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Polyquinolines and polyanthrazolines: synthesis and properties

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Contents

Abstract. The advances in the synthesis and studies of the properties of polyquinolines and polyanthrazolines are reviewed. The main attention is given to polymers prepared by the Friedlander reaction from the AB- and AA–BB-type monomers, *viz.*, rigid-rod polyquinolines, polyether quinolines, cardo polyquinolines and polymers containing tetraphenylsilyl and perfluorotetramethylene fragments. The approaches to the design of reactive oligo- and polyquinolines, the terminal groups of which have a curing effect on these systems, are considered. The use of polyquinolines for the preparation of composite and electroluminescent materials is discussed. The bibliography includes 155 references.

I. Introduction

Polyheteroarylenes (PHA) based on quinolines (polyquinolines, PQ) and anthrazolines (polyanthrazolines, PAZ) present substantial interest for both fundamental and applied investigations [1-6] due to their high heat resistances and high thermal stabilities.[7]

In the early stage (the 1970's), PQ and PAZ were used predominantly for the preparation of polymeric materials (films, fibres, composites, *etc.*) for the aerospace industry. Later (the 1990's), more attention was placed on their use for the preparation of materials for high-tech industrial domains, for optoelectronics, in particular.[8,9]

The results obtained in both stages of the investigations of these compounds are considered in this review.

II. Synthesis of polyquinolines and polyanthrazolines manifesting high heat resistances and high thermal stabilities

The past four decades have been marked by the synthesis of diverse PHA.[10-19] Some of them, *e.g.*, polyimides,[20-25] polyazoles,[26-30] polyphenylquinoxalines,[31-33] *etc.*), have found application in the design of materials retaining their operating characteristics at temperatures around 300 °C. To a considerable extent, such compounds satisfied the needs of the aircraft industry and rocket engineering for thermostable polymeric materials, but more recent demands are for materials able to withstand higher temperatures. Therefore, the efforts of investigators have switched over to a search for polymers surpassing the well-known PHA in heat resistances and thermal stabilities. Identification of the least stable fragments in the polymeric chains of conventional PHA and their replacement by more thermostable units seemed to be the most rational solution to this problem.

In-depth studies of the decomposition mechanisms of different classes of PHA have shown that the decomposition involves predominantly the heterocyclic fragments,[34-42] which suggests that it is the heterocyclic fragments of PHA that should be replaced by more thermostable components. A comparison of the thermal stabilities of various carbo- and heterocycles [43,44] has shown that quinoline is one of the most heat-resistant compounds.[44] The first attempt at synthesising polymers containing quinoline rings in the main chains starting from benzidine and bis(β-diketones), *viz.*, 4,4′-bis(acetoacetyl)diphenyloxide and 4,4′-bis(acetoacetyl)diphenylethane, was undertaken by Korshak *et al.*[45] (Scheme 1).

The polyanils formed in the first step were soluble in cresol, DMSO and H_2SO_4 (the reduced viscosities of their solutions in H_2SO_4 were 0.6–0.8 dl g^{-1}), while polyquinolines prepared by thermal cyclisation of polyanils *in vacuo* were insoluble in either of these solvents, which significantly limited their processing into articles.

Some time later, Shopov[46] succeeded in obtaining a soluble PQ by extrapolation of the Pfitzinger reaction[47] to the polymer synthesis.

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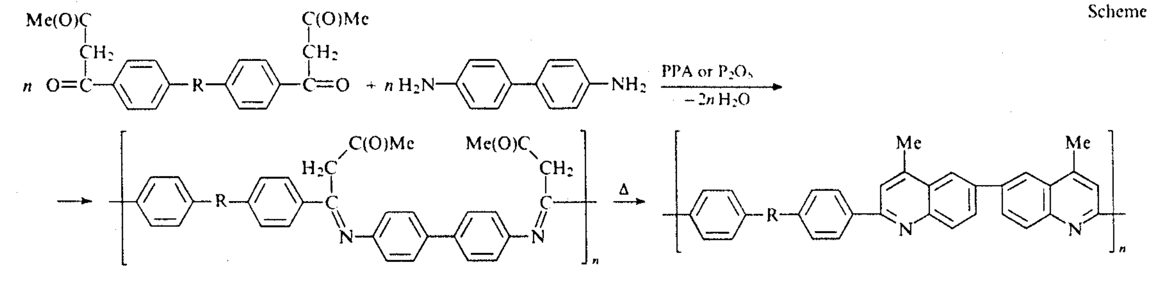
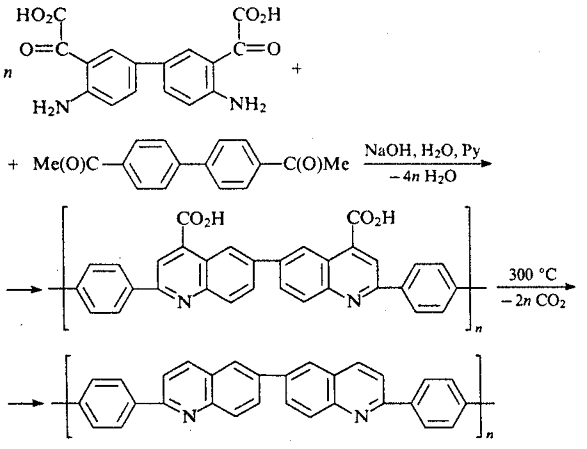
Scheme 1

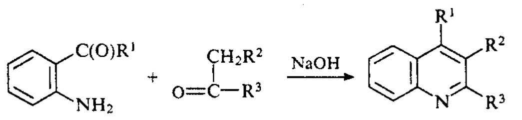


R = O, CH_2CH_2; PPA is polyphosphoric acid.



The carboxy-substituted PQ represented a dark-brown powder which was soluble in DMF, pyridine, DMSO and aqueous alkali and underwent decarboxylation to the target PQ upon heating to 300 °C. Unfortunately, no comprehensive analysis of the properties of the polymers obtained was reported.[45,46]

Yet another approach to the synthesis of PQ was realised by Stille *et al.*,[1-5,48-52] this was based on the Friedlander reaction.[1-5,53-56] In its classical version, this reaction consists of an alkali-catalysed condensation of aromatic *o*-aminocarbonyl compounds with methylene ketones.[54-56]

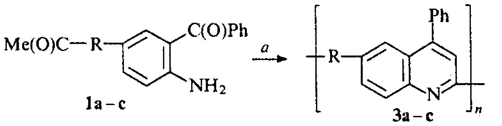


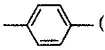
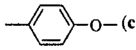
Formally, this reaction results in a Schiff base which undergoes subsequent aldol condensation[57] with involvement of the carbonyl group and the reactive methylene group.[58] It was shown[59-64] that acids are as effective as catalysts of the formation of the quinoline rings as alkalis.

The preparation of PQ by the Friedlander reaction may include both homocondensation of compounds containing *o*-aminocarbonyl and oxomethylene fragments[51,65-68] and co-condensation of bis(*o*-aminocarbonyl) and bis(oxomethylene) derivatives.[48-52] In both cases, synthesis of the starting compounds presents the major problem, since substituted *o*-aminocarbonyl derivatives are difficult to access.[58,64]

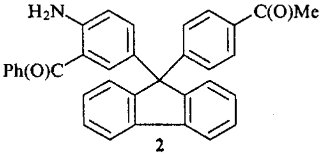
1. Synthesis of polyquinolines by homocondensation of AB-type monomers

5-Acetyl-2-aminobenzophenone (**1a**),[51,65,69] 4′-acetyl-4-amino-3-benzoylbiphenyl (**1b**),[65] 4′-acetyl-4-amino-3-benzoyldiphenyl oxide (**1c**)[66] and 9-(4-acetylphenyl)-9-(4-amino-3-benzoylphenyl)fluorene (**2**) were used as the AB monomers in the synthesis of PQ.[68] Homocondensation of the first three compounds in *m*-cresol – polyphosphoric acid (PPA) or *m*-cresol – P_2O_5 mixtures (according to ^{31}P NMR data, these systems represent mixtures of mono- and di-*m*-cresyl phosphate)[52] at 120 – 130 °C yielded the fibre-forming PQ **3a – c** containing lateral phenyl groups.



R is a bond (**a**),  (**b**),  (**c**).

(*a*) PPA (or P_2O_5), *m*-cresol, 120 – 130 °C;



2

5-Acetyl-2-aminobenzophenone (**1a**) yielded the polyquinoline **3a**, which precipitated from the reaction mixture after 24 – 30 h. The intrinsic viscosities of its solutions in sulfuric acid were 1.3 – 3.6 dl g^{-1}. According to X-ray diffraction data, the crystallinity of the polymer **3a** was close to 65%, as a result of which it was soluble only in sulfuric acid. The high crystallinity of the polymer **3a** is largely determined by the symmetry of its macromolecule due to the formation of only one geometric isomer of the PQ in the Friedlander reaction,[51,54] while three isomers of polyquinoxalines, which are structurally similar to polyquinolines, are formed.[31-33]

Dynamic thermogravimetric analysis (TGA, ΔT = 5 °C min^{-1}) revealed that the mass loss of the polymer **3a** began at 520 °C in air and at 570 °C in nitrogen; at 800 °C, the mass losses were 20%. Such a high thermal stability of polymer **3a** is explicable, especially if one takes into consideration the high extent of cyclisation[51] and high thermal stability of the quinoline ring.[44] The high rigidity and crystallinity of the PQ formed account for its high glass-transition (Tg = 415 °C) and melting (T_m = 552 °C) temperatures[1,49,65] and limited solubility significantly complicates its processing into articles.

The PQ **3b**, the homocondensation product of 4′-acetyl-4-amino-3-benzoylbiphenyl (**1b**), manifests similar characteristics. The comparative characteristics of the polymers **3a,b** are listed in Table 1.

Somewhat better solubilities of rigid-rod homocondensation products of the AB-type monomers could be achieved if copolycondensation of compounds **1a** and **1b** was carried out. Thus the random copolymer of 5-acetyl-2-aminobenzophenone (**1a**) with 4′-acetyl-4-amino-3-benzoylbiphenyl (**1b**) was soluble not only in sulfuric acid, but also in trifluoroacetic acid (see Table 1). The observed better solubilities of rigid-rod random copolymers in comparison with those of homopolymers is in keeping with previously reported data.[70,71]

Table 1. Some characteristics of polyquinolines **3a**,**b**.[65]

Polymer	Solubility[a]	$[\eta]$ /dl g^{-1} (see [b])	T_g /°C (DSC [c])	T_m /°C	T_d /°C (see [d]) (TGA)	
					air	N_2
3a	H_2SO_4	3.6	415	552	520	570
3b	H_2SO_4	11.6	–	580	605	610
See [e]	CF_3CO_2H, H_2SO_4	4.9	330	520	555	580

[a] In this case, the ability of the solvent to form 5% solutions of polymers is meant.

[b] The intrinsic viscosities $[\eta]$ were measured in concentrated H_2SO_4 at 25 °C.

[c] DSC is differential scanning calorimetry.

[d] The temperature at which the initial mass loss of the polymer was observed.

[e] A random copolymer (1 : 1) of the monomers **1a** and **1b**.

The polyquinoline **3c** based on 4′-acetyl-4-amino-3-benzoyldiphenyl oxide (**1c**) is soluble in chloroform, THF and DMF, and holds more promise as regards its processing. The high solubility of this polyheteroarylene may be attributed to the presence of ether bonds, which is consistent with the results of other authors.[72] The glass-transition temperature (Tg) of polymer **3c** is 235 °C; however, this compound has an amorphous structure and does not melt according to data from differential scanning calorimetry (DSC); its initial decomposition temperature is 513 °C.

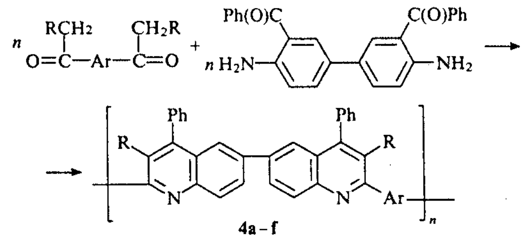
The introduction of 'cardo' groups,[73] of fluorene groups in particular, is yet another approach to the enhancement of the solubilities of PQ derived from AB-type monomers.[68] The corresponding monomer, 9-(4-acetylphenyl)-9-(4-amino-3-benzoylphenyl)fluorene (**2**) was prepared by an eight-step synthesis starting from fluorenone. Homocondensation of this monomer in a mixture of *m*-cresol with di-*m*-cresyl phosphate afforded a cardo polyquinoline containing fluorene groups. This polymer is amorphous, it is soluble in strong acids and *m*-cresol, and its Tg is 365 °C. However, the low characteristic viscosity of solutions of this polymer ($[\eta]$ = 0.24 dl g^{-1}) is its drawback.

A much larger panel of PQ has been synthesised by reactions of bis(*o*-aminocarbonyl) compounds with diacylarylenes and diphenacylarylenes.

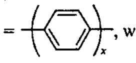
2. Synthesis of polyquinolines by co-condensation of bis(*o*-aminocarbonyl) compounds with diacyl- and diphenacyl arylenes

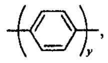
a. Rigid-rod polyquinolines

Polycondensation of 3,3′-dibenzoylbenzidine with various diacylarylenes affords rigid-rod poly(2,6-quinolines) with high glass-transition temperatures and limited solubilities.[65]



4a – f

R = H, Ar = , where x = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**);

R = Ph, Ar = , where y = 1 (**e**), 2 (**f**).

Some characteristics of rigid-rod PQ **4a – f** are listed in Table 2. Anisotropic solutions of these polymers in a *m*-cresol – di-*m*-cresyl phosphate mixture were used for the spinning of high-quality fibres.[65]

Poly(3,6-quinolines) **5a**,**b** were prepared by the reaction of 3,3′-dibenzoylbenzidine with diphenacylarylenes, *viz.*, 1,4-diphenacylbenzene and 4,4′-diphenacylbiphenyl in a *m*-cresol – di-*m*-cresyl phosphate mixture.[74]

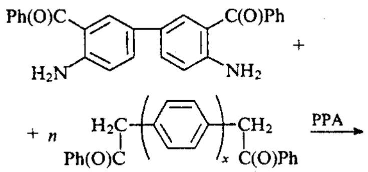
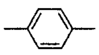
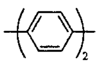
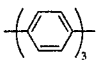
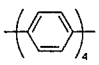
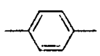
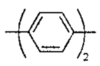
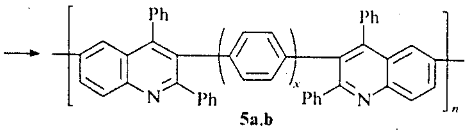


Table 2. Some characteristics of rigid-rod poly(2,6-quinolines) **4a – f**.[65]

Polymer	R	Ar	Solubility[a]		$[\eta]$ /dl g^{-1} (see [b])	Tg /°C (DSC)	T_m /°C	T_d /°C (TGA)	
			H_2SO_4	CF_3CO_2H				air	N_2
4a	H		ps	s	7.0	350	–	570	595
4b	H		ins	s	14.5 – 26.0	340	500	570	580
4c	H		ins	s	22.0	345	540	525	600
4d	H		ins	ins	–	350	–	580	600
4e	Ph		ins	s	17.0	370	555	580	590
4f	Ph		ps	s	22.0	360	–	570	595

[a] Hereinafter, ps is partly soluble, s is soluble, ins is insoluble. [b] The intrinsic viscosities $[\eta]$ were measured in CF_3CO_2H at 25 °C.

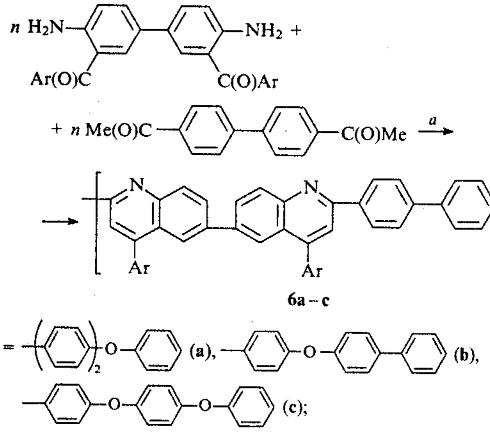


5a,b

Poly-mer	x	Solubility	$[\eta]$ /dl g^{-1}	T_g /°C (DSC)	T_m /°C	T_d /°C	
						air	N_2
5a	1	H_2SO_4	0.5	370	550	570	575
5b	2	*m*-cresol, H_2SO_4	2.4	390	530	570	585

The PQ **5a** prepared from 1,4-diphenacylbenzene is poorly soluble in H_2SO_4, while the PQ **5b** based on 4,4′-diphenacylbiphenyl is soluble in both H_2SO_4 and *m*-cresol. Polyquinolines **5a,b** have high glass-transition and melting temperatures; their initial thermal and thermooxidative decomposition temperatures are also high.[74]

Insufficient solubilities and high glass-transition temperatures of rigid-rod polyquinolines **4a – f** and **5a,b** made their processing problematic. Therefore, a search for approaches to the enhancement of the working characteristics of PQ was undertaken. Thus rigid-rod PQ **6a – c** containing extended arylene oxide fragments in the side chains were prepared by the condensation of 3,3′-diaroylbenzidines with 4,4′-diacetylbiphenyl.[75]



6a – c

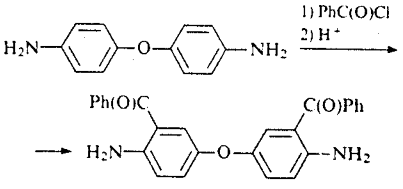
(*a*) *m*-cresyl phosphate, *m*-cresol, 136 – 138 °C, 48 h.

The glass-transition temperatures of polymers **6a – c** are in the interval 307 – 342 °C, while their melting temperatures are in the interval 416 – 505 °C. The solubilities of these PQ are similar to those of rigid-rod PQ containing lateral phenyl groups.[65]

b. Poly(ether quinolines)

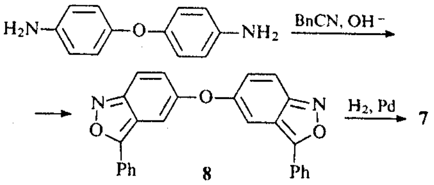
The introduction of ether bonds into macromolecules of PQ, *i.e.*, the synthesis of poly(ether quinolines) (PEQ) has significantly improved their solubilities. Such polymers are formed by the above-considered polycondensation of diphenacylarylenes with bis(*o*-aminocarbonyl) compounds where 4,4′-diamino-3,3′-dibenzoylbiphenyl was replaced by 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**7**).

The oxide (**7**) was synthesised by two methods.[51] One of them included direct benzoylation of 4,4′-diaminodiphenyl ether under drastic conditions to give compound **7**, which was difficult to purify (yields 6% – 13%).

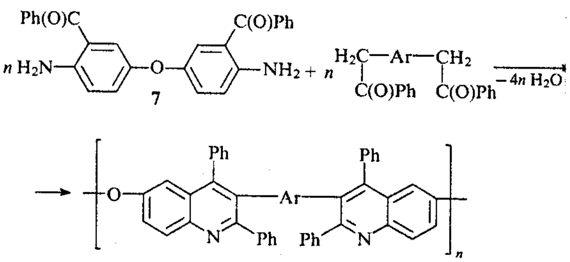


7 (6% – 13%)

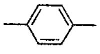
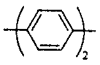
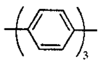
The second approach consisted of the reaction of 4,4′-diaminodiphenyl ether with phenylacetonitrile and subsequent reduction of the 5,5′-oxybis(3-phenyl-2,1-benzoisoxazole) (**8**) formed resulting in the monomer **7** (yield 85%).[51]



The synthesis of poly(ether 3,6-quinolines) **9a – c** from 4,4′-diamino-3,3′-dibenzoyldiphenyl oxide (**7**) has been described.[74]



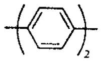
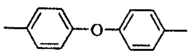
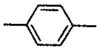
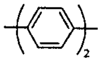
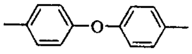
9a – c

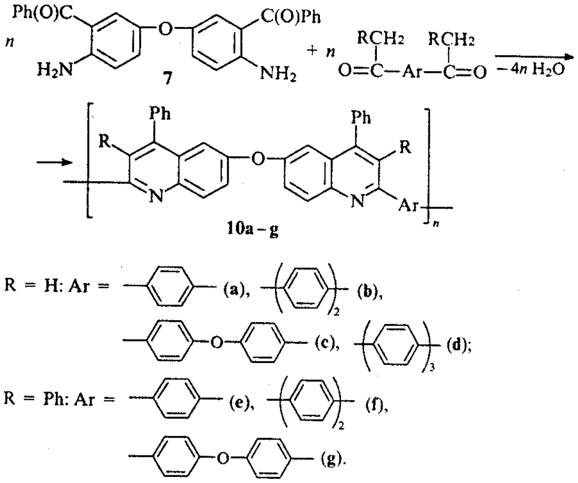
Poly-mer	Ar	Solubility	$[\eta]$ /dl g^{-1}	T_g /°C (DSC)	T_m /°C	T_d /°C	
						air	N_2
9a		$CHCl_3$	0.7	312	–	535	57
9b		TCE	3.6	325	–	530	55
9c		$CHCl_3$	1.2	255	–	530	57

Poly(ether quinolines) **9a – c** were soluble not only in H_2SO and *m*-cresol, but also in chloroform and tetrachloroethan (TCE). Their glass-transition temperatures were in the rang 255 – 325 °C; their melting temperatures could not be determined presumably due to the lower crystallinities of these flexible-chai polymers in comparison with the rigid-rod polymers.[76] Solution of PEQ in *m*-cresol, chloroform and tetrachloroethane were use for the preparation of strong transparent films by casting.

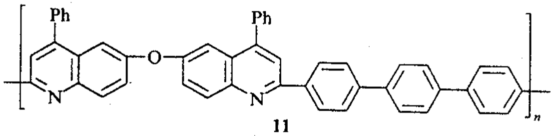
The reaction of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (7 with diacylarenes in *m*-cresol – PPA and *m*-cresol – P_2O_5 mixture was used for the synthesis of phenyl-substituted poly(ether 2, quinolines) **10a – g**.[77,78] The reaction conditions and the mai characteristics of some of these compounds are listed in Table 3

Table 3. Conditions of the synthesis and some characteristics of phenyl-substituted poly(ether 2,6-quinolines) **10**.[78]

Polymer	Ar	R	Conditions		Solubility	$[\eta]$/dl g^{-1}	Tg/°C	T_m/°C	T_d/°C
			T/°C	t/h					
10a		H	135 130	122 48	$CHCl_3$ $CHCl_3$	0.6 1.0	300	455	540
10b		H	130 130	41 48	*m*-cresol *m*-cresol	2.0 3.1	308	480	530
10c		H	135 130	49 48	$CHCl_3$ $CHCl_3$	1.0 1.6	266	448	545
10e		Ph	130	21	*m*-cresol	3.4	345	475	535
10f		Ph	130	21	*m*-cresol	4.1	351	480	540
10g		Ph	130	24	$CHCl_3$	2.0	305	476	530



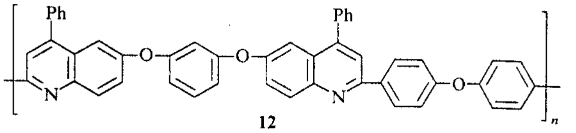
These polymers were soluble in chloroform and *m*-cresol. Even PEQ **11** was soluble in both sulfuric and formic acids and *m*-cresol.[78]



11

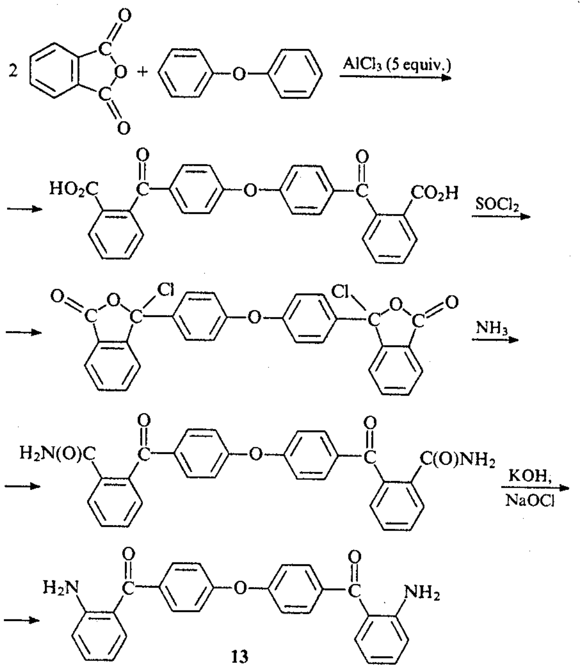
It was shown that the solubilities of phenyl-substituted PEQ were lower than those of the analogues devoid of the phenyl groups, which is in contrast with the data for other classes of rigid-rod polymers.[31–33,79,80] This can be attributed to the higher proneness of the former to aggregation due to hindered rotation of the quinoline rings.

Further increase in the number of ether bonds in the main chains of PEQ was achieved using resorcinol bis(4-amino-3-benzoylphenyl) ether as a monomer. Its condensation afforded PEQ **12**, which is soluble not only in formic acid and chloroform, but also in *N*-methyl-2-pyrrolidone (*N*-MP).[81] The softening temperature of PEQ **12** is 135 °C.



12

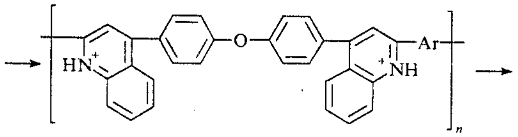
A method for the synthesis of 4,4′-bis(2-aminobenzoyl)diphenyl ether (**13**) was developed by Norris and Stille.[51]

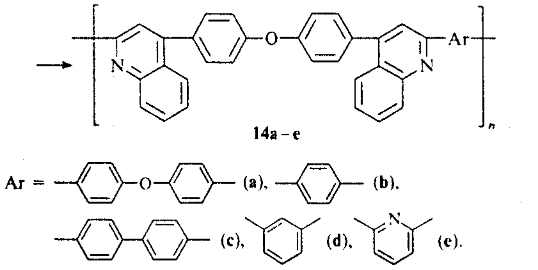


13

Its reaction with diacetylarenes yielded the polymers **14a – e** containing 2,4-substituted quinoline fragments.[48–50]

$$n\,\mathbf{13} + n\,\mathrm{Me(O)C{-}Ar{-}C(O)Me} \xrightarrow{\mathrm{PPA}}$$





This reaction proceeds especially smoothly in mixtures of *m*-cresol with PPA or P_2O_5; the formation of a protonated form of PEQ in these media is an essential feature as a result of which the polymer remains in the solution up to the end of the reaction. The reaction conditions and some characteristics of the PEQ synthesised are listed in Table 4.

Table 4. Conditions of the synthesis and some characteristics of PEQ **14a,c – e**.[50]

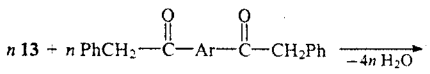
Polymer	Conditions		$[\eta]^a$ /dl g^{-1}	T_g /°C	T_m /°C	T_d /°C
	T/°C	t/h				
14a	125 130	50 13	0.62	251	483	510
14c	110 120 150	5 12 24	0.38	326	475	575
14d	100 130	16 45	0.36	268	see [b]	520
14e	100 135	18 48	0.08	–	–	–

[a] The intrinsic viscosity was measured in *m*-cresol.
[b] An amorphous polymer.

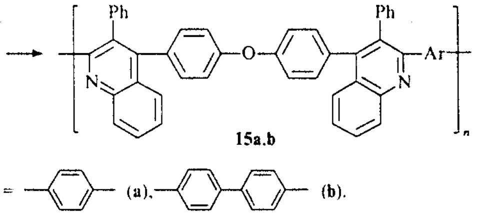
The polyquinolines **14a – e** have amorphous structures and are easily soluble in *m*-cresol and chloroform. Their softening temperatures are much lower than those of rigid-rod PEQ.

Properties of the PEQ polymer **14a** have been studied in much more detail.[48–50] The relatively high molecular mass (~50 000) and its good solubility in *m*-cresol and chloroform made it possible to use it as a starting material for the preparation of strong elastic films and fibres; subsequent orientation of the latter noticeably increased their crystallinities.[50,77] The polymer **14a** possessed high thermal stability upon dynamic and isothermal TGA. Thus dynamic TGA (air, ΔT = 5 °C min^{-1}) revealed that its initial decomposition temperature was 510 °C; a 10% mass loss in nitrogen occurred at 800 °C. According to data from isothermal TGA, the polymer retained its stability upon heating at 300 °C in circulating air over 100 h. It decomposed at 360 °C, the mass loss after 21 h being 10%. Complete decomposition of the polymer occurred after 39 h.

The reaction of 4,4′-bis(2-aminobenzoyl)diphenyl ether (**13**) with 1,4-diphenylacetylbenzene and 4,4′-diphenylacetylbiphenyl afforded phenyl-substituted poly(2,4-quinolines) **15a,b**.[48–50,69]



$$n\,\mathbf{13} + n\,\mathrm{PhCH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Ar{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2Ph} \xrightarrow[-4n\,H_2O]{}$$



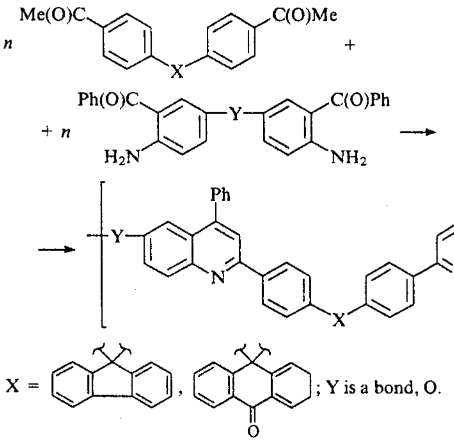
The polymers **15a,b** are soluble in *m*-cresol; their intrinsic viscosities are 0.26 and 0.57 dl g^{-1}, respectively. The polymer **15a** was not obtained in a crystalline state; its glass-transition temperature was 273 °C; the glass-transition and melting temperatures of the polymer **15b** were 345 and 500 °C, respectively.[68] Strong elastic films could be prepared from 15% – 25% solutions of these PEQ in $CHCl_3$ or a (3 : 1) TCE – *m*-cresol mixture, which became opaque upon slow evaporation of the solvents due to partial (~ 20%) crystallisation.

According to dynamic TGA (ΔT = 5 °C min^{-1}) the decomposition of the polymer **15a** in air and in nitrogen began at 530 – 545 °C and at 530 – 570 °C, respectively. In nitrogen, the mass loss of the polymer at 800 °C was only 15% – 26%. According to the data from isothermal TGA, no mass loss of the polymer **15b** in circulating air occurred over 100 h at 300 °C; over the same time at 371 °C, the mass loss was 48%.

c. Polyquinolines containing cardo, tetraphenylsilyl and perfluorotetramethylene groups

A series of cardo polymers[82,83] and PQ containing tetraphenylsilyl[84] and perfluorotetramethylene groups have been synthesised in order to improve the processibility of high-molecular-weight PQ.[85,86]

9,9-Bis(4-acetylphenyl)fluorene and 9,9-bis(4-acetylphenyl)-10-anthrone[82] were synthesised aimed at the preparation of cardo PQ. These were further introduced into reactions with bis(*o*-aminobenzophenones).[82]

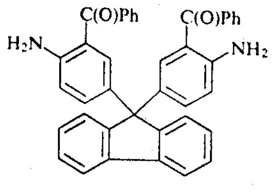


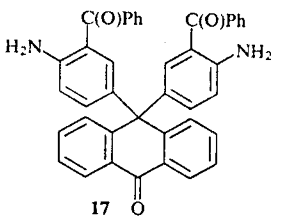
The majority of the cardo PQ thus prepared were soluble not only in *m*-cresol, but also in chloroform and TCE.

The introduction of cardo groups has made it possible to increase the glass-transition temperatures of PQ by 40 – 70 °C in comparison with PEQ. The PQ based on cardo diacetyl derivatives are characterised by extremely high thermostabilities; their decomposition began at the temperatures above 550 °C. The decomposition temperatures of anthronyl-containing PQ are 30 – 50 °C lower than those of fluorene-containing PQ.

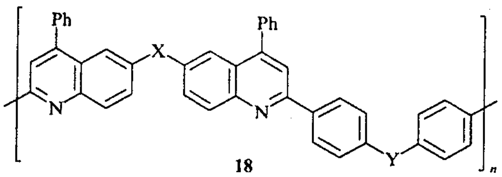
By virtue of their high molecular masses (up to 5.25 × 10^5 Da), some of these polymers[83] were successfully used for the preparation of strong films.

Polyquinolines prepared from cardo bis(*o*-amino ketones), *viz.*, 9,9-bis(4-amino-3-benzoylphenyl)fluorene (**16**) and 9,9-bis(4-amino-3-benzoylphenyl)-10-anthrone (**17**),[82] were soluble in chlorinated hydrocarbons and thermostable (up to 520–580 °C). Their glass-transition temperatures were 310–420 °C.


16

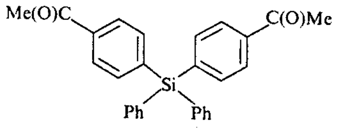

17

The use of comonomers each containing cardo groups for the synthesis of PQ has led to the polymers **18** which are soluble in chlorinated solvents ($CHCl_3$, TCE). Some properties of the cardo PQ **18** are listed in Table 5.


18

Studies of rigid-rod cardo PQ by dynamic TGA revealed that the polymers containing one cardo and one 4,4′-biphenyl group in the repeating unit of the polymer possessed better mechanical properties than the flexible-chain polymers containing one cardo and one 4,4′-diphenylene oxide group or two cardo groups in the polymer unit.

The silicon-containing diacetyl monomers **19** and **20** were synthesised[84] and introduced into the acid-catalysed polycyclocondensation with bis(*o*-aminobenzophenones) **7** and **16**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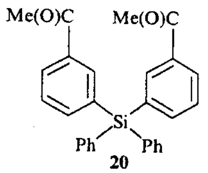
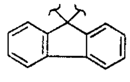
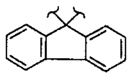
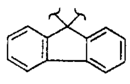
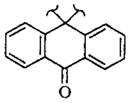
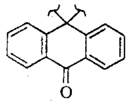
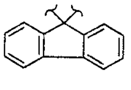
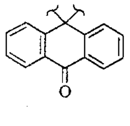
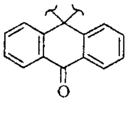
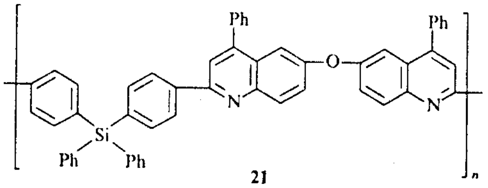
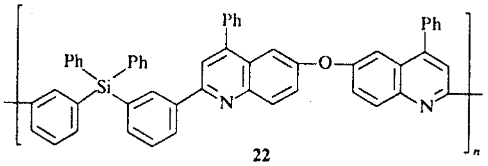

20

resulting in PQ **21**–**24**.

Table 5. Some characteristics of cardo PQ **18**.[82]

X	Y	[η] /dl g^{-1}	T_g /°C	T_d /°C
		0.58	390	580
		0.70	385	530
		1.30	405	540
		0.53	390	520


21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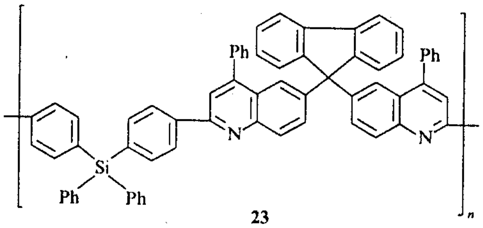
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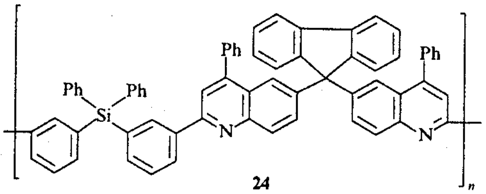
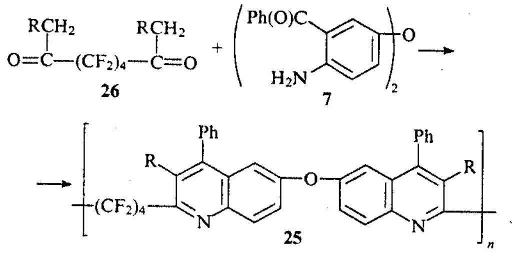

24

Both homo- and block-copolymers with fluorene-containing cardo blocks were prepared by condensation of equimolar amounts of compounds **7** and **16** with the diacetyl monomers **19** and **20** in *m*-cresol – di-*m*-cresyl phosphate at 140 °C.

The solubilities of the polymers **21**–**24** exceed those of the majority of PQ.[1–5] In addition, these compounds swell strongly in many solvents, such as *m*-cresol, chloroform, dichloromethane, *N*-MP, DMF, benzene and chlorobenzene.

Easily processable polyquinolines **25** (*Tg* = 142–183 °C) were prepared from comonomers **26** containing perfluorotetramethylene groups.[85,86]



Polymers **21**–**25** were used for the preparation of high-quality films[50,69,77,79] and fibres[50,69,77,87] some of which manifest high thermal characteristics.[50,69,77,87,88]

However, introduction of ether bonds or perfluoroalkylene groups aimed at improving the processability of PQ results in a decrease in the glass-transition or softening temperatures and, consequently, their operating temperatures. These can be increased by crystallisation of amorphous polymers. However, its practical realisation is rather a difficult task; therefore, an alternative approach, *viz.*, post-moulding curing of amorphous polymers, has been developed.

d. Reactive oligo- and polyquinolines

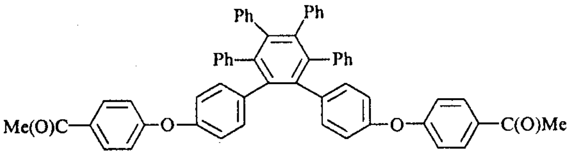
Reactive oligo- and polyquinolines can be prepared by several methods. These include

(1) introduction of terminal arylcyanate groups into PQ with subsequent cyclotrimerisation resulting in internodal *sym*-triazine fragments (Scheme 2);[89]

(2) introduction of biphenylene fragments,[52, 90–94] which undergo ring-opening at 350–400 °C to generate biradicals that further recombine into dimers and/or polymers;[90–96]

(3) introduction of terminal biphenylene groups and triple C–C bonds into the main chains of PQ.[94] This enables cross-linking of the polymers, if the reactions are carried out at high temperatures[95] or in the presence of nickel catalysts;[97]

(4) introduction of hexaarylbenzene fragments into macromolecules of PQ[98] using 1,2-bis[4-(acetylphenoxy)phenyl]-3,4,5,6-tetraphenylbenzene as a comonomer for PQ synthesis.



These hexaarylbenzene fragments are effective cross-linking agents, which enable preparation of polymers with enhanced thermal and mechanical properties, especially at temperatures exceeding the glass-transition temperatures of the original PQ;[99]

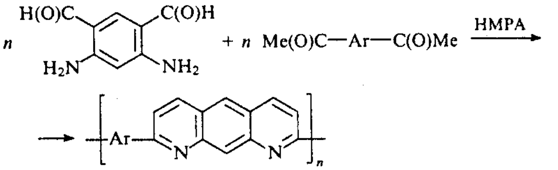
(5) introduction of terminal [2.2]paracyclophane groups[100] with subsequent curing of reactive PQ obtained due to the opening of the [2.2]paracyclophane rings.

All these approaches seem to hold much promise with regard to the design of novel composites with enhanced thermal and mechanical characteristics.[94]

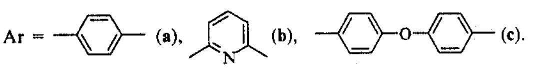
In addition to thermal and mechanical properties, considerable attention of investigators is given to the electrophysical characteristics of PQ.[98, 101] Thus materials with conductivities of $11\ \Omega\ cm^{-1}$ could be prepared by doping PQ devoid of bridging groups with AsF_5, iodine, sodium naphthalenide and anthracenide.[98, 101–107]. Among those, rigid-rod PQ prepared by doping with sodium anthracenide manifested the highest conductivities. However, PQ containing bridging groups possessed low permittivities ($\varepsilon \sim 2.8$)[108] comparable to those of the best fluorine-free PHA.[109]

e. Polyanthrazolines

The Friedlander reaction was successfully employed in the synthesis of polymers containing both substituted and non-substituted anthrazoline or isoanthrazoline rings in the main chains. Thus the reaction of 4,6-diaminoisophthalaldehyde with diacetylarenes in hexamethyl phosphorotriamide (HMPA)[110, 111] yielded the polymers **27a–c**.

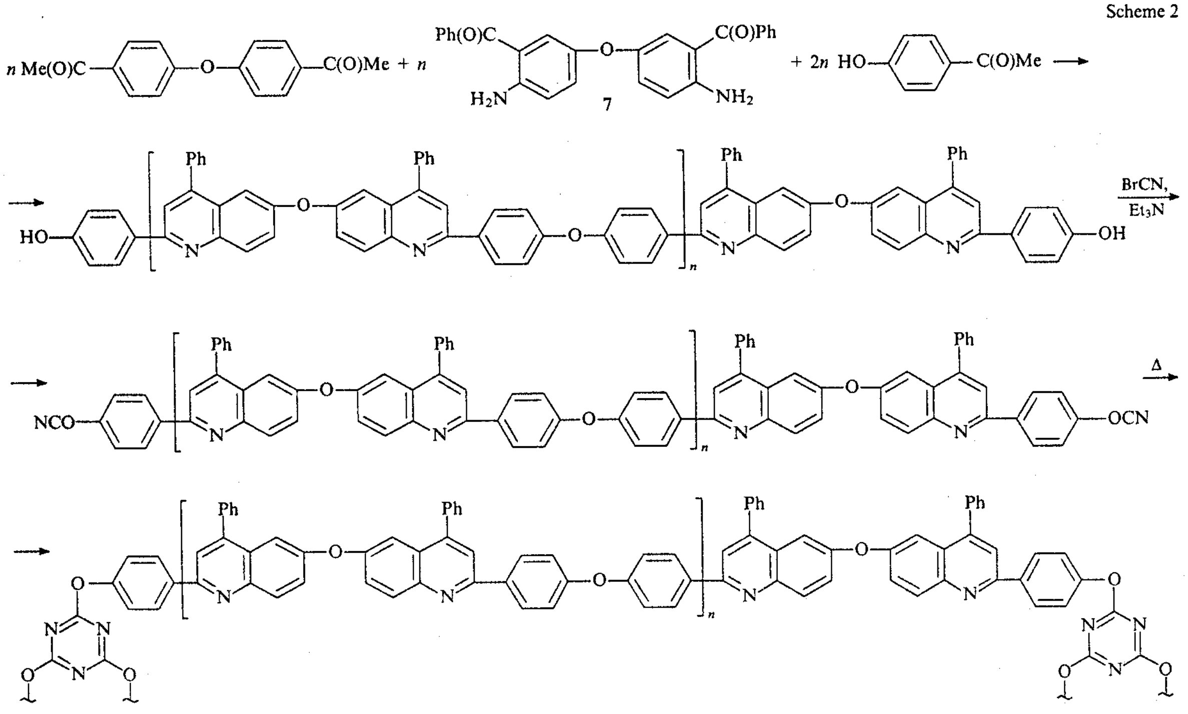


27a – c



The polyanthrazolines thus prepared possessed high thermostabilities: according to dynamic TGA ($\Delta T = 10\ °C\ min^{-1}$), the mass loss in air began at 450 °C, whereas in an inert atmosphere the 5% mass loss was observed at 600–650 °C. However, these polymers were soluble only in sulfuric acid. They sedimented from reaction solutions, which prevented the formation of high olecular mass products; the inherent viscosities of their solutions in sulfuric acid did not exceed 0.26 dl g^{-1}. Polyanthrazolines prepared from dibenzoylphenylenediamines instead of dialdehydodiamines as

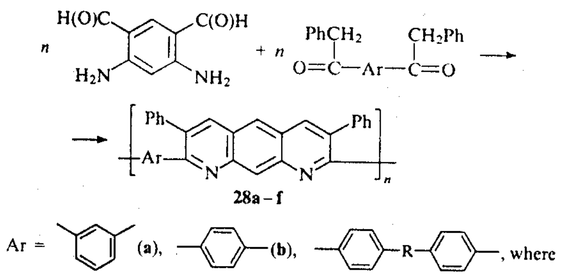
Scheme 2



n = 4, 10, 11.

the starting compounds or from bis(phenylacetyl)arenes instead of diacetylarenes were devoid of this drawback.[112,113]

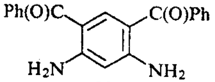
Acid- or base-catalysed reactions of 4,6-diaminoisophthalaldehyde with bis(phenylacetyl)arenes gave the phenyl-substituted PAZ **28a–f**,[113] which manifested better solubilities than their analogues bearing no phenyl groups.



R = bond (c), O (d), S (e), SO_2 (f).

A comparison of the polymers **27** and **28** having similar molecular masses revealed that the former were soluble only in strong acids, whereas the latter were soluble in chloroform. As a consequence, phenylated PAZ **28** did not precipitate from HMPA solutions in the course of their preparation. However, their viscosities were similar to those of non-phenylated PAZ **27**[110] (0.2–0.3 dl g^{-1}) (see Ref. 113), which may be attributed to side reactions involving the aldehyde groups. Studies of model reactions have shown[113] that the yields of target heterocyclic systems increase considerably on going from *o*-aminobenzaldehyde to *o*-aminobenzophenone and upon substitution of acid catalysts for basic catalysts.

Therefore, phenylated PAZ prepared from 4,6-dibenzoyl-1,3-phenylenediamine (**29**) and 2,5-dibenzoyl-1,4-phenylenediamine (**30**) as monomers in the presence of acid catalysts were used in further studies.[113]



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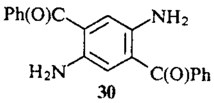

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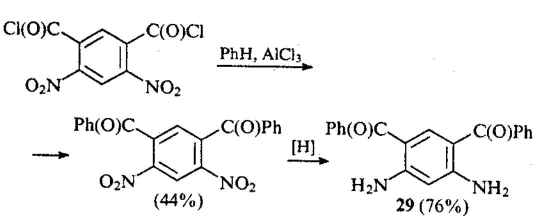
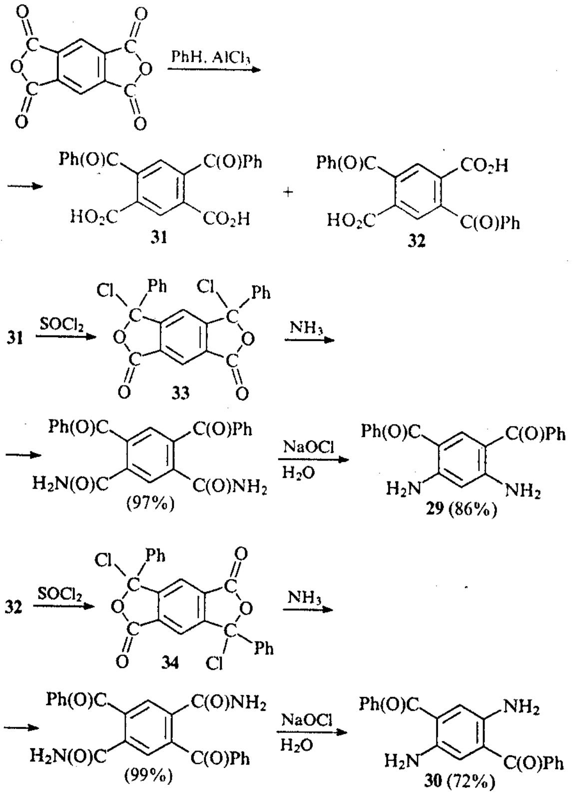
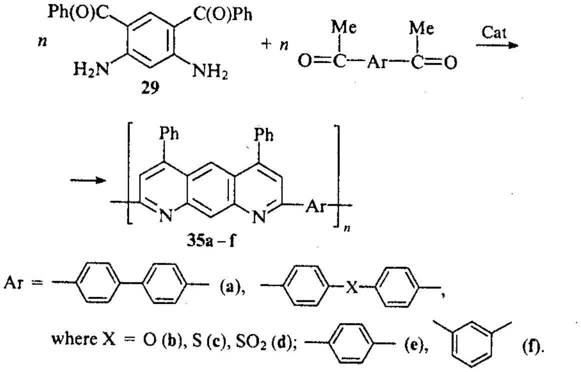
4,6-Dibenzoyl-1,3-phenylenediamine **29** was prepared by the Friedel–Crafts acylation of benzene with 4,6-dinitroisophthaloyl chloride with subsequent reduction of the 1,3-dibenzoyl-4,6-dinitrobenzene formed.[114]



4,6-Dibenzoyl-1,3-phenylenediamine (**29**) and its isomer **30** were also prepared from pyromellitic anhydride. The Friedel–Crafts reaction of the latter with benzene gives isomeric dibenzoyldicarboxylic acids **31** and **32**. After separation of isomers **31** and **32**, they were converted into pseudo-dibenzoyl dichlorides **33** and **34**; their amination with aqueous ammonia yielded the corresponding amides. The Hoffmann rearrangement of the latter afforded diamines **29** and **30**.

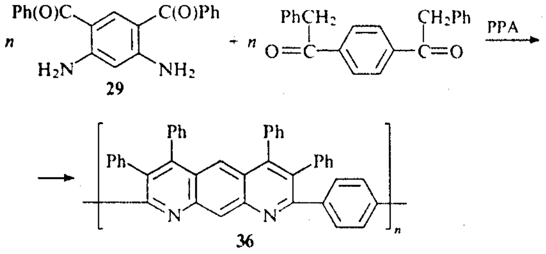


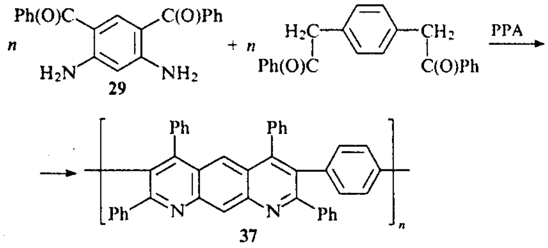
The reactions of 4,6-dibenzoyl-1,3-phenylenediamine (**29**) with diacetylarenes[112,113] were carried out in chlorobenzene, *m*-cresol, sulfolane and other solvents; HCl, H_2SO_4, P_2O_5 and H_3PO_4 were used as catalysts.



The polymers **35a–f** prepared in a *m*-cresol–PPA system manifested the best viscosity characteristics ($\eta_{\log} \approx 1.25$ dl g^{-1}). These PAZ were soluble in *m*-cresol, *N*-MP and formic acid. According to dynamic TGA data, their decomposition in air began at 500–560 °C, while that in an inert atmosphere occurred at 530–600 °C.

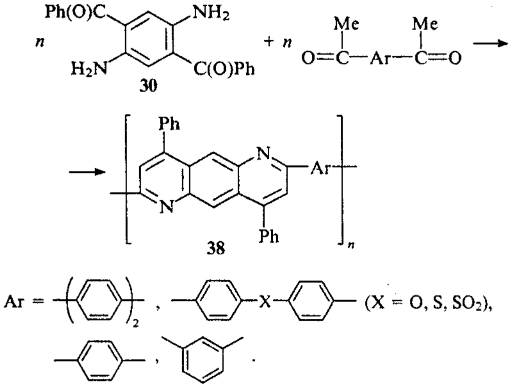
Isomeric PAZ **36** and **37** containing four phenyl substituents in each polymeric fragment were prepared by the reaction of diamine **29** with 1,4-bis(phenylacetyl)benzene and 1,4-diphenacylbenzene.[1,2,111,113]





The main characteristics of these polymers differ only insignificatly from those of the aforementioned phenylated PAZ **35a–f.**

The substitution of 2,5-dibenzoyl-1,4-phenylenediamine (**30**) for 4,6-dibenzoyl-1,3-phenylenediamine (**29**) gave polyisoanthrazolines **38**;[1,113] due to their greater symmetries, they possessed lower solubilities than those of the isomeric PAZ. The thermal characteristics of polymers **30** are similar to those of other PAZ.

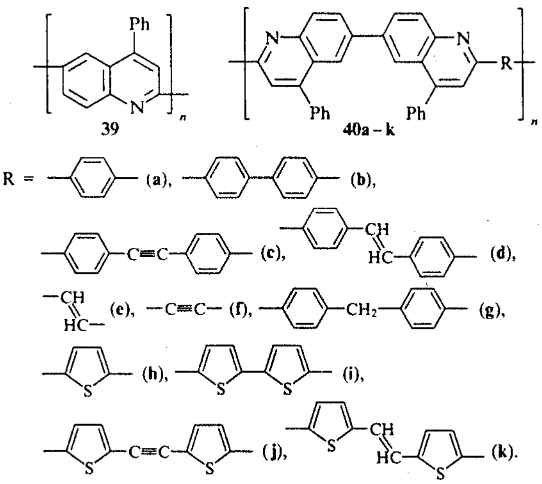


III. Polyquinolines possessing electroluminescent properties

Polymers possessing electroluminiscent properties attracted attention as materials for electrooptics, for the preparation of light-emitting diodes (LED), in particular.[115–124]

Considering that the majority of conjugated electroluminescent polymers form and transport 'holes' much more efficiently than electrons,[125–127] the construction of polymers with enhanced electron-transport properties is a topical task. It was found that polyquinolines with different structures possess remarkable electron-transport properties[8,9,128,129] and can be used for the preparation of electron-transport layers for LED.

The polymers **39** and **40a–k** were the subject of investigation in one of the first systematic studies of PQ and PAZ possessing high photoluminescent properties.[8,9,130]

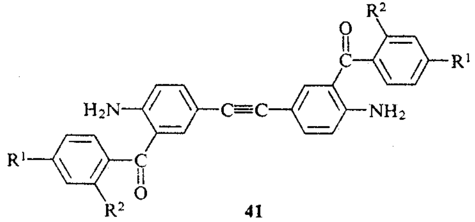


In-depth studies of these polymers, which differ in the length of their conjugation chains, have shown that the widths of thei optical forbidden bands differed by 1.0 eV. Thus the width of th optical forbidden band (E_g) of PQ **40b** containing a biphenyldiy fragment was equal to 2.81 eV, while that of PAZ **40j** containing dithienylvinylene fragment was 2.0 eV. Substitution of the thio phene groups for the phenylene groups caused a noticeable long wavelength shift of the absorption maxium (λ_{max}) (b 64–106 nm) with concomitant narrowing of the forbidden ban by 0.3–0.5 eV. Some characteristics of these PQ are presented i Table 6.

Table 6. Optical characteristics of conjugated PQ.[9]

Polymer	λ_{max} (film)	λ_{max} (solution)	E_g	log ε
39	410	389	2.65	4.16
40a	398	405	2.78	4.63
40b	394	429	2.81	4.83
40c	399	436	2.72	4.86
40d	408	467	2.65	4.88
40g	370	389	3.01	4.68
40h	441	493	2.49	4.78
40i	468	546	2.33	5.06
40j	469	567	2.26	–
40k	484	578	2.23	5.00

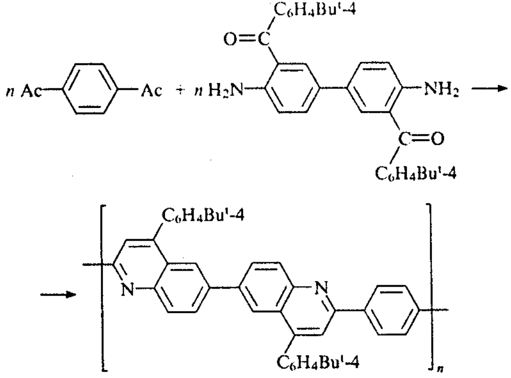
The monomers **41** were synthesised, and a novel procedure fo the introduction of the acetylenic fragments into PQ was proposed, which consisted of polycondensation with 5,5′-diacetyl-2,2′-bithiophene.[131]



41

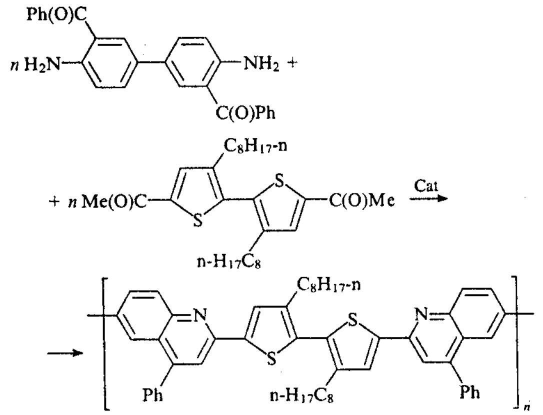
$R^1 = R^2 = H$; $R^1 = OMe$, $R^2 = H$; $R^1 = H$, $R^2 = F$.

An attempt has been made to overcome the limited solubilities of rigid-rod conjugated PQ by modifying them through introduction of alkyl substituents.[132–139] However, no enhanced solubility was observed for PQ **42** containing *tert*-butyl substituents in the *para*-position of the phenyl rings.[133, 134] Notwithstanding, this PQ was used for the preparation of electroluminescent films with a light-yellow emission (λ_{max} = 554 nm), proton/electron quantum efficiency of 0.26% and a brightness of 280 cd m^{-2} at a current density of 100 mA cm^{-2}.



42

The increase in the solubility of PQ is better achieved by introducing higher alkyl (*e.g.*, octyl) substituents.[135]

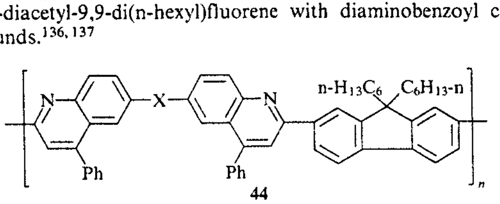


43

The polymer **43** thus prepared was soluble in formic acid and other protic solvents as well as in THF, toluene and CHCl$_3$. The absorption maximum of a solution of PQ **43** was 414 nm. Green emission (λ_{max} = 510 and 530 nm) was observed for a solution and a thin polymeric film, respectively.

Considerable attention has also been given to PQ that contained fluorene groups with alkyl substituents.[136–138]

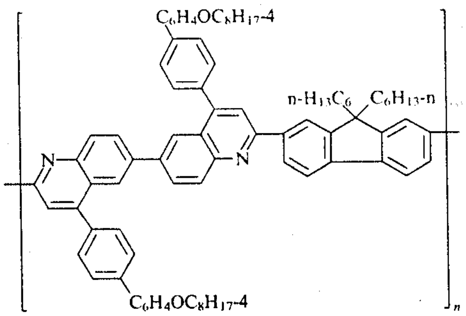
Polyquinolines with the general formula **44** containing 9,9-di(n-hexyl)fluorene fragments were prepared by the reaction of 2,7-diacetyl-9,9-di(n-hexyl)fluorene with diaminobenzoyl compounds.[136, 137]



44

X is a bond, O, S, CH = CH.

The PQ formed are soluble in CHCl$_3$, THF and chlorobenzene; their glass-transition temperatures lie in the range 195–243 °C. The electroluminescence spectra of PQ are characterised by blue emission (432 nm). The use of [4,4′-diamino-3,3′-bis(4′-octyloxybiphenyl-4-yl)carbonyl]biphenyl as a monomer allowed introduction of additional 4-octyloxybiphenyl groups into PQ **45**, which is soluble in CHCl$_3$, THF and dimethylacetamide.[138]



45

The electroluminescence maximum of PQ **45** lies around 530 nm (green emission). Mixing of this PQ with polyvinylcarbazole results in a blue shift of the maximum due to the dilution effect.[139]

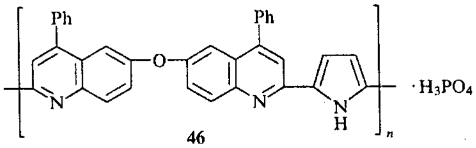
The effectiveness of formation of polymeric mixtures for the enhancement of the electroluminescent properties of the target materials has been reported.[140, 141].

IV. Conclusion

The data considered in the present review illustrate the indisputable progress in the area of the synthesis of PQ and PAZ and their use in the preparation of unique materials, *e.g.*, fibres, films, composite materials and electroluminescent systems.

Novel promising areas for the application of PQ have recently been outlined. In the first place, these include the construction of second [142–145] and third [146–148] generations of materials for non-linear optics.

Of considerable interest are the data related to the use of pyrrole-containing PQ for complex formation with strong acids.[149] Such complexes were used for the preparation of proton-exchange membranes,[149] which represent the most important components of fuel cells relevant to the key technologies of the 21st century.[150–154] Thus a proton-exchange membrane based on complex **46** manifests enhanced proton conductivity ($1.5 \times 10^{-5}\ \Omega\ cm^{-1}$ at 157 °C),[149] which surpasses that of the known polybenzimidazole–H$_3$PO$_4$ complexes ($7 \times 10^{-5}\ \Omega\ cm^{-1}$ at 150 °C).[155]



46

The remarkably high thermal conductivity of PQ·H$_3$PO$_4$ membranes opens up promising opportunities for their wide applications.

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