxane, it was prepared *in situ* and used for syntheses of poly(ether–amide)s by "one-pot procedures".



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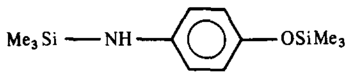

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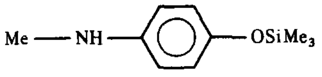

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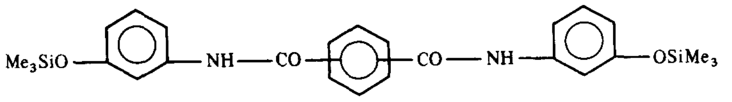
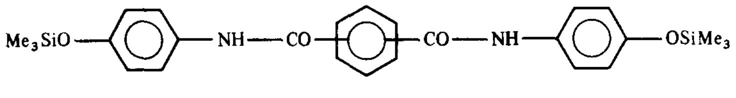


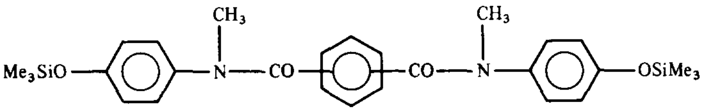
a: Isophthalic acid
b: Terephthalic acid

4 a,b



a: Isophthalic acid
b: Terephthalic acid

5 a,b

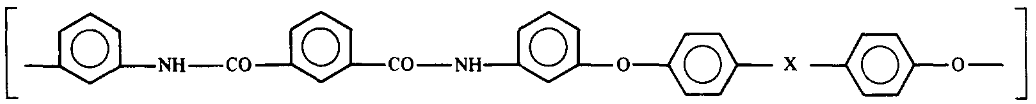


a: Isophthalic acid
b: Terephthalic acid

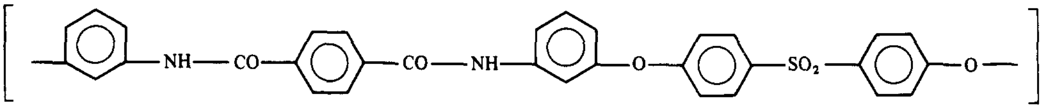
6 a,b

Poly(ether–amide)s based on 3- or 4-aminophenol

The poly(ether–amide)s **7–9** were prepared from silylated diphenols **4a, b** or **5a** by thermal bulk condensations with DFDPS or 4,4′-difluorobenzophenone. Three condensation procedures were compared. First, the isolated monomer **4b** or **5a** was subjected to bulk condensation with the fluoroaromatics in the presence of CsF in analogy with previously described syntheses of poly(ether–sulphone)s [12] or poly(ether-ketone)s [13] (method A in Table 2). Second, monomer **4a** or **4b** was prepared in toluene; after removal of solvent and chlorotrimethylsilane, the crude monomer **4a** or **4b** was condensed with DFDPS ph in the presence of KF (method B in Table 2). Third, monomer **4a** was prepared in toluene in the presence of a fluoroaromatic; after evaporation of solvent and



7 a,b **a**: X = SO_2
b: X = CO



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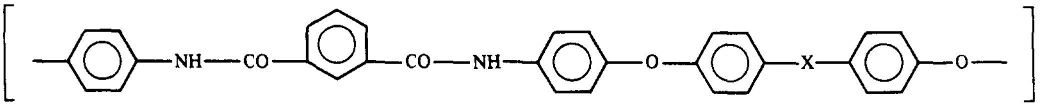


a: X = SO_2
b: X = CO

9 a,b

Table 2. Reaction conditions, yields and properties of poly(ester-amide)s prepared from silylated diphenols **4a**, **b** and **5a**

Polymer formula	Synth. Method	Temp.[a] (°C)	Time[a] (hr)	Yield (%)	η_{inh}^{b} (dl/g)	T_g^c (°C)	Elemental formula (Formula weight)	Elemental analyses	C	H	N
7a	A	230, 280 320	60, 30 60	85	0.20	195	$C_{32}H_{22}N_2O_6S$ (562.65)	Calcd Found	68.31 66.66	3.95 3.81	4.98 4.86
7a	B	260, 280 300, 320	30, 30 30, 30	95	0.35	216	$C_{32}H_{22}N_2O_6S$ (562.65)	Calcd Found	68.31 67.60	3.95 3.91	4.98 4.81
8	B	180, 200, 240 260, 280, 320	30, 30, 15 15, 15, 45	87	0.33	213	$C_{32}H_{22}N_2O_6S$ (562.65)	Calcd Found	68.31 67.50	3.95 3.81	4.98 4.85
8	C	210, 250, 280 320, 340	20, 30, 25 25, 25	96	0.38	213	$C_{32}H_{22}N_2O_6S$ (562.65)	Calcd Found	68.31 67.66	3.95 3.90	4.98 4.91
8b	C	240, 260 280	20, 20, 80	96	0.35	196	$C_{33}H_{22}N_2O_5$ (526.55)	Calcd Found	75.27 74.11	4.22 4.08	5.32 5.20
9a	A	220, 250, 280 320, 340	30, 10, 10 30, 60	85	0.34	230	$C_{32}H_{22}N_2O_6S$ (562.65)	Calcd Found	68.31 66.93	3.95 3.75	4.98 4.92
9a	A	220, 280 320, 340	30, 10 10, 90	83	0.50	249	$C_{32}H_{22}N_2O_6S$ (562.65)	Calcd Found	68.31 67.72	3.95 3.92	4.98 4.95
9b	A	220, 280 320	60, 15 30	70	0.33	188	$C_{33}H_{22}N_2O_5$ (526.57)	Calcd Found	75.27 73.47	4.22 4.17	5.32 5.44

[a] Cond. of isolated silyl monomers.
[b] Cond. of crude silyl monomers.
[c] One-pot procedure.

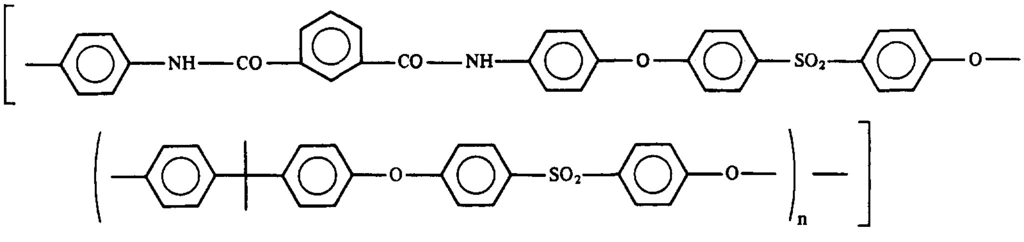
Table 3. Yields and properties of poly(ether-amide)s prepared from DFDPS ph and silylated diphenols **5a** or **5b** in combination with bistrimethylsilyl bisphenol-A

Silylated diphenols molar ratio	Yield (%)	η_{inh}^{a} (dl/g)	T_g^b (°C)	Elemental formula (Formula weight)	Elemental analyses	C	H	N	S
5a + Bis-TMS-bisphenol-A (1:1)	92	0.40	195	$C_{59}H_{44}N_2O_{10}S_2$ (1005.22)	Calcd Found	70.50 69.78	4.42 4.32	2.79 2.83	6.38 6.45
5a + Bis-TMS-bisphenol-A (1:3)	74	0.45	205	$C_{113}H_{88}N_2O_6S_4$ (1890.36)	Calcd Found	71.80 71.36	4.70 4.66	1.48 1.56	6.78 7.01
5b + Bis-TMS-bisphenol-A (1:1)	76	0.20	178	$C_{59}H_{44}N_2O_{10}S_2$ (1005.22)	Calcd Found	70.50 69.67	4.42 4.30	2.79 3.01	6.38 6.06
5b + Bis-TMS-bisphenol-A (1:3)	60	0.21	180	$C_{113}H_{88}N_2O_6S_4$ (1890.36)	Calcd Found	71.80 71.43	4.70 4.71	1.48 1.65	6.78 6.66

[a] Measured with $c = 2$ g/l at 20° in CH_2Cl_2/CF_3CO_2H (4:1 by volume).
[b] From DSC measurements with a heating rate of 20°/min.

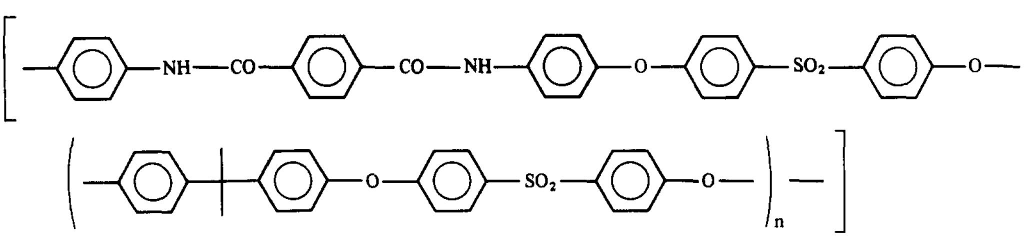
chlorotrimethylsilane, the crude residue and a catalytic amount of KF was gradually heated to 320° (method C in Table 2). This latter method may be considered to be a true "one-pot procedure". All condensations led to good yields, yet the inherent viscosities all fell in the range of 0.3–0.5 dl/g.

A particular advantage of the synthetic strategy of this work is the easy modification of the aromatic diamine unit. Cocondensation of monomers **4a, b** or **5a, b** with various silylated diphenols and activated fluoroaromatics should result in oligoether block containing in principle two primary amide end-groups (in the form of amide linkages). In order to demonstrate the usefulness of this strategy, monomers **5a** and **5b** were cocondensed with bistrimethylsilyl bisphenol-A and DFDPS ph. The data of Table 3 show that poly(ether-amide)s of structure **10** or **11** were indeed obtained. Again high yields but low molecular weights were found. Since under similar reaction conditions, poly(ether-sulphone)s or poly(ether-ketone)s with inherent viscosities above 1.0 dl/g were synthesized, the results of Tables 2 and 3 suggest that the amide groups of monomers **4a, b** and **5a, b** somehow affect the condensation.



a: n = 1
b: n = 3

10a,b



a: n = 1
b: n = 3

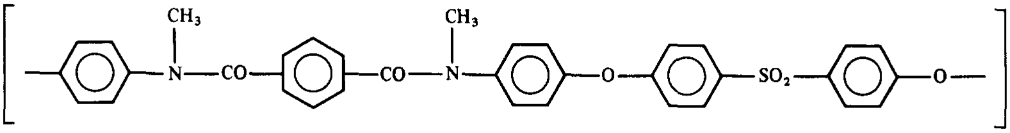
11a, b

Poly(ether–amide)s based on N-methyl-4-aminophenol

The syntheses of poly(ether–amide)s derived from monomers **6a** or **6b** have two aims. First, it should be ascertained whether amide groups with N-proton affect the polycondensation. Second, solubilities, crystallinities and glass transition temperatures of aromatic poly(ether–amide)s with similar structures with and without H-bonds should be compared.

When monomers **6a** and **6b** were condensed with DFDPS at temperatures up to 340°, polyamides (structures **12** and **13a**) with inherent viscosities >0.5 dl/g were indeed obtained (Table 4). Only a condensation conducted with a slight excess of DFDPS gave a lower viscosity. Therefore, further condensations were conducted using 4,4′-difluorobenzophenone as reaction partner. Yet the resulting poly(ether–ketone–amide) (**13b**) only showed a viscosity of 0.41 dl/g. When the condensation was repeated with 1% excess of 4,4′-difluorobenzophenone, the viscosity of the reaction product was even lower (0.38 dl/g). These results indicate that sublimation and side reactions of the fluoroaromatics are not the limiting factors for the molecular weights.

Finally two poly(ether–ketone–amide)s with short ether–ketone blocks were prepared by cocondensation of monomer **6b** with 4,4′-bistrimethylsiloxy-



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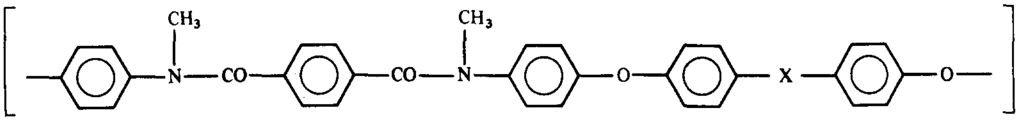
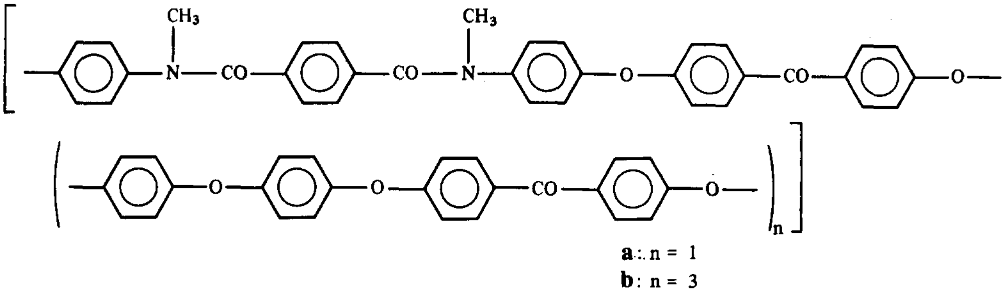


13 a,b a: X = SO_2
b: X = CO

Table 4. Reaction conditions, yields and properties of poly(ether–amide)s based on *N*-methyl-4-aminophenol (prepared from **6a** or **b** with various difluoroaromatics)

Polymer formula	Temp.[a] (°C)	Time[a] (hr)	Yield (%)	η_{inh}^{b} (dl/g)	T_g^c (°C)	Elemental formula (Formula weight)	Elemental analyses			
								C	H	N
12	190, 200, 240 260, 290, 340V	30, 10, 20 40, 15, 40V	87	0.60	190	$C_{34}H_{26}N_2O_6S$ (590.65)	Calcd Found	69.14 69.01	4.44 4.45	4.74 4.73
13a	180, 190, 250 250–340, 340V	60, 15 20, 75V	66	0.80	205	$C_{34}H_{26}N_2O_6S$ (590.65)	Calcd Found	69.14 68.27	4.44 4.33	4.74 4.66
13b	210, 220 250–280, 280V	60, 20 40, 60V	84	0.41	178	$C_{35}H_{26}N_2O_5$ (554.60)	Calcd Found	75.80 74.37	4.73 4.90	5.05 4.99
14a	220, 240, 260 280, 280V	60, 15, 15 15, 30V	91	0.50	160	$C_{60}H_{42}N_2O_9$ (935.00)	Calcd Found	77.08 76.26	4.53 4.78	3.00 3.08
14b	220, 240, 260 300, 300V	60, 30, 15 20, 30V	88	0.81[d]	155	$C_{110}H_{74}N_2O_{17}$ (1695.80)	Calcd Found	77.91 76.92	4.40 4.69	1.65 1.73

[a] The reaction temperature was raised in a stepwise manner.
[b] Measured with $c = 2$ g/l at 20° in CH_2Cl_2/CF_3CO_2H (4:1 by volume).
[c] From DSC measurements with a heating rate of 20°/min.
[d] Measured with $c = 2$ g/l at 20° in CH_2Cl_2/CH_3SO_3H (4:1 by volume).



14a,b

diphenylether (**14a** and **14b**). The condensations yielded again inherent visocisites around 0.5 and 0.8 dl/g (Table 4). The lower viscosity of **14a** may result from the lower reaction temperature and shorter reaction time.

Properties of poly(ether–amide)s

i.r. Spectra are well suited for characterization of the chemical structures of all poly(ether–amide)s and for differentiation between poly(ether–amide)s derived from 3- or 4-aminophenol and those derived from *N*-methyl-4-aminophenol. As demonstrated in Fig. 1, the NH-stretch vibrations give rise to a strong band at 3100–3600 cm − 1 for polyamides such as 7-9, whereas they are absent for polyamides derived from monomers **6a** or **6b** (Fig. 2). When ether–ketone blocks are present, the ketone-stretch vibration absorbs at nearly the same wave length as the amide stretch vibration (1653 cm^{-1}, Fig. 2). However, the molar fraction of the ether–ketone blocks is indicated by the intensity of the C—O and C=C stretch vibrations at *ca* 1250 and 1490 cm^{-1} (Fig. 2).

DSC measurements conducted at a heating rate of 20°/min revealed that all poly(ether–amide)s of this work with the exception of **14b** are amorphous materials. Even annealing for 1 hr at 200° did not result in crystallization. The glass transition temperatures (T_gs) listed in Tables 2–4 show the following tendencies. Poly(ether–amide)s prepared from **4a, b** or **5a, b** do not show clear differences. Higher T_gs were found for polymers containing SO_2 groups (**7a, 9a**) than for those with CO groups (**7b, 9b**). For the poly(ether–sulphone–amide)s **10a, b** and **11a, b** again a clear tendency is lacking. Interestingly, the absence of H-bonds does not lower T_g as indicated by poly(ether–amides) **12** and **13a, b** (Table 4). Incorporation of ether–ketone blocks [**14a** and **14b** reduces T_g towards the lower T_g of the pure poly(ether–ketone)]. The long ether–ketone blocks of **14b** render this polymer a slowly crystallizing material as demonstrated by the DSC traces of Fig. 3. Finally, it is worth noting that all poly(ether–amide)s of this work were soluble in mixtures of chloroform or

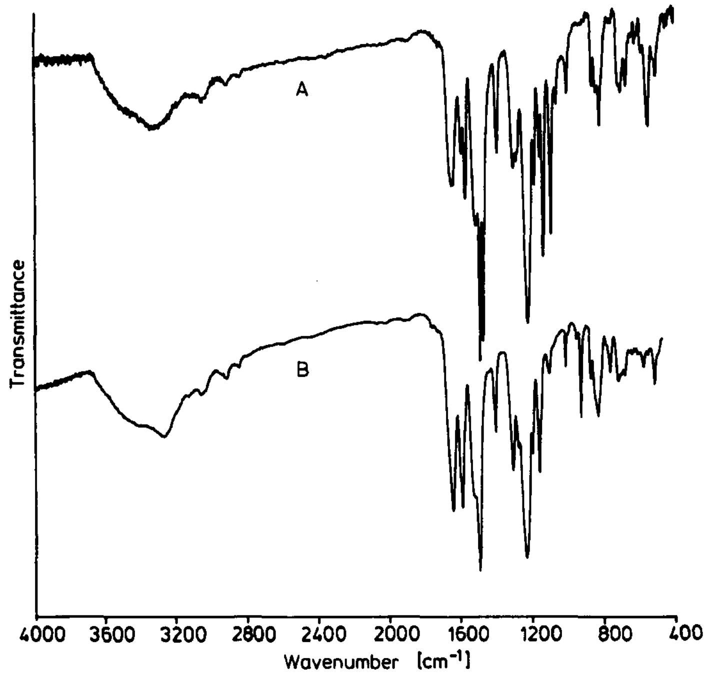


Fig. 1. i.r. Spectra (measured with KBr discs) of (A) poly(ether-ketone–amide) **9b** and (B) poly(ether–sulphone–amide) **9a**.

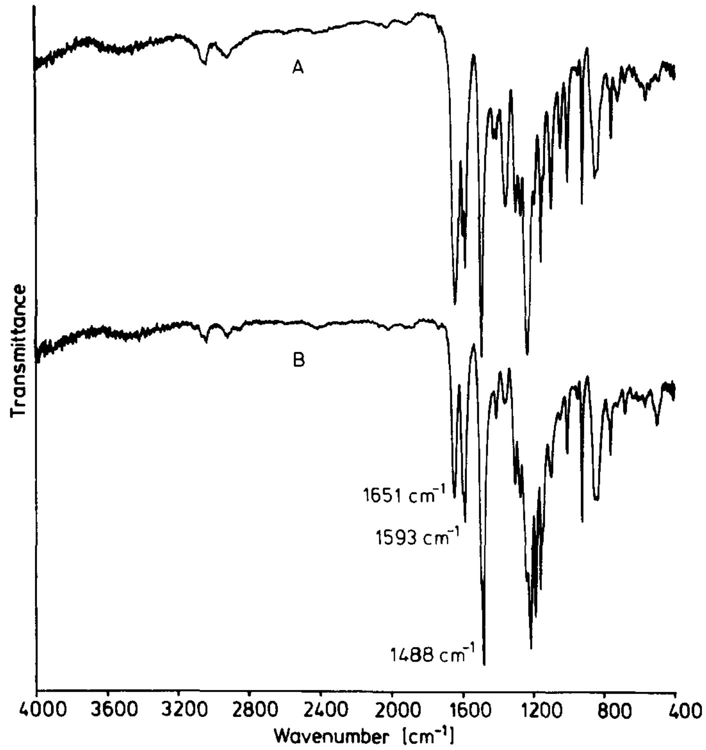


Fig. 2. i.r. Spectra (measured with KBr discs) or (A) the poly(ether–ketone–amide) **13** and (B) poly(ether–ketone–amide) **14b**.

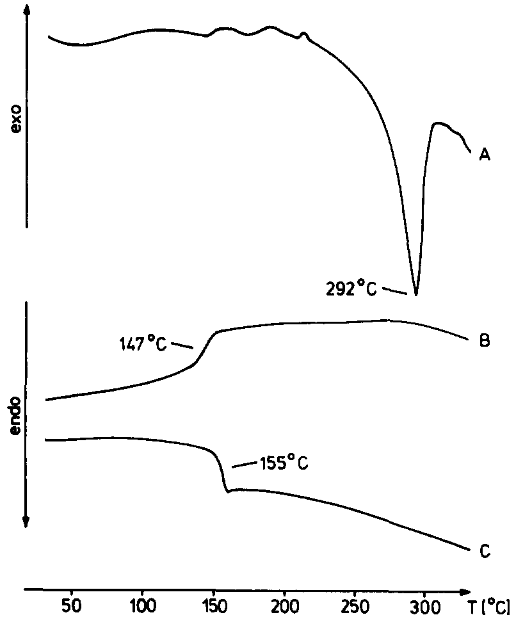


Fig. 3. DSC measurements (heating and cooling rate 20°/min) of poly(ether-ketone-amide) **14b**.

dichloromethane and trifluoroacetic acid in contrast to polyamides such as Nomex or Kevlar. In the case of **12** and **13a, b**, even solubility in pure dichloromethane was observed.

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