

CHEMISTRY

Now Electrochromic Polyphenylquinoxalines

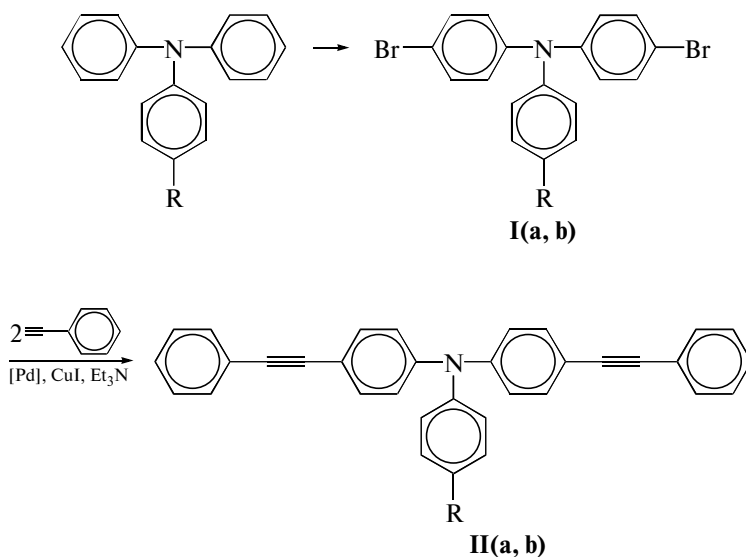
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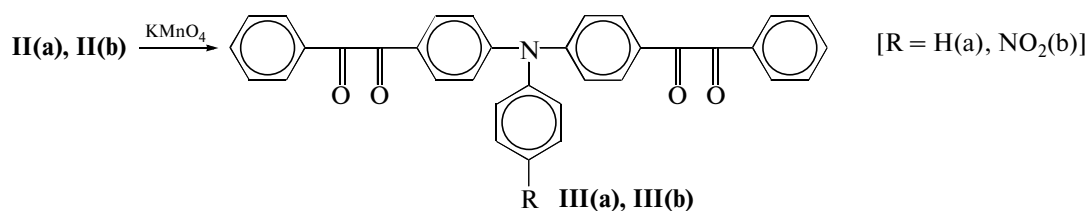
π -Conjugated triaryl-containing polymers have received considerable recent attention not only as efficient hole-transport materials but also as promising electrochromic materials [1–3]. The electrochemical oxidation of triarylamine (TAA) readily yields a stable radical cation with high charge mobility and long lifetime, which is accompanied by a noticeable change in color [4, 5]. This renders TAA an attractive anodic electrochromic “building block.” Various polyimides, polyamides, polyphenylenes, and polyazomethines with TAA units in the backbone, combining high thermal stability and favorable photochemical and electrochromic properties, have been synthesized [6–9]. Polyphenylquinoxalines (PPQs) with TAA fragments are not only efficient electron-transport *n*-type blocks

with high electron affinity and thermostability [10, 11] but also exhibit excellent electrochromic properties. However, TAA-containing PPQs have not been studied as candidates for electrochromic materials. The introduction of bulky TAA units into PPQs not only enhances the solubility without detriment to useful properties, but also imparts to polymers hole-transport and electrochromic properties and improves charge-carrier transport. With the aim of obtaining TAA-containing PPQs, we synthesized a series of new bis- α -diketones **III**. To this end, TAA was brominated to give bis(4-bromophenyl)arylamine **I**, which was then cross-coupled with phenylacetylene. Compound **II** thus obtained was oxidized to target bis- α -diketone **III** (Scheme 1).



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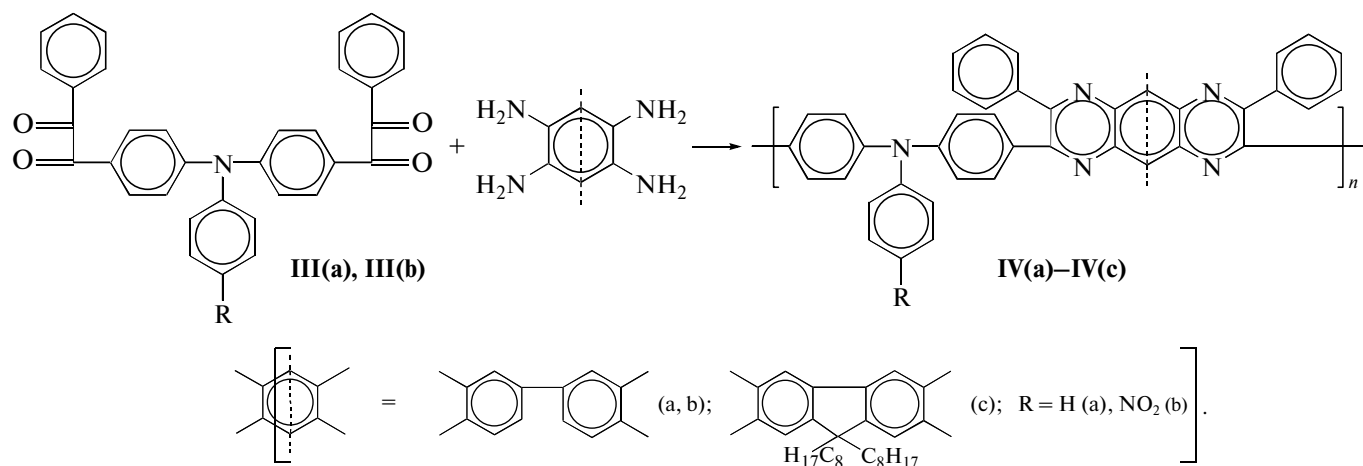


Scheme 1.

The composition and structure of compounds **I**, **II**, and target product **III** were confirmed by elemental analysis, IR spectroscopy, and ^1H and ^{13}C NMR. In particular, the IR spectra of bis- α -diketone **IIIb** shows characteristic bands α -diketone group stretches (1674 cm^{-1}). The ^1H NMR spectrum shows four doublets at 8.21, 8.00, 7.81, and 7.21 ppm due to five types of protons and two trip-

lets at 7.67 and 7.77 ppm caused by overlap of the signals of the *meta* and *para* protons of free phenyl groups. The ^{13}C NMR spectrum shows two signals of the carbonyl groups of the α -diketone fragment at 195.12 and 194.66 ppm.

Bis- α -diketones **IIIa** and **IIIb** were used for synthesizing PPQs **IV** according to Scheme 2.



Scheme 2.

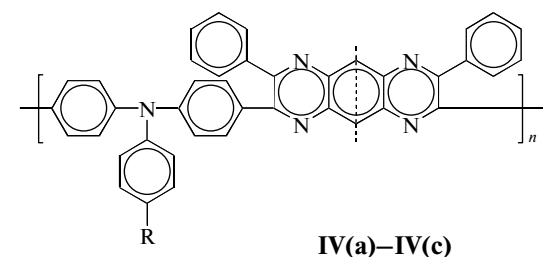
PPQs were synthesized in *m*-cresol for 5 h at 160°C . The process occurred under homogeneous conditions and afforded polymers with relatively high reduced viscosity ($\eta_{\text{red}} = 0.79\text{--}0.92\text{ dL/g}$).

The structure of polymers **IV** was confirmed by IR spectroscopy.

The spectra of all polymers show absorption bands at $1640\text{--}1545\text{ cm}^{-1}$ typical of $\text{C}=\text{N}$ stretches in quinoxaline rings and lack the bands in the regions $1660\text{--}1680$ and $3200\text{--}3400\text{ cm}^{-1}$ due to the $\text{C}=\text{O}$ and NH_2 stretching vibrations of the initial compounds. The glass transition temperatures of PPQs found from DSC curves are in the range $224\text{--}315^\circ\text{C}$ (Table 1). The temperatures of 10% weight loss in argon and air are in the range $420\text{--}577$ and $414\text{--}550^\circ\text{C}$, respectively. The solubility of PPQs in aprotic solvents

allowed us to obtain films with the breaking strength $\sigma = 85\text{--}95\text{ MPa}$ and the percent elongation $\varepsilon = 8\text{--}10\%$. The absorption spectra of the polymers in solutions and thin films show strong absorption with maxima in the ranges $410\text{--}450$ and $405\text{--}445\text{ nm}$, respectively. Under the same conditions, the fluorescence maxima are observed in the ranges $535\text{--}600$ and $530\text{--}560\text{ nm}$, respectively.

The electrochemical properties of the polymers were studied by cyclic voltammetry (Table 2). All polymers exhibit reversible redox properties and show a redox couple in the range $E_{1/2} = 0.92\text{--}1.25\text{ eV}$. Typical cyclic voltammograms for polymer **IVa** are shown in Fig. 1. PPQ **IVa** shows a reversible redox couple at $E_{1/2} = 1.04\text{ V}$ which is assigned to the radical cation that emerges on removal of an electron from the nitrogen atom of the TAA fragment [12]. The band gap

Table 1. Some characteristics of PPQs of general formula

Polymer	R		$\eta_{\text{red}}, \text{ dL/g}$ (<i>m</i> -cresol, 25°C)	$T_{\text{st}}, ^\circ\text{C}$	$T_{10\%}, ^\circ\text{C}^*$ (TGA, $\Delta T = 20 \text{ K/min}$)	Tensile properties of films	
						$\sigma, \text{ MPa}$	$\varepsilon, \%$
IVa	H		0.81	308	$\frac{550}{577}$	95	8
IVb	NO ₂		0.92	315	$\frac{507}{529}$	90	8
IVc	H		0.79	224	$\frac{414}{420}$	85	10

* The numerator pertains to heating in air and the denominator, to heating in argon.

Table 2. Some optical and electrochemical properties of polymers **IVa–IVc**

Polymer	$\lambda_{\text{max}}^{\text{abs}} *1$	$\lambda_{\text{max}}^{\text{fl}} *1$	$\lambda_{\text{onset}}^{\text{abs}}$	HOMO *2	LUMO *3	$E^{\text{opt}} *4$	$E_{1/2}$
	nm			eV			V
IVa	$\frac{435}{432}$	$\frac{535}{530}$	495	5.40	2.89	2.51	1.04
IVb	$\frac{410}{405}$	$\frac{600}{560}$	482	5.61	3.04	2.57	1.25
IVc	$\frac{450}{445}$	$\frac{535}{533}$	510	5.28	2.85	2.43	0.92

*1 In the numerator are absorption and luminescence maxima in chloroform ($c = 10^{-4} \text{ mol/L}$) and in the denominator, the same in thin films.

*2 $\text{HOMO}_{\text{polym}} = 4.8 \text{ eV} (\text{HOMO}_{\text{Fc/Fc}^+}) + E_{1/2}(\text{polym}) - 0.44 \text{ eV}$ ($E_{1/2} = \text{Fc/Fc}^+$), where $\text{HOMO}_{\text{Fc/Fc}^+}$ is the standard in vacuum, and $E_{1/2}(\text{polym})$ is the external redox standard.

*3 $\text{HLUMO} = \text{HOMO} - E^{\text{opt}}$.

*4 $E^{\text{opt}} = 1240/\lambda_{\text{onset}}^{\text{abs}}$.

width (E^{opt}), HOMO, and LUMO of the polymers were determined from the half-wave potential ($E_{1/2}$) and the absorption onset wavelength $\lambda_{\text{onset}}^{\text{abs}}$ in the spectra of films (Table 2). Comparison of the electro-

chemical data in Table 2 shows that polymer **IVc** ($E_{1/2} = 0.92 \text{ eV}$) is more readily oxidized than polymers **IVa** ($E_{1/2} = 1.04 \text{ V}$) and **IVb** ($E_{1/2} = 1.25 \text{ V}$). It is likely that the introduction of electron-donor groups

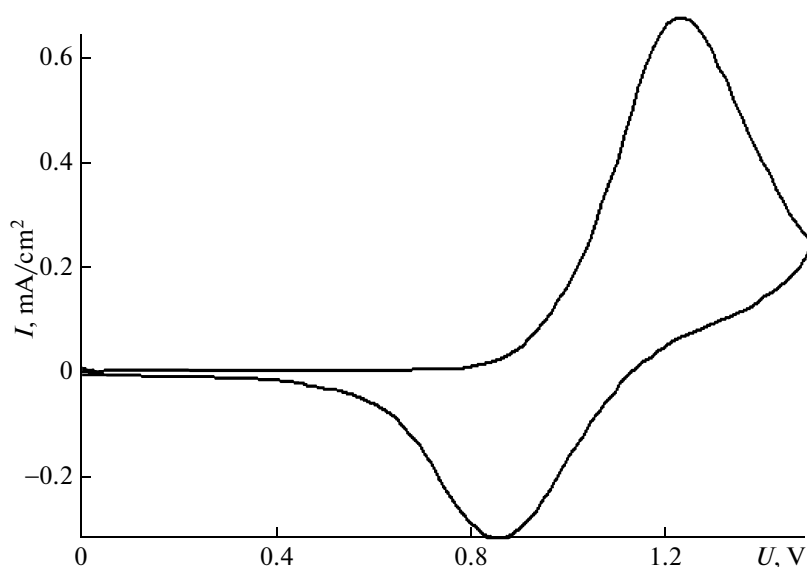


Fig. 1. Cyclic voltammograms of PPQ **IVa** in a 0.1 M tetrabutylammonium perchlorate–acetonitrile solution at a sweep rate of 50 mV/s.

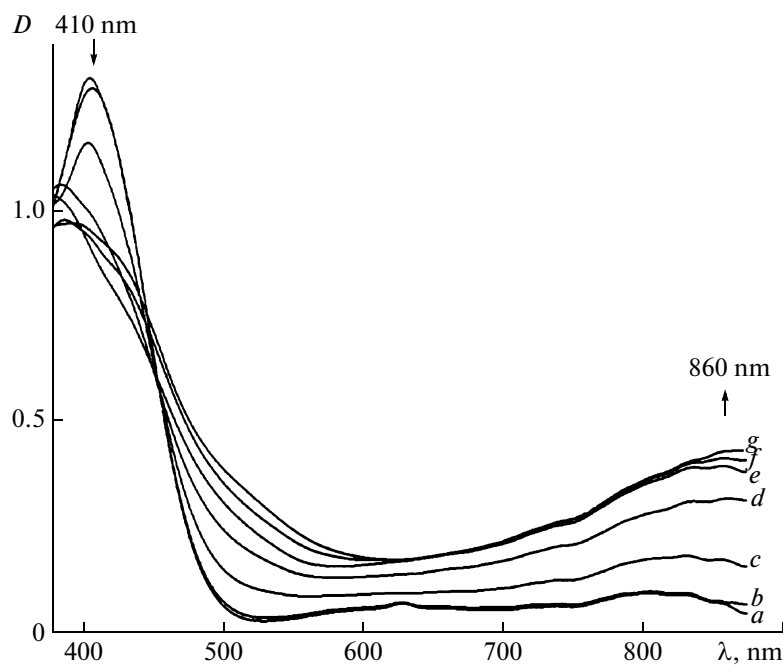


Fig. 2. Electronic absorption spectra of PPQ **IVb** in a 0.1 M tetrabutylammonium perchlorate–acetonitrile solution (vs. Ag/AgCl). Potentials, V: (a) 0, (b) 1.0, (c) 1.2, (d) 1.3, (e) 1.5, (f) 1.7, and (g) 1.9.

decreases the oxidative potential of electroactive polymers.

The electrochromic properties of PPQs were studied by means of an optically transparent thin-layer electrode interfaced with a UV-VIS spectrophotometer. Typical electrochromic absorption spectra of polymer **IVb** recorded at different potentials are shown in Fig. 2. With increasing the applied potential from 0 to

1.9 V in the course of oxidation, the characteristic peak at 410 nm corresponding to the neutral form of PPQ **IVb** becomes gradually weaker and shifts to 391 nm; at the same time, a broad signal appears at 860 nm, which gradually builds up with increasing applied potential due to the formation of the stable radical cation assigned to the TAA fragment. This is accompanied by a change in the film color from yellow

(neutral form) to claret (oxidized form). The time of color switching was estimated by means of the stepped potential absorption profile as the time it takes for the 90% change in complete absorption to be achieved after applying the potential. In particular, for polymer **IVc** ($\lambda = 800$ nm), the color switching time was found to be 5.5 s and the bleaching time was 0.9 s at 1.1 V. Owing to the high stability of films and good adhesion between the polymer and the ITO electrode surface after 15 continuous cycles, PPQs revealed high stability and reversibility of electrochromic characteristics.

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