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Molecular design of new π-conjugated poly(ketanil)s with tunable spectroscopic properties

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New conjugated aryl-substituted poly(azomethine)s, termed poly(ketanil)s, have been synthesised from 1,4-phenylenediamine (or 3,3′,5,5′-tetramethylbenzidine) and two different diketones *via* polycondensation with the goal to obtain new materials with tunable spectroscopic properties. It is demonstrated that both the absorption and photoluminescence spectra of these poly(ketanil)s can be modified not only by changing the chemical constitution of both repeating subunits in the polymer main chain but also *via* acid-base doping involving the protonation of the ketimine groups. By combining these two methods it is possible to precisely tune the absorption and emission spectra of the poly(ketanil)s. The use of bifunctional protonating agents, containing plasticising groups, for example 1,2-(di-2-ethylhexyl)ester of 4-sulfophthalic acid (**DEHEPSA**), in addition to modifying the spectroscopic properties of the polymers, leads to a lowering of their glass transition temperature (T_g), improving in such a manner the flexibility of the prepared poly(ketanil)s materials.

Introduction

Conjugated polymers have aroused widespread interest during the last two decades, because of their useful electronic, optoelectronic, electrochemical and nonlinear optical properties. Among conjugated polymers, those with extended π systems involving alternating C=C and C–C bonds are predominant. This is the case of many prototypical conjugated polymers, such as poly(acetylene), poly(*p*-phenylene) and poly(*p*-phenylenevinylene) (PPV). Since the –CH=N– group is isoelectronic with the –CH=CH– group, the incorporation of nitrogen atoms into the conjugated system leads to another class of conjugated polymers closely related to poly(*p*-phenylenevinylene)s, namely aromatic poly(azomethine)s (PAZ), which are also extensively studied in recent years because of their interesting electronic and optical properties.[1–5] Conjugated poly(ketanil)s, abbreviated in the subsequent text as **PKs**, can be considered as simple derivatives of the corresponding poly(azomethine)s in which the hydrogen atom of the azomethine group is replaced by an aryl group. The chemical structure of the simplest conjugated poly(ketanil) is presented in Fig. 1 and compared with those of the simplest PAZ and the simplest PPV with the goal to demonstrate the similarities between these three families of conjugated polymers.

Literature data concerning the synthesis and the investigation of optical properties of **PKs** are scarce.[6–8] This is rather surprising because **PKs** seem to be excellent candidates for various applications such as optical sensors or organic semiconductors in plastic electronics and optoelectronics devices.[9] In particular they should combine a rather facile tuning of their spectroscopic properties with improved thermal stability as compared to other conjugated polymers. This last property is of significant technological importance since conjugated polymer based materials used, for example, in organic electronics and optoelectronics frequently suffer from insufficient thermostability and photostability.[10–21]

Moreover, because of the presence of an electron lone pair at the nitrogen atom in the ketimine groups, **PKs** can be protonated with Brønstedt acids or complexed with Lewis acids. This opens up an additional possibility to tune their physical properties *via* dopant engineering. Several examples of dopant induced polymer modifications are known from the literature. Acid-base doping may not only render the conjugated polymer conductive but also lower its glass transition temperature, T_g, provided that specially designed plasticising dopants are used.[22] It may also alter the polymer spectroscopic properties. For example, protonation of poly(*p*-phenylenevinylene) derivatives containing bipyridine subunits results in a significant increase of the photoluminescence Stokes shift of this polymer.[23] Finally acid-base doping can be used for the preparation of poly(ketanil) supported heterogeneous catalysts since basic centres on the polymer surface can easily bind catalytically active centres of the Lewis or Brønsted acid types.

A rather unique feature of **PKs** synthesised in this research is the possibility of a precise tuning of their spectroscopic properties by a combination of chain and dopant engineering methods. In this perspective, the determination of the structure-spectroscopic properties relationship, for this new family of polymers, is important not only from the point of view of basic research but also in view of their possible applications. To achieve this goal we first study the spectroscopic properties of **PKs** in their base form and then in the protonated (doped) form. As the protonating agent we use 1,2-(di-2-ethylhexyl)ester of 4-sulfophthalic acid (**DEHEPSA**), which due to the presence of plasticising groups improves the processibility of **PKs** by lowering their T_g.

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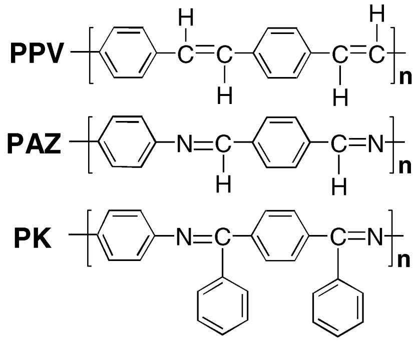


Fig. 1 Chemical structures of poly(*p*-phenylenevinylene) (PPV), the simplest poly(azomethine) (PAZ) and the simplest poly(ketanil) (PK).

Experimental

Materials

Acetone was dried and distilled in the usual manner. *meta*-Cresol (MC) was purified by distillation. Methanol, hexane, dimethylacetamide (DMA) were used without any purification. 3,3′,5,5′-Tetramethylbenzidine (Aldrich) was used without further purification. 1,4-Phenylenediamine (Aldrich) was sublimed. Aniline (Aldrich) and 2,6-dimethylaniline (Aldrich) were distilled prior to their use. The protonating agent, 1,2-(di-2-ethylhexyl)ester of 4-sulfophthalic acid (abbreviated as **DEHEPSA**), was prepared as described in ref. 24. *p*-Dibenzoylbenzene (**DB**) and *p*-dibenzoylxylene (**DK**) were synthesized using the Friedel–Crafts reaction as described in ref. 25.

DB. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ: 7.58 (m, 4H), 7.71 (m, 2H), 7.81 (m, 4H), 7.87 (s, 4H). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ: 128.21, 128.93, 129.17, 132.52, 136.33, 139.87, 194.84. Mp 161 °C. FTIR (KBr, cm^{-1}): 3084, 1657 (C=O), 1595, 1576, 1447, 1270, 1158, 1109, 1070, 858, 783, 708, 677. Anal. calcd for $C_{20}H_{14}O_2$: C, 83.90%; H, 4.93%; found: C, 83.56%; H, 4.86%.

DK. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ 2.19 (s, 3H), 2.28 (s, 3H), 7.14 (m, 2H), 7.26 (m, 2H), 7.29 (m, 2H), 7.82 (s, 4H). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ 18.53, 19.88, 128.23, 129.23, 130.53, 130.91, 132.57, 134.35, 137.42, 140.36, 196.93. Mp 119 °C. FTIR (KBr, cm^{-1}): 3025, 2962, 1659 (C=O), 1569, 1500, 1451, 1261, 1157, 1112, 1041, 949, 843, 826, 4 747,695. Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18%; H, 6.48%; found: C, 84.04%; H, 6.37%.

Characterisation techniques

The obtained polymers were characterised by the following techniques: elemental analysis (240C Perkin–Elmer analyser), ^{1}H-NMR and ^{13}C-NMR (Varian Inova 300 spectrometer, $CDCl_3$ solvent against TMS as an internal reference unless otherwise specified in the text), and FTIR (BIO-RAD FTS 40 A spectrometer, KBr pressed pellet technique).

Molecular weights of the synthesised compounds were determined using size-exclusion chromatography (SEC). The determinations were carried out on a Spectra Physics 8800 chromatograph, at a temperature of 308 K, using a Shodex SE61 differential refractometer as a detector. Tetrahydrofurane (THF) was used as the eluent and polystyrene (PS) samples of narrow polydispersity as standards.

Glass transition temperatures (T_g) of the synthesised polymers (sample weight of *ca.* 20 mg, scanning rate of 20 K min^{-1}) were determined by differential scanning calorimetry (DSC) on a TA-DSC 2010 apparatus using sealed aluminium pans under nitrogen atmosphere (flow rate of *ca.* 30 ml min^{-1}). Thermogravimetric analyses (TG) were performed on a Paulik–Erdey apparatus at a heating rate of 10 K min^{-1} under nitrogen.

UV-vis solution absorption spectra were recorded using a Hewlett–Packard 8452A spectrophotometer whereas the photoluminescence solution spectra were registered on a Fluorolog 3.12 Spex spectrometer with a 450 nm excitation line (450 W xenon lamp as the light source).

Wide angle X-ray diffraction patterns were recorded using powder samples on a HZG-4 diffractometer working in typical Bragg geometry (CuK_α radiation).

Synthesis of model compounds MI and MII

Two model compounds were synthesised: one having methyl substituents in the subunit originating from the amine and the other in the subunit originating from the diketone. Diketone **DK** (1 mmol) and 10 ml of aniline with 0.06 g of *p*-toluenesulfonic acid were refluxed with stirring for 10 h (**MII**). When diketone **DB** and 2,6-dimethylaniline (10 ml) were used the mixture was stirred and heated at 200 °C for 12 h (**MI**). **MI** and **MII** were precipitated with 100 ml of hexane and methanol, respectively. They were then filtered, washed and dried at 60 °C under vacuum for 12 h, and finally crystallised from an acetone–hexane mixture (1 : 1 v/v).

MI. Anal. calcd for $C_{36}H_{32}N_2$: C, 87.77%; H, 6.55%; N, 5.69%; found: C, 87.37%; H, 6.75%; N, 5.69%. ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 130.63 (C1), 137.20, 136.47 (C4), 166.61 (C5), 141.44, 139.87, 138.90 (C6), 148.70 (C10), 125.67 (C11), 122.80 (C13), 127.84, 128.36, 129.23, 127.74 (C7, C3, C2, C12), 18.53 (CH_3) FTIR (KBr, cm^{-1}): 3077, 3025, 2941, 2913, 2850, 1618, 1591, 1489, 1465, 1444, 1401, 1372, 1313, 1299, 1277, 1252, 1210, 1178, 1149, 1110, 1090, 1030, 1000, 979, 961, 947, 913, 861, 827, 775, 766, 697, 677, 542, 464. UV-vis (nm): 274 and 369 (DMA); 320 and 400 (MC).

MII. Anal. calcd for $C_{36}H_{32}N_2$: C, 87.77%; H, 6.55%; N, 5.69%; found: C, 87.30%; H, 6.58%; N, 5.62%. ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 129.83 (C1), 136.03 (C4), 168.06 (C5), 141.17 (C6), 150.73 (C10), 120.76, 120.61 (C11), 123.67 (C13), 128.57, 128.47 (C8), 134.69 (C9), 129.18, 128.66, 132.08, 129.47, 129.29, 128.35, 128.17 (C7, C3, C2, C12). FTIR (KBr, cm^{-1}): 3035, 2965, 2919, 2862, 1613, 1589, 1559, 1495, 1483, 1447, 1407, 1376, 1309, 1297, 1280, 1197, 1170, 1150, 1108, 1070, 1027, 995, 950, 903, 894, 861, 764, 751, 733, 695, 676, 619, 546, 528, 472, 460. UV-vis (nm): 280 and 349 (DMA); 340 and 370 (MC).

Polymer synthesis

In a typical preparation 1 mmol of a given diketone and 1 mmol of a diamine were heated and stirred at 180 °C for 24 h under nitrogen atmosphere. The mixture was then cooled to room temperature, scraped and powdered. The polymers (**PK1**, **PK2**, **PKK1**, and **PKK2**) were purified by Soxhlet extraction with methanol, then with acetone and finally dried at 60 °C under vacuum for 24 h.

PK1. FTIR (KBr, cm^{-1}): 3055, 3026, 1660, 1608, 1597, 1556, 1489, 1444, 1402, 1306, 1278, 1223, 1178, 1152, 1102, 1074, 1028, 1012, 1000, 954, 938, 916, 858, 840, 790, 774, 751, 701, 579. Anal. calcd for $C_{36}H_{28}N_2$: C, 87.15%; H, 5.03%; N, 7.82%; found: C, 86.58%; H, 5.11%; N, 7.40%.

PK2. FTIR (KBr, cm^{-1}): 3474, 3255, 3024, 2911, 2856, 1661, 1622, 1564, 1467, 1445, 1400, 1375, 1313, 1274, 1202, 1161, 1089, 1020, 1000, 937, 923, 860, 774, 749, 698, 668. Anal. calcd for $C_{36}H_{30}N_2$: C, 88.24%; H, 6.16%; N, 5.70%; found: C, 87.46%; H, 6.14%; N, 5.99%.

PKK1. FTIR (KBr, cm^{-1}): 3374, 3203, 2924, 2863, 1659, 1607, 1598, 1568, 1515, 1501, 1451, 1404, 1302, 1291, 1261, 1204, 1128, 1041, 1016, 989, 949, 901, 875, 843, 826, 758, 747, 721, 679, 582, 514, 468. Anal. calcd for $C_{30}H_{26}N_2$: C, 86.96%; H, 6.28%; N, 6.76%; found: C, 86.50%; H, 6.37%; N, 6.88%.

PKK2. FTIR (KBr, cm^{-1}): 3469, 3387, 3256, 3019, 2965, 2913, 2855, 1663, 1623, 1564, 1470, 1444, 1377, 1264, 1202, 1091, 1015, 951, 861, 815, 751. Anal. calcd for $C_{40}H_{38}N_2$: C, 87.91%; H, 6.95%; N, 5.13%; found: C, 86.77%; H, 6.41%; N, 5.70%.

Results and discussion

Characterisation of the model compounds

The results of the elemental analysis, ^{13}C-NMR, and FTIR spectroscopic investigations are fully consistent with the chemical structure of the model compounds schematically depicted in Fig. 2.

In particular, in the FTIR spectra, the absorption band at 1618 and 1613 cm^{-1} for **MI** and **MII**, respectively, which is characteristic of the –CH=N– group, confirms the presence of the ketanil units. This finding is consistent with the ^{13}C NMR data. In the spectrum of **MI** a clear signal characteristic of the carbon atom in the –CH=N– group is seen at *ca.* 167 ppm. The presence of the methyl groups in the diketone originating subunit results in a downfield shift of this signal by *ca.* 1.5 ppm. The proposed assigments of the NMR lines registered for **MI** and **MII** are listed in the Experimental (*vide supra*).[26] The splitting of the signals observed for carbon atoms C4 and C6 may indicate the presence of both *cis* and *trans* structures in model compound **MI**.

Consistent with the chemical nature of the model compounds, the UV-vis spectra of **MI** and **MII** show the presence of two bands ascribed to electronic transitions in the benzene ring and in the ketimine group, respectively. In **MI** these bands are located at 280 nm and 349 nm (DMA solvent), in **MII** at 274 nm and 369 nm in the same solvent. Both model compounds are solvatochromic: a large bathochromic shift is observed for both bands if an aprotic solvent such as DMA is replaced by a protic one (MC). The model compounds studied readily crystallise, which is facilitated by their symmetry and rigid structure. Their X-ray diffractograms reveal a set of well-defined Bragg reflections.[27]

Characterisation of the polymers

The main goal of the studies involving the model compounds was to determine basic structural and spectroscopic properties of the aromatic-ketimine systems on perfectly monodispersed samples and to verify the influence of the increasing chain length on these properties.

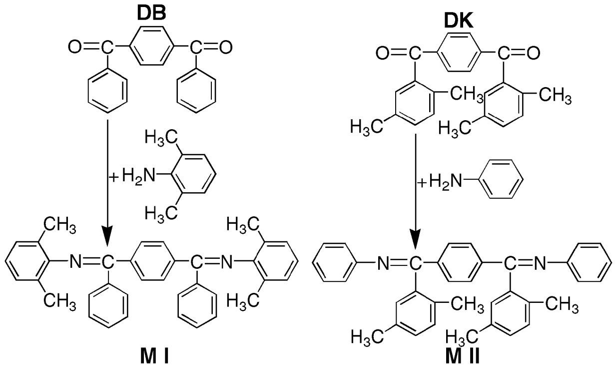


Fig. 2 Chemical structure of the ketanil model compounds **MI** and **MII**.

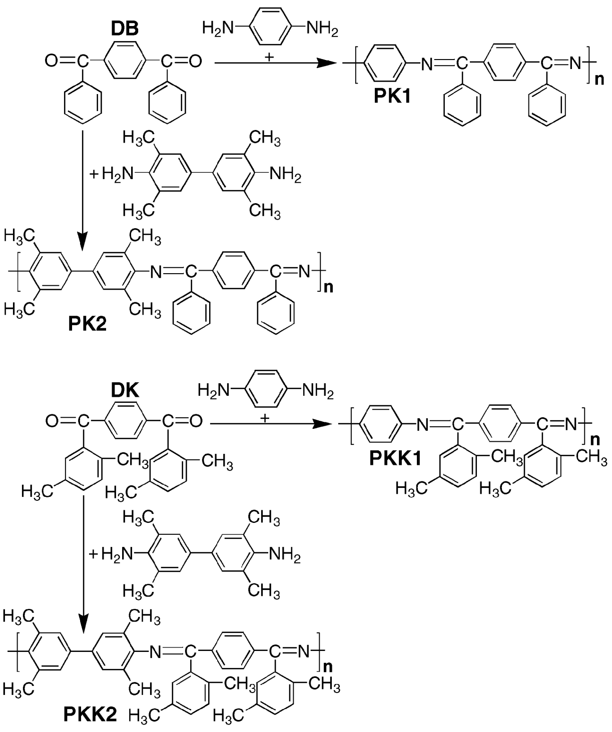


Fig. 3 Chemical structure of the synthesised poly(ketanil)s.

The chemical structures of the synthesised polymers are presented in Fig. 3. As seen from the SEC results (Table 1) their degree of polymerisation is rather low.

In the case of polyconjugated systems the results of SEC studies, using PS standards, must be considered only as a rough approximation of the real molecular weight. In principle the calibration with PS sharp fractions leads to an underestimation of the molecular weight of conjugated polymers for $M_n < 2.0$ kDa and its overestimation for M_n significantly higher than 2.0 kDa.[28] Thus, the apparent difference in M_n between **PK1** and **PK2** may in reality be smaller.

The presence of ketimine groups is confirmed by FTIR spectroscopy since in each case the band characteristic of the C=N stretching deformations is detected. The exact position of this band varies in the spectral range 1607–1623 cm^{-1}, shifting towards higher wavenumbers for the polymers with the methyl groups at the *ortho* position in the amine used for synthesis of the polymers (*i.e.*, for **PK2** and **PKK2**). This can be considered as a manifestation of the influence of steric effects on the conjugation. A similar shift, although of a lower value, is also observed in the case of the model compounds (*vide supra*). In Fig. 4 the IR spectrum of **PK1** is presented, which can be considered as typical of all the **PKs** discussed here. In addition to the C=N stretching band at 1608 cm^{-1}, a band at 1597 cm^{-1} can be distinguished and ascribed to the C=C stretching deformations in the aromatic ring. Because of the rather low molecular weight of the systems studied, end groups can also be spectroscopically detected. In particular a clear band characteristic of the carbonyl end group is present at 1660 cm^{-1}. It is shifted towards lower wavenumbers as a result of its conjugation with the π-bonding system of the polymer chain. A

Table 1 Molecular weights and polydispersity coefficients of the poly(ketanil)s determined by SEC

	M_n/kDa equiv. PS	M_w/kDa equiv. PS	M_w/M_n	DPn
PK1	1.45	1.89	1.3	~4
PK2	6.79	12.90	1.9	~14
PKK1	2.89	4.91	1.7	~7
PKK2	4.30	10.32	2.4	~8

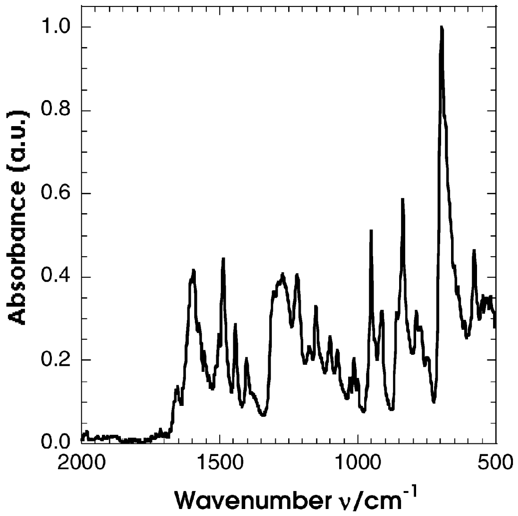


Fig. 4 FTIR spectrum of **PK1**.

weak band at 3385 cm^{-1} (not shown in Fig. 4) can, in turn, be ascribed to the end groups of the amine type.

In Table 2 the results of the ^{13}C NMR studies are collected, together with the proposed assignment of the observed signals.[26] The peak at *ca.* 167 ppm is characteristic of the carbon atom in the –CH=N– group. For the ketimine structure two isomers are possible (*cis* and *trans*), even though the *trans* structure is always supposed to be thermodynamically more stable. A splitting of the signals in the ^{13}C NMR spectrum seems to confirm the coexistence of both isomers.

The changes in the chemical shifts, observed upon modification of the chemical constitution of the diamine originating subunit, are consistent with the assignment proposed in Table 2. In the case of **PK2** and **PKK2**, the presence of methyl groups in the *ortho* position with respect to nitrogen results in a downfield shift of the signal related to C10 and C11 carbons and a slightly smaller upfield shift of the line ascribed to the C5 carbon in comparison with the polymers synthesised from 1,4-phenylenediamine. In contrast to the model compounds, the synthesised **PKs** are amorphous, as confirmed by X-ray diffraction. In the DSC investigations they give similar profiles with no melting endotherms and a clear glass transition temperature, T_g. These findings additionally corroborate their amorphous nature. The measured T_g values are collected in Table 3.

PK2 exhibits a significantly higher T_g as compared to **PK1** and especially **PKK1**. A similar increase in T_g, induced by the presence of a methyl group at the *ortho* position with respect to nitrogen, was previously observed in polyimides.[29,30] Finally, it should be stressed that the amorphous nature of the synthesised polymers revealed by X-ray diffraction and DSC studies unequivocally explains their facility to form good optical quality films on an appropriate substrate.

Conjugated polymers exhibit several physical properties that facilitate their technological application. Among them, the optical properties of these polymers have been extensively studied in view of their application as nonlinear optical materials, optical sensors of various types, semiconducting active layers in organic light emitting diodes (OLEDs), to name a few.[31–34] In this perspective detailed studies of the spectroscopic properties of the newly synthesised poly(ketanil)s is of crucial importance. They seem to be good candidates for technological applications since they exhibit enhanced thermal stability as compared to the majority of conjugated polymers. Moreover, as already mentioned, their absorption and luminescence spectra can be precisely tuned by a combination of chain and dopant engineering methods.

Typical solution UV-vis spectra of a conjugated poly(ketanil) and a **DEHEPSA** protonated poly(ketanil) are presented in Fig. 5.

As in the case of the model compounds (**MI** and **MII**) two types of chromophore groups in conjugation can be distinguished in the poly(ketanil) macromolecule: the aromatic ring and the ketimine group. Spectroscopic signatures of both groups are clearly seen in their UV-vis solution absorption spectra and consist in two more-or-less overlapping bands. The band at shorter wavelengths, usually in the range of 270–290 nm in DMA solution and 280–320 nm in MC solution, can be ascribed to the π–π* transition in the aromatic ring. The second absorption band is located in the spectral range of 308–383 nm for DMA solutions and 380–390 nm for MC solutions and can be ascribed to the ketimine chromophore. Independently of the solvent used, for **PKs** with the methyl groups at the *ortho* position with respect to nitrogen (**PK2** and **PKK2**), this band is slightly hypsochromically shifted as compared to the analogous bands in **PK1** and **PKK1** (see Table 4).

It is clear from the data collected in Table 4 that, similarly to their model compounds, **PKs** are solvatochromic. Solvatochromism is a common phenomenon in conjugated polymers and its origin is molecular.[35,36] It arises from conformational changes of the polymer chains as a result of their interactions with solvent molecules. In polyconjugated systems the width of the band gap is strictly related to the extent of conjugation. In other words, more planar conformations assure better overlap of the p_z orbitals in the sp^2 hybridised macromolecule and make the band gap narrower. Thus, solvents that improve the planarity of the macromolecule induce a bathochromic shift of the bands originating from the electronic transitions associated with the π-bonding system. In the case of the **PKs** studied a systematic bathochromic shift in the position of both bands is observed if aprotic DMA is replaced by MC, which is a protic solvent. This behaviour clearly indicates that MC is not an inert solvent and that it strongly interacts with the polymer chain, modifying its conformation towards higher planarity. This can occur *via* hydrogen bond formation between the imine-type nitrogens of **PKs**, which are hydrogen bonding acceptors, and the hydroxyl group of MC, which is a good hydrogen bonding donor. Another mechanism of solvent-polymer interactions may, in this case, involve the protonation of imine nitrogens by MC. Phenols are much more acidic than aliphatic alcohols ($pK_a < 10$) and in some cases are capable of protonating polymers with basic centres.[37,38]

Photoluminescence (PL) spectra of the polymers investigated are also solvent-dependent (see Table 5). The simplest conjugated **PKs** with no substituents in the main chain (**PK1** and **PKK1**) in DMA solution emit blue radiation. Similarly to the UV-vis absorption spectra, the replacement of DMA by MC results in a bathochromic shift of the photoluminescence band. This effect is more pronounced in polymers with no substituents in the main chain (**PK1** and **PKK1**). On the contrary **PK2** and **PKK2** exhibit significantly higher Stokes shifts as compared to **PK1** and **PKK1** since they absorb at lower wavelengths and emit at higher wavelengths, independently of the solvent (DMA or MC). Typical PL spectra of the **PKs** are shown in Fig. 6.

Our preliminary data on the luminescence spectra of **PKs** in the solid state show that **PK1** and **PKK1** exhibit a photoluminescence band maximum at essentially the same wavelength, *ca.* 505 nm. This value is intermediate between the photoluminescence maxima recorded for these polymers in DMA and MC solutions. In the case of **PKK2** the maximum of the photoluminescence band in the solid state at 520 nm is hypsochromically shifted not only with respect to the spectrum measured for MC solution (561 nm) but also as compared to the band registered in DMA solution (543 nm). The observed photoluminescence shifts when going from DMA solution to MC solution and finally to the solid state clearly indicate that

Table 2 ^{13}C NMR data (δ in ppm) of the poly(ketanil)s **PK1**, **PK2**, **PKK1**, and **PKK2**

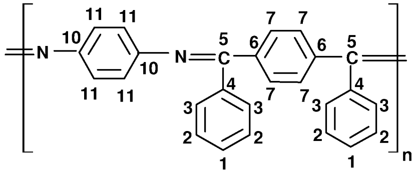
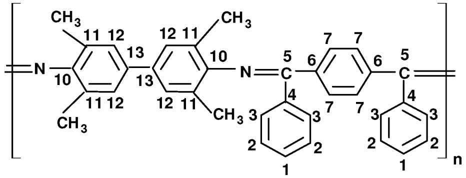
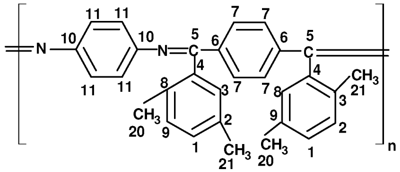
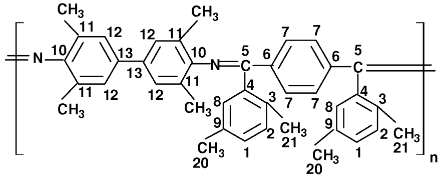
Chemical Structure	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C20	C20	CH_3
PK1 	130.07	128.74 128.63 128.34	128.14 127.99	137.32 135.99 139.44	167.56	138.58 139.07	129.49 129.12	—		146.88	121.48	—	—	—	—	—
PK2 	130.02	128.24	128.22	136.42 137.01 135.85	166.70 166.68	139.08	129.16	—		147.81	122.78	125.93	129.72	—	—	17.76 18.66
PKK1 	131.08 131.49	128.98 128.49	133.91 133.60	137.74 138.24	167.51	141.10	129.92	129.42 129.22	134.90 134.82	146.73	121.16	—	—	20.80	19.60	—
PKK2 	131.13	128.08	133.96	137.78 138.12 138.25 138.38	166.12	141.25 141.48 141.65 141.94	129.97	129.27	134.95	146.07 146.54 149.68 149.84	122.09 121.96	126.78 126.26	131.53	20.86	19.65	18.75 17.80 17.31

Table 3 DSC results obtained for undoped and **DEHEPSA** protonated polyketanils and their model compounds

	mp/ °C		T_g/°C	
	Undoped PK	PK-**DEHEPSA**	Undoped PK	PK-**DEHEPSA**
MI	202	140	$57^{\pm 10}$	$6^{\pm 10}$
MII	226	151	$61^{\pm 10}$	$6^{\pm 10}$
PK1	N.D.	N.D.	$179^{\pm 10}$	$31^{\pm 10}$
PK2	N.D.	N.D.	$244^{\pm 10}$	$27^{\pm 10}$
PKK1	N.D.	N.D.	$114^{\pm 10}$	$23^{\pm 10}$

N.D. = not detected

this property is principally governed by the local conformation of the polymer chain.

The presence of an electron lone pair at the nitrogen atom of the ketimine group enables the protonation of **PKs** with Brønstedt acids. However, contrary to the case of polyaniline and its derivatives protonation does not transform **PKs** into organic conductors. Since **PKs** remain semiconductors after the acid-base doping their properties characteristic of the semiconducting state can be additionally tuned by appropriate dopant engineering. An instructive example of this approach is given below. In our research we have selected 1,2-di(2-ethylhexyl) ester of 4-sulfophthtalic acid (**DEHEPSA**) as the protonating agent. This choice is rationalised by the fact that this molecule is bifunctional and acts simultaneously as a Brønstedt acid and as a plasticising agent. The protonating diester is in fact a simple derivative of di(2-ethylhexyl) phthalate—the most popular industrial plasticiser of PVC. It has been proved to lower the T_g of doped poly(aniline) and to improve its stretchability while retaining its excellent electrical transport properties.[39–42] **DEHEPSA** was added to the MC solution of the **PKs** studied in a 1 : 1 ratio with respect to imine nitrogen in order to assure full protonation of the polymer. The samples for the DSC study were obtained by casting from MC solutions. The plasticising effect of the protonating agent is clearly visible. All DSC data obtained for the **DEHEPSA**-protonated polymers and model compounds are collected in Table 3. The **DEHEPSA**-induced plasticising results in a significant decrease of the T_g values, which, for all polymers studied, only slightly exceed the room temperature. This, protonation-induced plasticising effect facilitates solution processing of the **PK** films and improves their optical quality because of the amorphous nature of the plasticised material.

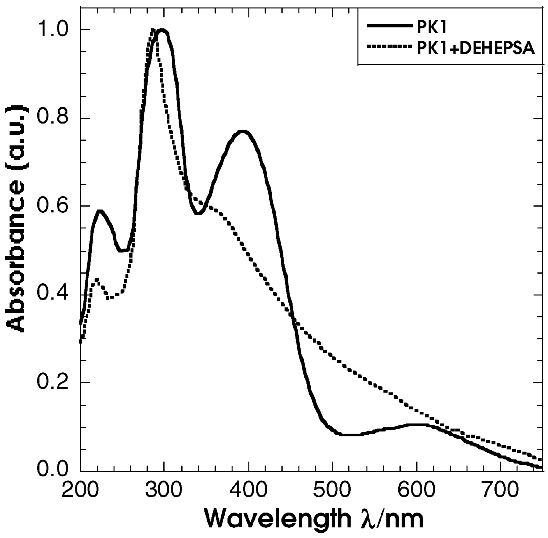


Fig. 5 Solution UV-vis spectra of **PK1** before and after protonation with **DEHEPSA** in MC.

Table 4 UV-vis spectroscopic data obtained for undoped and **DEHEPSA** protonated poly(ketanil)s

	λ_{max} (DMA)/nm in DMA	λ_{max} (MC)/nm	λ_{max} (MC + **DEHEPSA**)/nm
PK1	268, 383	300, 390, 610	290, 410
PK2	290, 370	310, 380	305, 390
PKK1	269, 308, 400	280, 390, 620	280, 400
PKK2	270	320, 380	300, 390

The model compounds **MI** and **MII** are crystalline. Protonation with **DEHEPSA** lowers their melting point by 62 and 75 °C, respectively. A similar effect is observed in the T_g values measured after the amorphisation of the samples by quenching with liquid nitrogen. Thus the protonation-induced plasticising effect is clearly observed both in the polymers studied and in their model compounds.

In addition to the plasticising effect protonation alters the spectroscopic properties of the **PKs**. In general, the first band in the UV-vis absorption spectra, corresponding to the π–π* transition of the benzene ring, is little affected by protonation. On the contrary, the band ascribed to the C=N chromophore in the conjugated polymer backbone significantly broadens and changes its position, indicating strong interactions of this group with the protonating agent. In Fig. 5 the effect of protonation on the UV-vis spectrum of **PK1** is shown as an example; all spectroscopic data are collected in Table 4.

As expected, protonation with **DEHEPSA** has a rather pronounced effect on the PL spectra of the **PKs** investigated and, with the exception of **PKK2**, produces an even larger bathochromic shift in the position of the PL band as compared to that induced by pure MC (see Table 5). Similar behaviour has already been reported for other conjugated polymers, for example, for PPV derivatives containing bipyridine units.[23]

Table 5 Photoluminescence emission bands (λ_{exc} = 450 nm) of undoped and **DEHEPSA** protonated poly(ketanil)s

	λ_{emis} (DMA)/ nm	λ_{emis} (DMA + **DEHEPSA**)/ nm	$\Delta\lambda_{emis}$/ nm	λ_{emis} (MC)/ nm	λ_{emis} (MC + **DEHEPSA**)/ nm	$\Delta\lambda_{emis}$/ nm
PK1	452	491	+39	519	542	+23
PK2	516	496	−20	519	548	+29
PKK1	487	493	+6	520	563	+43
PKK2	543	494	−49	561	552	−9

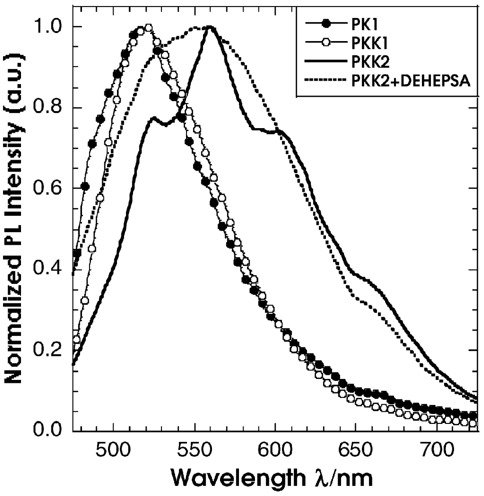


Fig. 6 Photoluminescence (PL) solution spectra of **PK1**, **PKK1**, **PKK2** and **PKK2** protonated with **DEHEPSA** in MC. λ_{exc} = 450 nm.

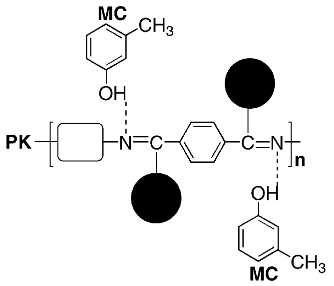


Fig. 7 Proposed schematic model for the PK-MC system (MC-PK: H-bonding interactions).

Evidently, in both cases the protonation lowers the luminescent excited state. It is clear, from the above-presented data, that the optical properties of **PKs** can be tuned not only by chain engineering but also by dopant (protonating agent) engineering.

The double role of the protonating agent should be highlighted once again. In addition to the tuning of the photoluminescence properties it improves the processibility and mechanical properties of the polymer *via* a plasticising effect. The practical importance of this effect cannot be underestimated.

Spectroscopic data discussed above clearly indicate that MC is not an inert solvent and strongly interacts with the polymer chain, modifying its conformation towards higher planarity, possibly by hydrogen bonding as schematically depicted in Fig. 7.

We have studied this problem in greater detail using ^{1}H NMR spectroscopy. In particular, we have prepared mixtures of **PKs** with MC in a 1 : 1 stoichiometric ratio of OH to C=N so as to assure the interaction of each hydroxyl group with each ketimine group. Fig. 8 shows the NMR spectrum of the **PK1**–MC mixture as an example. First we notice a slight downfield shift of the line attributable to the OH group of MC and its significant broadening as compared to the line of "free" MC, that is MC without the presence of poly(ketanil), recorded under the same experimental conditions. These changes are indicative of H-bonding type interactions between the polymer and MC. **PKK1**–MC gives very similar results.

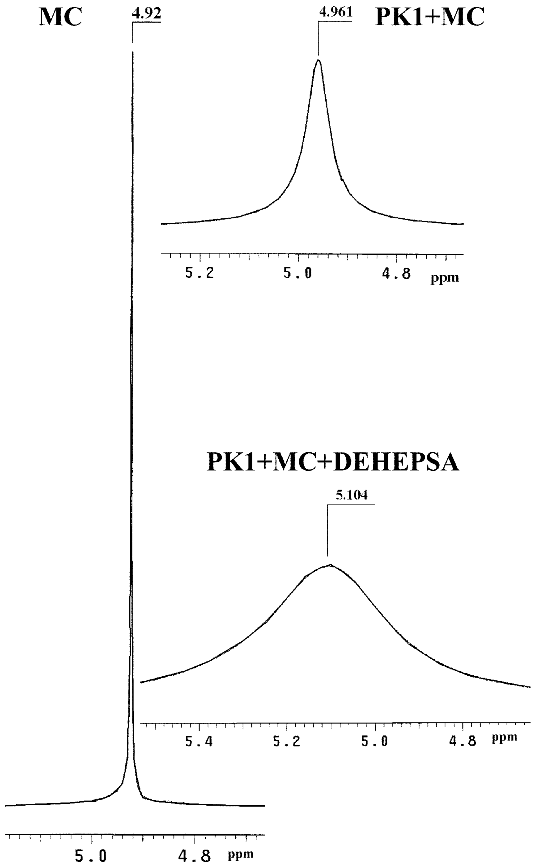


Fig. 8 ^{1}H NMR spectra of "free MC", **PK1** + MC, **PK1** + MC + **DEHEPSA** in $CDCl_3$.

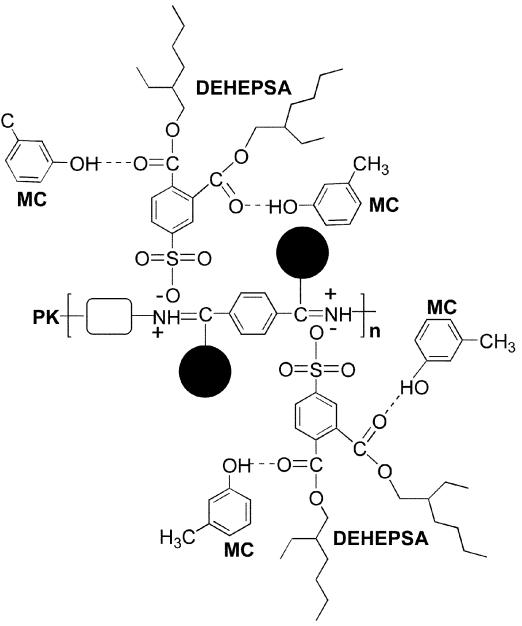


Fig. 9 Proposed schematic model for the PK–**DEHEPSA** + MC system (MC–**DEHEPSA**: H-bonding interactions; PK–**DEHEPSA**: acid-base interactions).

We have also studied the protonation of **PKs** with **DEHEPSA**, in the presence of MC. Thus, we have prepared mixtures of polyketanils with MC and **DEHEPSA** in a 1 : 1 : 1 stoichiometric ratio of OH to C=N to SO_3H. The protonation is manifested by a clear absence of the signal attributable to the OH group of **DEHEPSA** and a further downfield shift and further broadening of the line ascribed to the OH group of MC (see Fig. 8). We postulate that in this case MC forms H-bonds with **DEHEPSA** since the lone pair of the imine nitrogen is no longer available due to protonation (Fig. 9)

Thus, the NMR results firmly confirm strong interactions of MC and **DEHEPSA** with **PKs**, which by modifying the chain conformation lead to significant changes in the polymer photoluminescent properties.

Conclusions

To summarise, we have synthesised a new family of π-conjugated poly(ketanil)s whose spectroscopic properties can be tuned either by a change in the chemical constitution of their building blocks or by doping with an appropriately designed protonating agent. The latter not only constitutes a convenient tool for absorption and emission colour tuning but also lowers significantly the polymer glass transition temperature, T_g, and improves the material processibility.

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