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Processable Fully Aromatic Quinoline-Based Polymers

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ABSTRACT: Quinoline-based homo- and copolymers have been synthesized by the acid-catalyzed Friedlaender condensation between bis(*o*-aminoketone)s and silicon-containing bis(ketomethylene) monomers. The polymers contain quaternary silicon atoms and are fully aromatic; they show improved solubility compared to known polyquinolines with approximately unchanged softening and decomposition temperatures of the final material. A new solubilization method was developed for these materials. In addition two block copolymers based on an aramid block containing fluorene cardo units and polyquinoline were prepared.

Introduction

Thermally stable transparent materials open promising opportunities in fields such as electronics, optoelectronics, and nonlinear optics,[1−4] but the requirements in such applications comprise long-term stability at moderately high temperature (80−100 °C), good mechanical properties, easy processing, and high glass-transition temperatures (T_g). This portfolio of characteristics is rarely met by organic materials. Often, thermo- and photochemical stability are as critical as high T_g, e.g., for the electrooptical (EO) response of poled polymer films.[5,6] The required high transparency in both the visible region and the near infrared in this example[7] restricts the choice to amorphous materials.

Polyaromatics with limited conjugation along the main chain show high promise; many systems have been used as matrixes for chromophores in quest/host systems or directly as active materials, e.g. aramides,[8] polyimides,[9] and polyarylenes;[10] polyquinolines, which have been shown to possess outstanding thermo-oxidative stability[11,12] and promising characteristics for processing,[13−16] have been investigated much less frequently.

Polyquinolines were first introduced by Stille et al.[17−19,25−29] who used the Friedlaender condensation[30] as a polymerization step. To date, some quinoline-based polymers with excellent chemical, optical, and thermal properties have been prepared[17−20] and employed in guest/host systems[21] as well as side-chain second-order[22,23] and third-order NLO polymers[14,24] and as electron transport agents in LEDs.[31,32] As for most fully aromatic polymers, these systems also exhibited poor solubility and high softening temperatures, which made polyquinolines in general difficult to process, both from solution and the melt, unless Lewis or protic acids are used. In this case, thin films could be spun in a gel form, retrieving the neutral polymer form after a treatment with a base; the disadvantages of this method, based on a deprotonation/precipitation phenomenon, are in the material shrinkage and in the residual acid/salt content, deleterious respectively for applications in optics (because of scattering) and electrooptics (because of conductivity decreasing the poling efficiency). Several attempts have been made to enhance the solubility of polyquinolines by chemical derivatization, either by incorporating flexible linkages in the polymer backbone,[20] through pendent side chains,[18] or by restricting the molecular weight of the samples to the oligomeric range.[28] Here we attempt to obtain soluble polyquinolines with fully aromatic structure and good thermal resistance through other means.

We report on the synthesis and characterization of “semirigid” silicon-containing polyquinolines. The silicon atom was introduced into the aromatic backbone with the hope of enhanced torsional flexibility of the main chain, and, hence, increased solubility and improved processability of the final polymers. In addition, flexible aryl ether linkages or a cardo unit were introduced, (the cardo structure, a pendent bulky fluorene unit, was surmised to confer improved solubility and amorphous structure to the resulting material[29]). Furthermore, block copolymers with an aramid with cardo moieties were synthesized; a similar strategy had been used by Hedrick et al. for the solubilization of block polyimides.[33]

We also sketch a solubilization method based on neutralization and extraction in solvent mixtures such as toluene/DMF or *m*-cresol/DMF.

Results and Discussion

Monomers. Our polymers are all obtained from bis(acetophenyl) monomers and bis(*o*-aminobenzophenone) monomers. The Friedlaender reaction joins an acetophenyl moiety with an *o*-aminobenzophenone structure to a diphenylquinoline group ($Ph_1-CO-CH_3 + Ph_2(NH_2)-CO-Ph_3 \rightarrow Ph_1-Q-Ph_3$). Silicon atoms were introduced in the acetophenyl-containing monomers in *p* and *m* positions, indicated in the monomer label by the letters **p** and **m**, respectively (Scheme 1), through a two-step process (Scheme 2).

At first, 4-bromoacetophenone (and analogously, 3-bromoacetophenone) was protected as ethylene glycol acetal (catalyzed by *p*-toluenesulfonic acid). The water formed in the reaction was removed by azeotropic distillation with benzene and the progress of the reaction monitored by FT-IR: at completion of the reaction, the carbonyl

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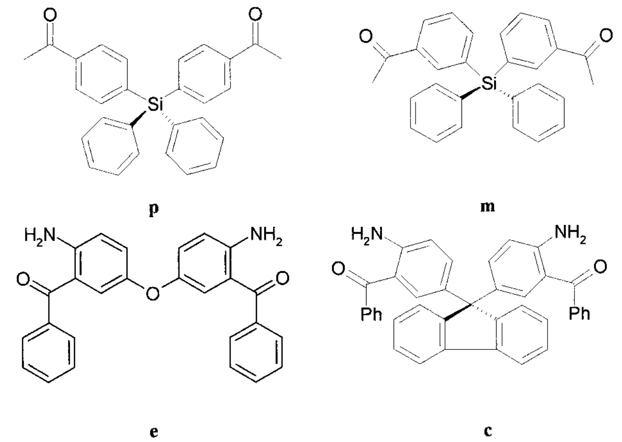
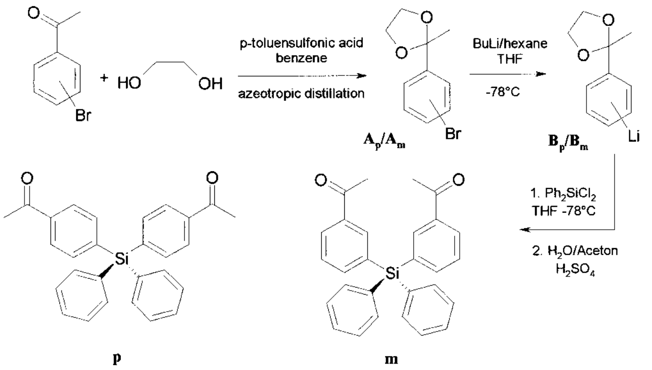
Scheme 1. Monomers



Scheme 2. Synthesis of Monomers p and m



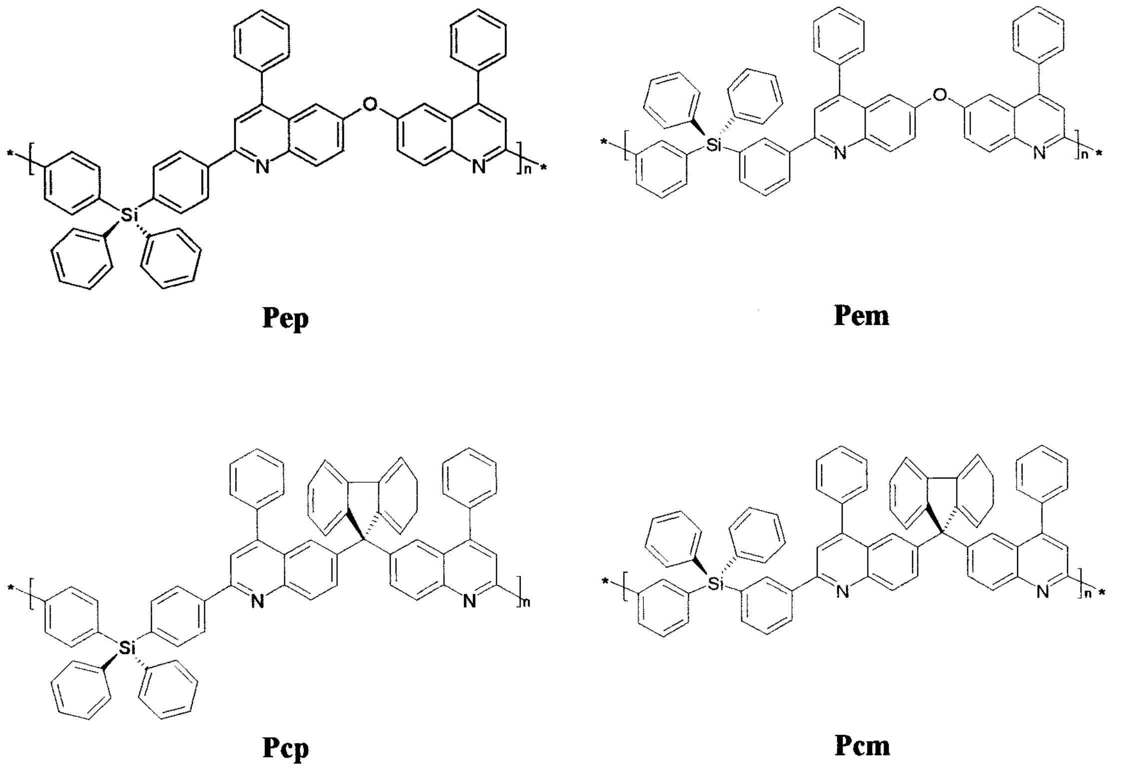
stretching absorption (1688 cm^{-1}) disappeared. The resulting product $\mathbf{A_p}$ (and $\mathbf{A_m}$) was then converted to the corresponding lithium derivative $\mathbf{B_p}$ (and $\mathbf{B_m}$), by halogen/metal exchange with *n*-butyllithium at −78 °C, and then reacted *in situ* with diphenyl-dichlorosilane. The monomer **p** (and **m**) was obtained after acid workup.

The two bis(*o*-aminobenzophenone) comonomers **e** (with an aryl**e**ther structure) and **c** (with the **c**ardo moiety) were prepared according to the literature.[27,29]

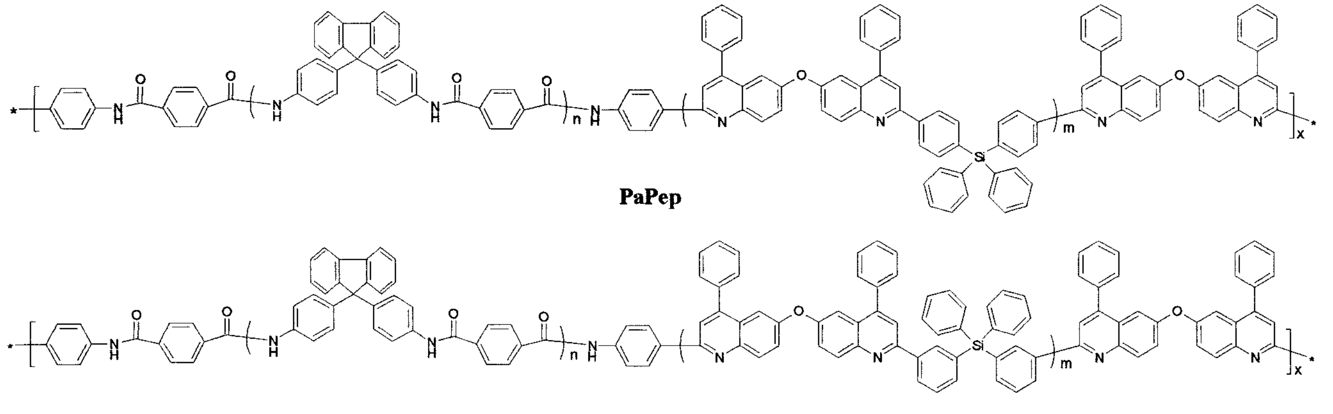
Polymers. The quinoline homopolymers were prepared with an equimolar mixture of the appropriate bis(*o*-aminobenzophenone) (**p**, **m**) and diacetyl monomer (**e**, **c**) at 140 °C, in a solution of *m*-cresol and di-*m*-cresyl phosphate. The di-*m*-cresyl phosphate is not commercially available and was synthesized according to the literature,[19] and its purity was checked by ^{31}P NMR. The polymer structures are sketched in Scheme 3: they are denoted by **P** followed by the letters indicating the monomers used (hence, **Pep**, **Pem**, **Pcp**, and **Pcm**). Random and block copolymers were also prepared by polymerizing monomers **p** and **m** with **e**; reacting an equimolar mixture of **p** and **m** with **e** yielded a random copolymer (**Pemp**), while condensation of oligomeric **Pem** and oligomeric **Pep** afforded the block copolymer **PemPep**. The conversions of all the polymerizations ranged between 80 and 90%.

We have also synthesized two block copolymers with cardo-bearing aramid blocks **Pa**, see Scheme 4). The two copolymers **PaPep** and **PaPem** were obtained starting from oligomeric **Pep** and **Pem**, respectively, chain-extending them with a fluorenyl-containing aramid oligomer. The amide block **Pa** was obtained by solution polycondensation of 9,9-bis(4-aminophenyl)fluorene (prepared as described in the literature[29]) at room temperature (Scheme 5). The two reagents were mixed in a 9:10 ratio and produced chloride-terminated chains, which were further reacted with 4-aminoacetophenone; the acetyl-end-capped oligomer was then isolated and characterized. Separately, oligomers of **Pep** and **Pem** were prepared with a slight excess of **e**, in order to obtain oligomers with *o*-aminoketone chain ends; the reaction mixture was kept at 140 °C for 24 h (half the

Scheme 3. Polyquinolines



Scheme 4. Poly(aramid-*block*-polyquinoline)s



PaPep

PaPem

Scheme 5. Synthesis of the Oligoaramid Pa

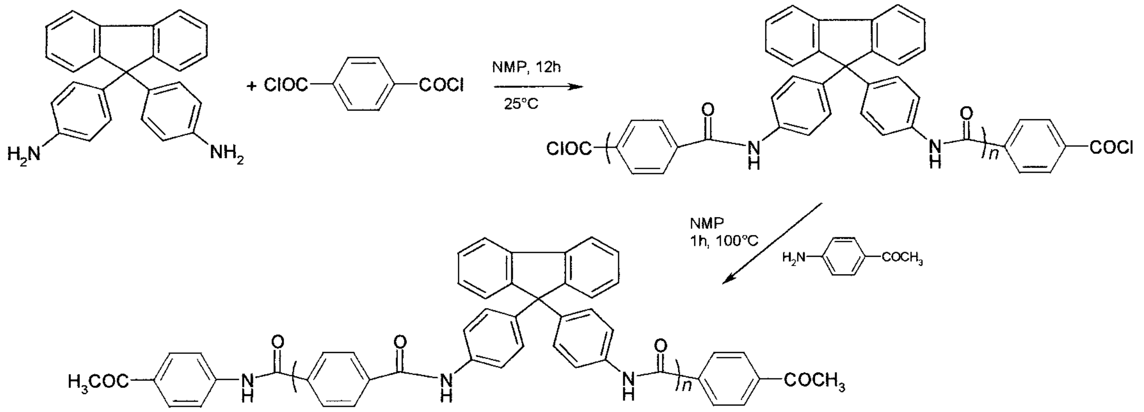


Table 1. Properties of Polyquinolines

polymer	T_g[a] (°C)	T_d[b] (°C)	λ_{max}[c] (nm)	$\epsilon(\lambda_{max})$[d] (10^4 L/[mol·cm])	$[\eta]$[e] (dL/g)
Pep	280	596	347	34	1.67
Pem	280	580	355	44	0.81
Pcp	267	597	362	32	0.62
Pcm	269	587	356	50	0.32
Pemp	260	565	357	30	0.25
PemPep	330	590	357	43	0.35

[a] DSC, second heating, 10°C/min, nitrogen flow. [b] TGA, onset of decomposition, 20°C/min, air flow. [c] Wavelength at the absorption maximum. [d] Per mole quinoline units. [e] Intrinsic viscosity in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C, measured with an Ubbelohde viscometer.

Table 2. Properties of the Aramid−Polyquinoline Block Copolymers

polymer	T_g[a] (°C)	T_d[b] (°C)	λ_{max}[c] (nm)	$\epsilon(\lambda_{max})$[d] (10^4 L/[mol·cm])	$[\eta]$[e] (dL/g)	% PQ[f]
PaPep	240	580	348	24	0.37	45
PaPem	183	573	349	120	0.20	20

[a] DSC, second heating, 10°C/min, nitrogen flow. [b] TGA, onset of decomposition, 20°C/min, air flow. [c] Wavelength at the absorption maximum. [d] Per mole of quinoline units. [e] Intrinsic viscosity in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C, measured with an Ubbelohde viscometer. [f] Quinoline repeating units as mole fraction of all repeating units in the block copolymer; average of the results from ^{1}H NMR, elemental analysis, and amounts of residual SiO_2 after TGA.

time necessary to obtain high-molecular-weight polyquinolines), and then the amide oligomer **Pa** was added.

The intrinsic viscosities were determined by dilution viscometry in a mixture of *m*-cresol and 5% w/w di-*m*-cresyl phosphate at 100 °C. The values are reported in Tables 1 and 2.

^{1}H and ^{13}C NMR spectra of the block copolymers **PaPep** and **PaPem** were recorded in deuterated DMF. The 8.6−6.9 ppm range of the ^{1}H NMR spectra of the aramid **Pa** (bottom) and of the copolymer **PaPep** (top) in are compared in Figure 1. From these spectra, the quinoline content of the copolymer is readily available.

PaPep and **PaPem** have different quinoline contents. An interpretation could be that monomer **m** undergoes condensation less readily than monomer **p**; indeed, the homopolymers with **m** exhibit significantly lower intrinsic viscosities (by a factor of ca. 2) than their **p**-containing analogues (see Table 1). A similar ratio in intrinsic viscosity is observed with **PaPep** and **PaPem** and it seems reasonable to surmise shorter **m**-containing than **p**-containing blocks. This effect might be further enhanced by the shorter reaction time used for the preparation of the aramid−polyquinoline block copolymers when compared to the quinoline-only polymers. The blocks might even be so short that a significant amount of bis(*o*-aminoketone) monomer was not converted at all so that the quinoline groups that would have formed from their reaction were not created; as a result some of the quinoline content in **PaPem** would be lower than in **PaPep**, as was indeed observed (see Table 2).

Solution Behavior. As for most polyquinolines,[14,15] all polymers described here are soluble in the presence of protic or Lewis acids; for our polymers, pure formic acid can already be used as solvent. As neutral molecules, the quinoline-only polymers (see Table 1) are not soluble in common organic solvents such as *m*-cresol,

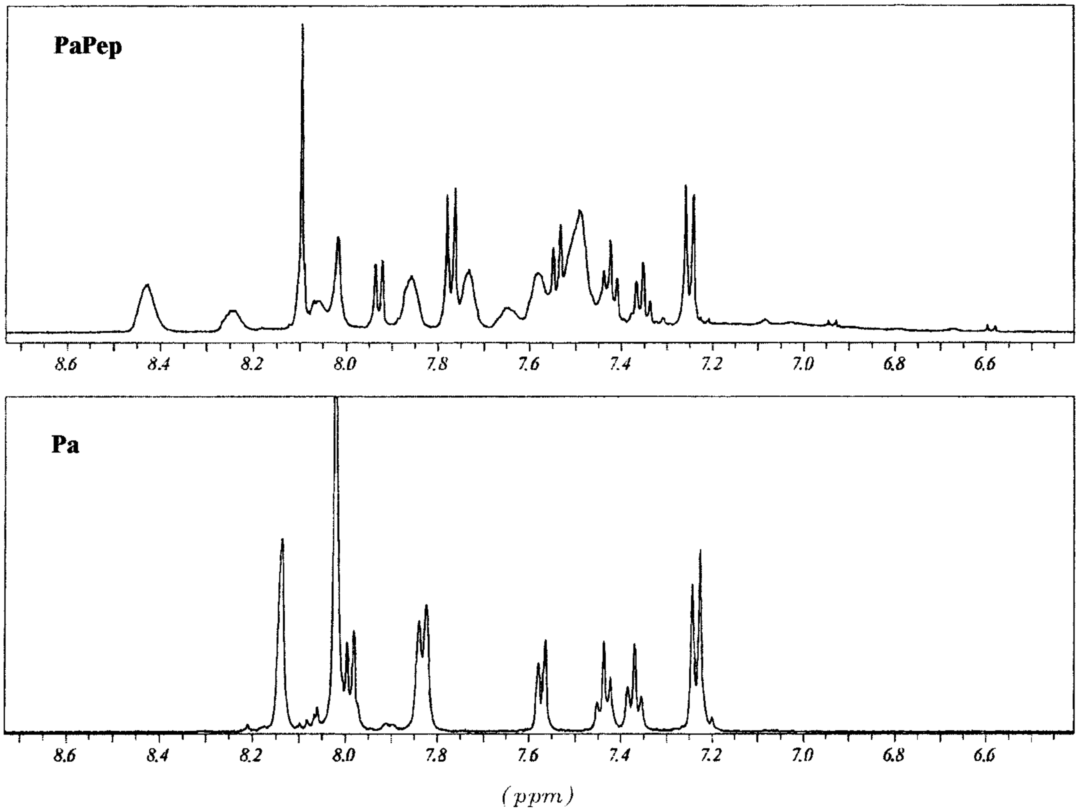


Figure 1. The 8.6–6.9 ppm range of the ^{1}H NMR spectra of the amide-based oligomer **Pa** (bottom) and of **PaPep** (top). Peak assignments are reported in the experimental part.

Table 3. Solubilization Experiments with Pem

neutral solvent[a]	protic solvent[a]	solubility	stabilizing solvent	stability after neutralization
(none)	DMCPA	yes	(none)	
(none)	formic acid	yes	(none)	
(none)	formic acid + hexafluoro-2-propanol	yes	(none)	
m-cresol	DMCPA	yes	DMF	unstable
ODCB	DMCPA	yes	DMF	stable
toluene	DMCPA	yes	DMF	stable
chlorobenzene	DMCPA	yes	DMF	stable
2-chlorophenol	DMCPA	yes	not necessary	stable
toluene	TsOH	no	(none)	
toluene	benzoic acid	swelling	(none)	
ODCB	benzoic acid	no	(none)	
2-chlorophenol	formic acid	yes	not necessary	stable
DMF	formic acid	no	(none)	
DMSO	formic acid	no	(none)	
dichloromethane	formic acid	yes	DMF	unstable
chloroform	formic acid	yes	DMF	unstable
1,2-dichloroethane	formic acid	yes	DMF	stable

[a] DMCPA: di-*m*-cresyl-phosphoric acid. ODCB: 1,2-dichlorobenzene. TsOH: *p*-toluenesulfonic acid.

1,2-dichloroethane, chloroform, methylene chloride, *N*,*N*-dimethyl formamide (DMF), *N*-methylpyrrolidone (NMP), benzene, or *o*-dichlorobenzene (ODCB), but different from most literature polyquinolines, significant swelling was observed. The hydrogen-bonding solvents (NMP, DMF, and *m*-cresol) showed the highest degree of swelling; from this, we assumed a process based on solvent exchange from an acid to a protic/aromatic solvent mixture might possibly lead to the dissolution of the polymers.

It could be argued that the enhanced solubility can come not only from the chemical structure (introduction of the silicon atom), but also from rather low molecular weight (see viscosity).

In a typical experiment, the polymer was dissolved in a small volume of the acidic solution used for polymerization (see above) and then diluted with a water-immiscible solvent (e.g., OCDB). The solution was then extracted with aqueous base (Na_2CO_3, pH = 11) in order to remove acidic compounds (e.g., *m*-cresol and di-*m*-cresyl phosphate), and a stabilizing, hydrogen-bonding solvent (e.g., DMF) was then immediately added. The mixed solution was dried over Na_2SO_4 to remove residual water and then characterized by UV–vis and fluorescence spectroscopy. Several solvent systems were used, and the results are summarized in Table 3.

Different from systems described in the literature,[14,15,20] where protonated polyquinolines had been processed and where deprotonation was only effected in the final form, e.g., as spun film, with our method neutral polyquinolines can be brought into solution in

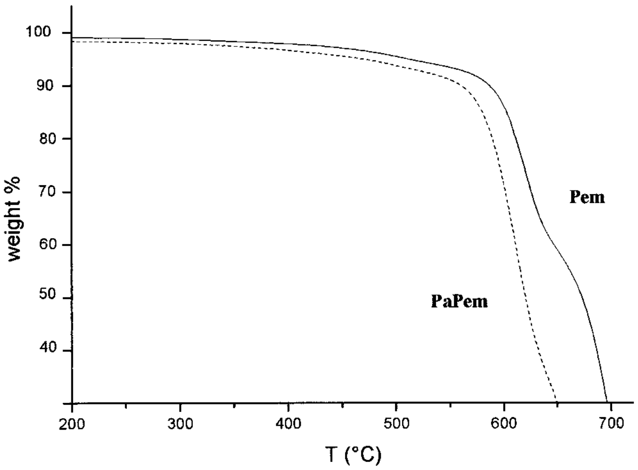


Figure 2. TGA of **Pem** (solid line) and **PaPem** (dashed line) at a heating rate of 20 °C/min, under air.

fairly volatile solvents, such as toluene, cholorobenzene and OCDB. As an alternative, the polymers can be solubilized in a partially protonated form in volatile weak acids, such as formic acid or *p*-chlorophenol, which do not require basic treatments too. Acid-free solutions of the polyquinolines **Pep** and **Pem** were spun into thin films on glass substrates, yielding colorless films in good optical quality (the protonated form is of red color).

The aramid–polyquinoline block copolymers **PaPep** and **PaPem** are readily soluble in NMP at room temperature and in DMF at 120 °C, and thin films of high quality can be spun from NMP.

Thermal Characteristics. The polymers were examined by DSC and TGA measurements. All have exceptionally high thermal stability: TGA showed the onset of decomposition between 570 and 600 °C (see Table 1, the decomposition temperature curves are shown in Figure 2), consistent with literature values[20] on other polyquinolines. The glass temperatures of the quinoline-only polymers were in the range 260–330 °C (see Table 1), while **PaPep** and **PaPem** are characterized by lower values (**PaPep**, 240 °C; **PaPem**, 183 °C). The copolymers are characterized by the same (presynthesized) **Pa** block and the **Pep** and **Pem** homopolymers show indistinguishable T_g values; the T_g difference between the two copolymers must thus be correlated with the quinoline content (see Table 2), which for the aramid–polyquinoline block copolymers was estimated from ^{1}H NMR spectra, elemental analysis, and the determination of residual SiO_2 after thermogravimetric analysis in air.

None of the polymers showed any sign of crystallinity, neither in X-ray diffraction nor in DSC on heating to 400 °C (only the glass transition is visible).

Optical Properties. The protonated quinoline-only polymers (Table 1) exhibit absorption maxima at wavelengths in the range 355–362 nm. Solutions of the neutral polymers (after the neutralization/extraction procedure previously described) show maxima around 350 nm in toluene/DMF, corresponding to the absorption of the quinoline rings. These and the corresponding extinction coefficients in solution are collected in Table 1. Values for λ_{max} for **Pem** in different solvents are reported in Table 4, and the corresponding spectra are shown in Figure 3. There is no traditional solvatochromic effect; the reddish color of the protic solution is evidently due to band broadening.

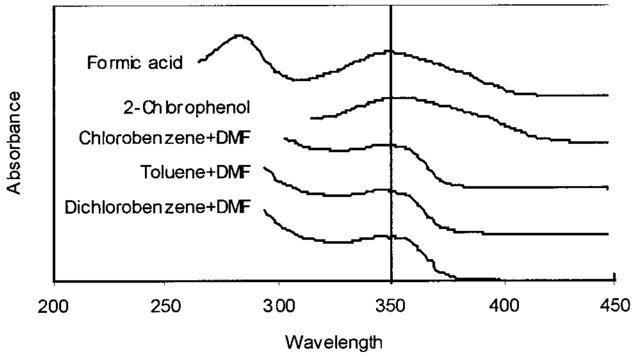


Figure 3. UV spectra of solutions of neutral **Pem** in different solvents.

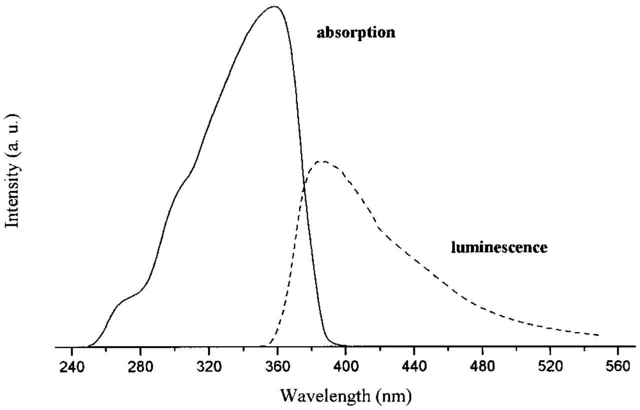


Figure 4. UV/VIS absorption (solid line) and photoluminescence spectra (dashed line) of **PaPep** in NMP solution.

Table 4. Absorption Maxima of Pem in Different Solvents

solvent	λ_{max} (nm)
chlorobenzene + DMF	350
toluene + DMF	346
1,2-dichlorobenzene + DMF	349
2-chlorophenol	350
formic acid	283/350

Photoluminescence spectra were also obtained on neutral solutions of the **Pep** and **Pem** and contained a double emission band with maxima around 380 and 415 nm for excitation in the range 300–360 nm. **PaPep** and **PaPem** in NMP solution showed intense absorption peaks at 280 and 350 nm (Table 2) and emissions bands in the violet-blue region (370–420 nm). Figure 4 displays absorption and emission spectra of **PaPep** in NMP.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich (Buchs, Switzerland) or Fluka (Buchs, Switzerland) and were used as received unless otherwise specified. Tetrahydrofuran (THF) was distilled twice on a liquid mixture of sodium and potassium, with benzophenone under nitrogen. *N*-methyl-2-pyrrolidone (NMP) was refluxed over calcium hydride for some hours and then distilled and collected on molecular sieves. All glass systems used for reaction were flamed out and kept under nitrogen.

NMR spectra were collected on a BRUKER FT NMR 300 MHz spectrometer. Optical absorption spectroscopy was performed on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. Fluorescence spectra were obtained from a Spex 0.22m Fluorolog spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out under nitrogen or air with a Perkin-Elmer DSC-7 and a Mettler TG50 apparatus, at a rate of 10 or 20 K/min.

Specific viscosities were measured in an Ubbelohde viscometer and extrapolated to zero concentration to obtain intrinsic viscosities. X-ray diffraction patterns were recorded in a STOE powder diffractometer (STADI P, Ge monochromator; Cu Kα_1 = 1.540 56 Å, PDS detector).

2-Methyl-2-(4-bromophenyl)-1,3-dioxalane. In a two-necked flask, 3.79 g (0.022 mol) of *p*-toluenesulfonic acid was dissolved in 500 mL of benzene by heating to reflux. Ethylene glycol (43.5 g, 0.700 mol) and 4-bromoacetophenone were then added. A Dean−Stark water-absorption trap was connected to the system and the reaction was run for 2 days under nitrogen. Aliquots of reaction product were periodically collected and the progress of the reaction was monitored by FT-IR. After 2 days, the water collection stopped at 100% of the theoretical yield and the IR spectrum showed that the reaction was complete. The solution was allowed to cool to room temperature, the *p*-toluenesulfonic acid neutralized and extracted with ice-cooled aqueous base (NaOH). The organic layer was separated and dried with sodium sulfate, and benzene was removed at reduced pressure. The oil so obtained was distilled at 0.1 mbar and 110 °C and provided a crystalline product, mp 39−40 °C. Yield: 93%.

IR (KBr): 2989 (m), 2954 ($\nu_{as}(CH_3)$), 2888 ($\nu_s(CH_3)$, $\nu_s(CH_2)$), 1591 (ν(C−C)), 1483 (ν(C−C)), 1443 (ν(C−C)), 1393, 1373, 1250, 1196 (ν(C−O)), 1079 (ν_{as}(C−O)), 1040 (ν(C−Br)), 1010, 947, 874, 826 (δ(C−H) oop para subst.), 766 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.43 (s, 2H, Φ); 7.35 (d, 2H, Φ); 4.01 (m, 2H, CH_2); 3.73 (m, 2H, CH_2); 1.6 (s, 3H, CH_3) ppm.

2-Methyl-2-(3-bromophenyl)-1,3-dioxalane. The same procedure was used as for 2-methyl-2-(4-bromophenyl)-1,3-dioxalane, but with 3-bromoacetophenone as the starting reagent. Yield: 77%.

IR (KBr): 2989 (m), 2888 ($\nu_s(CH_3)$, $\nu_s(CH_2)$), 1569 (ν(C−C)), 1471 (ν(C−C)), 1417 (ν(C−C)), 1373, 1273, 1238, 1201, 1117 (ν(C−O)), 1068 (ν_{as}(C−O)), 1039 (ν(C−Br)), 997, 948, 874, 793 (δ(C−H) oop meta subst.), 704 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.64 (s, 1H, Φ); 7.30 (m, 3H, Φ); 4.04 (m, 2H, CH_2); 3.77 (m, 2H, CH_2); 1.63 (s, 3H, CH_3) ppm.

Bis(*p*-acetophenyl)diphenylsilane (monomer p). 2-Methyl-2-(4-bromophenyl)-1,3-dioxalane (5.21 g, 0.0214 mol) was transferred under nitrogen into a three-necked flask and diluted with 50 mL of anhydrous THF. The solution was cooled to −78 °C, and a 1.6 M solution of butyllithium in hexane (13.4 mL, 0.0214 mol) was added slowly through seal. After being stirred for 15 min, the solution was warmed to −40 °C for some minutes to complete the reaction. The bath was then cooled again to −78 °C and diphenyldichlorosilane (2.72 g, 0.0107 mol) diluted in 50 mL of dry THF was added drop by drop. After 20 min, the solution was allowed to warm slowly to room temperature and stirred overnight. The THF was then removed at reduced pressure and the remaining liquid was diluted in 130 mL of acetone and 130 mL of water. Concentrated sulfuric acid (3 mL) was added, the solvent was then removed, and the resulting solution was extracted with methylene chloride and washed with water. The organic layer was dried with Na_2SO_4 and the product (yield 86%) purified by column chromatography on silica gel with a eluant gradient, from pure methylene chloride to a mixture of CH_2Cl_2 and 5% ethyl acetate. A microcrystalline white solid was obtained (final yield of 57%).

IR (KBr): 3096, 3048, 3021 (ν(CH)), 3008 ($\nu(CH_3)$), 1686 (ν(C=O)), 1595 (ν(C−C)), 1428, 1388, 1358, 1266, 1198, 1112, 957, 821 (δ(C−H) oop para subst.), 741 (δ(C−H) oop mono subst.), 701 (ν(C−Si)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.95 (d, 4H, Φ); 7.67 (d, 4H, Φ); 7.54 (d, 4H, Φ); 7.37−7.50 (m, 6H, Φ); 2.61 (s, 6H, CH_3) ppm. ^{13}C NMR: 26.72 (CH_3), 127.43, 128.23, 130.21, 132,59, 136.32, 136.60, 138.03, 140.20, 198.30 (C=O) ppm. Anal. Calcd for $C_{28}H_{24}O_2Si$: C, 79.96; H, 5.75. Found: C, 79.84; H, 5.86.

Bis(*m*-acetophenyl)diphenylsilane (monomer m). The same procedure was used as for monomer **p**, but with 2-methyl-2-(3-bromophenyl)-1,3-dioxalane (5 g, 0.0206 mol), butyllithium (12.9 mL, 0.0103 mol), diphenyldichlorosilane (2.61 g, 0.0103 mol), and 100 mL of dry THF as starting materials and solvent. Column chromatography yielded a clear viscous liquid that slowly crystallized in white needle crystals. Final yield: 60%.

IR (KBr): 3069, 3052, 3023 (ν(CH)), 3009 ($\nu(CH_3)$), 1686 (ν(C=O)), 1584 (ν(C−C)), 1428 (ν(C−C)), 1355, 1258, 1109, 793 (δ(C−H) oop meta subst.), 741 (δ(C−H) oop mono subst.), 698 (ν(C−Si)) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.17 (m, 2H, Φ); 8.03 (dd, 2H, Φ); 7.76 (dt, 2H, Φ); 7.37−7.58 (m, 8H, Φ); 2.51 (s, 6H, CH_3) ppm. ^{13}C NMR: 26.59 (CH_3), 128.21, 128.34, 129.66, 130.15, 132.80, 134.65, 135.99, 136.27, 136.67, 140.86, 198.22 (C=O) ppm. Anal. Calcd for $C_{28}H_{24}O_2Si$: C, 79.96; H, 5.75. Found: C, 79.89; H, 5.94.

Polyquinoline Pep. A mixture of bis(*p*-acetophenyl)diphenylsilane **p** (1.030 g, 2.448 mmol) and 4,4′-diamino-3,3′-dibenzoyldiphenyl ether **e** (1.000 g, 2.448 mmol), di-*m*-cresyl phosphate (17 g), and freshly distilled *m*-cresol (7 g) was placed in a two-necked flask. The stirred reaction mixture was flushed with nitrogen, heated in an oil bath to 140 °C, and allowed to react for 60 h under an inert atmosphere. The solution turned dark red and had a viscous consistency. Still hot, the solution was poured into an agitated solution of 500 mL of methanol, containing 20% v/v of triethlylamine. The precipitated polymer was recovered, vacuum-dried, and then redissolved in 150 mL of a mixture of di-*m*-cresyl phosphate containing 10% v/v of *m*-cresol. The solution was precipitated again in the same mixture of methanol and triethlylamine. The polymer was collected, centrifuged, and continuously extracted in a Kumagawa extractor for 24 h with a solution of methanol containing 20% triethylamine. Drying at 100 °C for 24 h afforded 1.52 g (82%) of pure polymer.

IR (KBr): 3062 (ν(C−H)), 1611 (ν(C−C)), 1589 (ν(C−C)), 1535, 1486 (ν(C−C)), 1457 (ν(C−C)), 1400, 1355, 1234, 1205, (ν(C−O)), 1109, 828 (δ(C−H) oop para subst.), 766 (δ(C−H) oop mono subst.), 699 (ν(C−Si)). T_g = 280 °C. Thermal stability: 5% weight loss up to 580 °C. Intrinsic viscosity (solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta]$ = 1.67 dL/g. Anal. Calcd: C, 85.68; H, 4.79; N, 3.70. Found: C, 84.69; H, 5.04; N,3.80.

Polyquinoline Pem. The same procedure was used as for polyquinoline **Pep**, but with monomer **m** (2.800 g, 6.657 mmol) and **e** (2.719 g, 6.657 mmol) as starting materials. Di-*m*-cresyl phosphate and *m*-cresol were used as the reaction medium. Yield of 90%.

IR (KBr): 3062 (ν(C−H)), 1611 (ν(C−C)), 1589 (ν(C−C)), 1544, 1489 (ν(C−C)), 1457 (ν(C−C)), 1234, 1206, (ν(C−O)), 1110, 828, 798 (δ(C−H) oop meta subst.), 699 (ν(C−Si)). T_g = 280 °C. Thermal stability: 5% weight loss up to 595 °C. Intrinsic viscosity (solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta]$ = 0.81 dL/g. Anal. Calcd: C, 85.68; H, 4.79; N, 3.70. Found: C, 82.73; H, 4.86; N, 3.82.

Polyquinoline Pcp. The same procedure was used as for polyquinoline **Pep**, but with an equimolar amount of monomers **p** and **e** as starting materials. Di-*m*-cresyl phosphate and *m*-cresol were used as the reaction medium.

IR (KBr): 3035 (ν(C−H)), 1586 (ν(C−C)), 1534, 1485 (ν(C−C)), 1447 (ν(C−C)), 1119, 1058, 828 (δ(C−H) oop para subst.), 739 (δ(C−H) oop mono subst.), 699 (ν(C−Si)). T_g = 270 °C. Thermal stability: 5% weight loss up to 585 °C. Intrinsic viscosity (solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta]$ = 0.62 dL/g. Anal. Calcd: C, 88.90; H, 4.90; N, 3.09. Found: C, 87.39; H, 5.30; N, 3.19.

Polyquinoline Pcm. The same procedure was used as for polyquinoline **Pep**, but employing an equimolar amount of monomers **m** and **c** as starting materials. Di-*m*-cresyl phosphate and *m*-cresol were used as the reaction medium.

IR (KBr): 3039 (ν(C−H)), 1587 (ν(C−C)), 1543, 1488 (ν(C−C)), 1447 (ν(C−C)), 1114, 1077, 882, 829, 798 (δ(C−H) oop meta subst.), 742 (δ(C−H) oop mono subst.), 698 (ν(C−Si)). T_g = 270 °C. Thermal stability: 5% weight loss up to 600 °C. Intrinsic viscosity (solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta]$ = 0.32 dL/g. Anal. Calcd: C, 88.90; H, 4.90; N, 3.09. Found: C, 87.43; H, 5.29; N, 3.30.

Random Copolymer Pemp. A mixture of bis(*p*-acetophenyl)diphenylsilane **p** (0.244 g, 0.5806 mmol), bis(*m*-acetophenyl)diphenylsilane **m** (0.244 g, 0.5806 mmol) and 4,4′-diamino-3,3′-dibenzoyldiphenyl ether **e** (0.474 g, 1.161 mmol) in di-*m*-cresyl phosphate (14 g) in freshly distilled *m*-cresol (4 g) was allowed to react at 140 °C, for 60 h, under nitrogen. The viscous solution was poured in methanol containing 20% triethylamine and the obtained polymer was collected, dissolved again in a mixture of di-*m*-cresyl phosphate/10% *m*-cresol, and precipitated in methanol with 20% triethlylamine. After extraction in a Kumagawa extractor with methanol and triethlylamine, the random copolymer was dried under vacuum and characterized.

IR (KBr): 3045 (ν(C−H)), 1661 (ν(C−C)), 1589 (ν(C−C)), 1535, 1488 (ν(C−C)), 1458 (ν(C−C)), 1235, 1205 (ν(C−O)), 1117, 828 (δ(C−H) oop paras), 798 (δ(C−H) oop meta subst.), 764 (δ(C−H) oop mono subst.), 699 (ν(C−Si)). $T_g = 260$ °C. Thermal stability: 5% weight loss up to 565 °C. Intrinsic viscosity (solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta] = 0.25$ dL/g. Anal. Calcd: C, 85.68; H, 4.79; N, 3.70. Found: C, 69.07; H, 4.27; N, 3.34.

Block Copolymer PemPep. Bis(*m*-acetophenyl)diphenylsilane **m** (0.377 g, 0.8971 mmol, 8 equiv), and 4,4′-diamino-3,3′-dibenzoyldiphenyl ether **e** (0.412 g, 1.009 mmol, 9 equiv) were dissolved in a flask with di-*m*-cresyl phosphate (10 g) and freshly distilled *m*-cresol (4 g). In a separate flask, bis(*p*-acetophenyl)diphenylsilane **p** (0.424 g, 1.009 mmol) and 4,4′-diamino-3,3′-dibenzoyldiphenyl ether **e** (0.366 g, 0.897 mmol, 8 equiv) were dissolved in the same reaction medium. Both solutions were stirred for 24 h at 140 °C, under nitrogen. The first solution was then quantitatively transferred into the second flask, and the mixture was allowed to react for 3 days more at 140 °C, under nitrogen. The resulting viscous solution was poured into a solution of methanol containing 20% v/v triethylamine. The precipitated material was collected and purified as described for **Pemp**.

IR (KBr): 3050 (ν(C−H)), 1611 (ν(C−C)), 1589 (ν(C−C)), 1535, 1488 (ν(C−C)), 1457 (ν(C−C)), 1234, 1205 (ν(C−O)), 1117, 830 (δ(C−H) oop para subst.), 798 (δ(C−H) oop meta subst.), 766 (δ(C−H) oop mono subst.), 699 (ν(C−Si)). $T_g = 330$ °C. Thermal stability: 5% weight loss up to 590 °C. Intrinsic viscosity (solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta] = 0.35$ dL/g. Anal. Calcd: C, 85.68; H, 4.79; N, 3.70. Found: C, 69.07; H, 4.27; N, 3.34.

Aramid Oligomer with Cardo Units (Pa). The cardo monomer 9,9-bis(4-aminophenyl)fluorene (1.000 g, 0.00287 mol) and freshly sublimated terephthaloyl dichloride (0.647 g, 0.00319 mol) were dissolved in cold, freshly distilled *N*-methyl-2-pyrrolidone (NMP). The solution was stirred at 5 °C for 1 h and then at room temperature for 12 h. Finally, 4-aminoacetophenone (0.0431 g, 0.319 mmol) was added and the reaction was allowed to proceed for 2 h at room temperature and then for 1 h at 100 °C. After cooling, the solution was poured into 200 mL of methanol. The resulting solid was dissolved in 20 mL of DMF, precipitated again in methanol, collected and dried at 40 °C under vacuum.

^{1}H NMR (DMF-*d*): $\delta = 10.45$ (s, 1H), 8.14 (s, 4H), 7.99 (d, 2H), 7.83 (d, 4H), 7.57 (d, 2H), 7.42 (t, 2H), 7.37 (t, 2H), 7.23 (d, 4H) ppm. IR (KBr): 1664 (ν(C=O)), 1597, 1527, 1510 (ν(CN), δ(CN)), 1447, 1406, 1385, 1322, 1297, 1276, 1259, 1182, 1097, 1075, 1018, 890, 886, 819, 749, 733 cm^{-1}.

Aramid−Polyquinoline Block Copolymer PaPep. Monomers **p** (0.371 g, 0.88 mmol, 9 equiv) and **e** (0.400 g, 0.98 mmol, 10 equiv) were added to a mixture of di-*m*-cresyl phosphate (7 g) and *m*-cresol (3 g) and stirred under nitrogen at 140 °C. After 24 h, the reaction mixture was diluted with 10 mL more of *m*-cresol and the amide oligomer **Pa** was added. The mixture was allowed to react for 48 h at 140 °C, under nitrogen. After cooling, the copolymer was precipitated in a mixture of methanol with 20% triethylamine and dissolved in NMP. This procedure was repeated twice, and then the resulting polymer washed with methanol/triethylamine, centrifuged and dried at 40 °C at reduced pressure. Yield: 86%.

^{1}H NMR (DMF-*d*, 70 °C): $\delta = 9.93$ (s, 1H), 8.43 (broad, 2H), 8.24 (broad, 1H), 8.09, 8.06 (s, 4H), 7.93 (d, 2H), 7.85, 7.77 (d, 4H), 7.73, 7.65, 7.58, 7.54 (d, 2H), 7.49, 7.42 (t, 2H), 7.36 (t, 2H), 7.24 (d, 4H) ppm. IR (KBr): 1685, 1676, 1670, 1664 (ν(C=O)), 1654, 1648, 1611, 1592, 1534, 1522, 1508, 1487, 1458, 1405, 1258, 1236, 1207, 1111, 710, 700 (ν(C−Si)) cm^{-1}. $T_g = 240$ °C, thermal stability up to 580 °C. Intrinsic viscosity (polymer solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta] = 0.37$ dL/g.

Aramid−Polyquinoline Block Copolymer PaPem. The same procedure as for copolymer **PaPep**, except that the quinoline blocks were prepared starting from monomers **m** and **e** in a mixture of di-*m*-cresyl phosphate/*m*-cresol; after 24 h, the oligoamide block **Pa** was added, and the reaction proceeded for 48 h at 140 °C, under nitrogen. The copolymer was obtained with a final yield of 80%.

^{1}H NMR (DMF-*d*, 70 °C): $\delta = 10.43$ (s, 1H), 8.76 (broad, 2H), 8.47 (broad, 2H), 8.13 (s, 4H), 8.02 (broad), 8.82 (d, 2H), 7.72 (broad), 7.45 (broad), 7.23 (d, 4H) ppm. IR (KBr): 1701, 1696, 1684, 1654, 1647, 1636, 1617, 1559, 1540, 1522, 1507, 1490, 1458, 1384, 1207, 1180, 1110, 700 (ν(C−Si)) cm^{-1}. $T_g =$ 183 °C, thermal stability up to 573 °C. Intrinsic viscosity (polymer solutions in di-*m*-cresyl phosphate/5% *m*-cresol, at 100 °C) $[\eta] = 0.20$ dL/g.

Conclusions

A number of novel silicon-based polyquinolines were synthesized using Stille's[12,18,20,25−29] synthetic procedures, and the resulting materials were characterized. It was demonstrated that they are completely amorphous in the solid state and can be dissolved as neutral chains.

The introduction of silicon atoms into the polyquinoline main chain did not decrease the outstanding stability compared to the corresponding non-silicon-containing polymers but, on the contrary, even slightly improved the thermo-oxidative resilience. The remarkable difference is, however, that the new polyquinolines can be solubilized as neutral molecules.

The use of para- or meta-substituted phenyl rings apparently did not affect the thermal, optical, and solubility properties, and the chain constitution, i.e., the random or blocky structure of copolyquinolines, did also not lessen the remarkable stability.

In solution, these polymers exhibit optical and NMR spectra analogous to the corresponding soluble aramid−polyquinoline block copolymers, indicating that with the solvent exchange process the neutral molecules were effectively molecularly dispersed (although aggregation of the polyquinoline segments in solution is to be expected).

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