Color reactions of polyarylenesulfophthalides in aniline—cyclohexanone mixtures in air

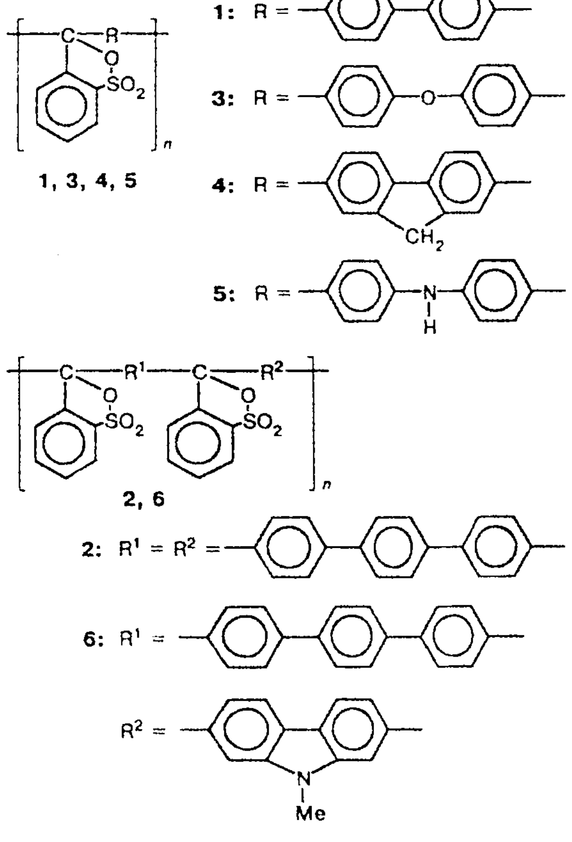
N. M. Shishlov, Sh. S. Akhmetzyanov, and V. N. Khrustaleva*

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation,
Fax: 007 (374 2) 35 6066. E-mail: root@chemorg.bashkiria.su

Slow color reactions occur when some polyarylenesulfophthalides are dissolved in an aniline—cyclohexanone mixture; these reactions involve generation of triarylmethyl type radicals that were characterized by ESR and UV spectroscopy.

Key words: polyarylenesulfophthalides, radicals; electronic spectra; ESR spectra.

Previously,[1] synthesis of new polymers, polyarylenesulfophthalides, has been reported. When these polymers are dissolved in aniline—cyclohexanone mixtures, color develops and paramagnetic species are formed. In the present paper, we studied this process in relation to polymers **1—6**.



Solutions of all these polymers in an aniline—cyclohexanone mixture exhibit ESR signals that gradually appear, increase up to a certain maximum, and then disappear (Fig. 1 and Table 1). These signals usually have poorly resolved HFS (in the form of inflections) with uneven numbers of lines. Only for polymer **3**, was a relatively resolved signal characterized by discernible HFS with splitting of ~0.6 Oe detected. The variation of the ESR signals of these polymers with time correlates with variation of the intensities of some absorption bands (see Table 1). Shaking the solutions or purging them with air leads to disappearance of the ESR signals and the absorption bands associated with them; subsequently, the ESR signals and the absorption bands (color) are restored almost up to their original level. These procedure of disappearance—appearance of paramagnetic species can be repeated several times. Furthermore, even during storage of the solutions, some fluctuations of the intensities of the ESR signals and absorption bands occur, which is apparently due to the complex character of this reaction-and-diffusion system involving atmospheric oxygen. This is an interesting ex-

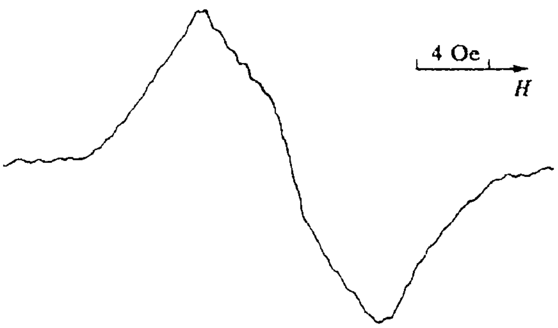


Fig. 1. ESR spectra of the polymer 1—aniline—cyclohexanone system 1 h after mixing of the components.

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Table 1. Properties of the polymers and characteristics of the resulting radicals

Polymer	[η] /dL g^{-1}	λ_{max} /nm	[Radicals] · 10^5 /mol L^{-1}	*g*	*H*/Oe	t_{max} /min
1	0.84	420* 580**	2	2.0026	10.0	150
2	0.78	434* 642*	48	2.0029	9.4	70
3	0.20	400* 540 640	7	2.0027	9.8	80
4	0.80	390* 603**	1	2.0027	10.0	30
5	0.05	450* 590	5	2.0027	10.0	90
6	0.40	420* 480* 566 640*	16	2.0025	9.2	50

Note: t_{max} is the approximate time needed to attain the maximum concentration of radicals and the maximum intensity of coloration.

* λ_{max}, assigned to the radicals.

** Absorption bands that correlate with ESR signals but do not refer directly to triarylmethyl radicals.

ample of a "living" chemical system. The ESR signals observed and the color centers associated with them also disappear when the solutions are exposed to the full light from a xenon lamp, and then appear again.

Sulfophthalein dyes incorporating sulfophthalide rings are known to easily generate triarylmethyl radicals upon various types of treatment.[2] Taking into account the structure of polymers **1**—**6** (the presence of the labile sulfophthalide ring in a chain unit) and parameters of the ESR spectra,[3,4] the ESR signals observed can be assigned tentatively to triarylmethyl type radicals. The absorption bands at 400—500 nm also correspond to this type of radicals.[5]

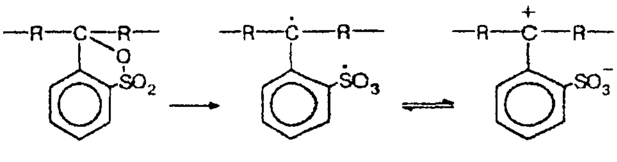
In the case of polymer **2**, the highest concentration of radicals is achieved and the longest lifetime of these radicals is observed (~10 days in air at 20 °C). The band at 642 nm is manifested only at large radical concentrations. The position and the low intensity of this band (E_{434}/E_{642} ~ 60) and its full correlation with the band at 434 nm make it possible to assign it to a forbidden transition of the radical. A weak band at 640 nm is also observed in the spectrum of polymer **6** at high concentrations of radicals. The intense and stable absorption band observed at 640 nm in the spectrum of polymer **3** is not associated with radicals.

Previously, we detected the formation of triarylmethyl type radicals in a study of thermolysis of polymer **1** and poly(triphenylmethanol) obtained from it.[6]

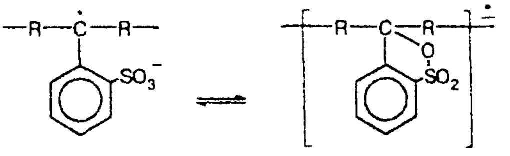
The intensities of the absorption band at 580 nm for compound **1** and of the band at 603 nm for **4** are higher that those of the short-wavelength absorption bands at 420 and 390 nm; therefore, they cannot be attributed to forbidden transitions. To interpret these bands, at least three suggestions can be made. These bands may be due to charge transfer complexes of radicals,[7] quinoid structures like the Chichibabin hydrocarbon,[8] or zwitterions (or ionic forms related to them) that result from the cleavage of the sulfophthalide ring and exist in an equilibrium with radicals.[2] Unambiguous assignment of these bands requires additional studies.

The paramagnetic species that we observed behave toward oxygen as monomeric triarylmethyl radicals (the Schmidlin test[9]), although no peroxide radicals was detected in our experiments.

At present, the mechanism of the formation of the radicals is not entirely understood; however, it can be assumed that the sulfophthalide ring is opened under the action of aniline:[10]



In an earlier paper,[2] it has been suggested that radicals exist in equilibrium with zwitterions. However, the ring-opening may also occur upon transfer of an electron from aniline, and in this case, the resulting radicals would be stabilized in a radical-ion form, which, in turn, can exist in an equilibrium with radical anion (formed without ring opening):



Formation of radicals characterized by the same ESR parameters was observed for polymer **1** when other primary arylamines (*para*-phenylenediamine, anisidine, toluidine) were used instead of aniline, but not with secondary amines (diphenylamine, dimethylamine) or tertiary amine (triphenylamine).

The polymeric nature of sulfophthalide molecules plays an important or, perhaps, the critical role in the generation and stabilization of observed intermediate species, because the phenomena described above are not observed in the case of their monomeric analogs.

It has been reported that ketones[11] and micellar surfaces[12] exert so-called differentiating effects on the equilibrium between different forms of sulfophthalein dyes. Apparently, in this case, we observed a joint effect of cyclohexanone and the surface of macromolecules on the equilibrium between the ionic and radical forms of the sulfophthalide ring formed under the action of amine.

Experimental

Polymer 1.[1] 3-(4-Biphenyl)-3-chloro-2,1-benzoxathiol 1,1-dioxide (8 g, 22.4 mmol), nitrobenzene (11.2 mL), and $SbCl_5$ (0.14 mL) were placed under a flow of argon in a three-necked flask equipped with a mechanical stirrer and an air-cooled condenser, and the mixture was kept for 10 h at 100 °C. The resulting polymer was dissolved in DMF, precipitated with ethanol, filtered off, washed with ether, and dried for 10 h at 90 °C to give 7.0 g (97%) of polymer 1 as a white amorphous powder. Found (%): C, 70.60; H, 3.91; S, 9.54. $(C_{19}H_{12}SO_3)_n$. Calculated (%): C, 71.25; H, 3.75; S, 10.0.

Polymers 3—5 were prepared in a similar way.

Polymer 2. This polymer was prepared as a white powder from 4,4"-bis(3-chloro-3-sulfophthalide-1,1':4',1"-terphenyl (8 g, 12.5 mmol), 1,1':4',1"-terphenyl (2.9 g, 12.5 mmol), nitrobenzene (22.4 mL), and $SbCl_5$ (0.24 mL) under the same conditions as polymer 1. Yield 9.4 g (95%). Found (%): C, 75.4; H, 3.70; S, 7.70. $(C_{50}S_2O_6H_{28})_n$. Calculated (%): C, 76.10; H, 3.55; S, 8.12.

Polymer 6 was obtained in a similar way using *N*-methylcarbazole as a comonomer.

Viscosity was measured at 25 °C using the Ubbelohde viscometer. ESR spectra were recorded on an SE/X-2544 ESR spectrometer (Radiopan) in glass tubes of diameter ~4 mm at 20 °C. Electronic spectra were recorded on a Specord M-40 spectrophotometer in 2 mm-thick quartz cells. Freshly distilled aniline and cyclohexanone were used.

A weighed portion of the polymer (20 mg) was dissolved in 1 mL of aniline (or cyclohexanone) and mixed with 1 mL of cyclohexanone (or aniline). A part of the mixture was placed in an ESR tube, and some of the mixture was placed in a cell of the spectrophotometer.

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A simple synthesis of non-solvated galliumtrialkyls

L. I. Zakharkin,* V. V. Gavrilenko, and N. P. Fatyushina

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085

A simple synthesis of non-solvated galliumtrialkyls is proposed based on the reaction of alkyl iodides with a mixture or an alloy of magnesium and gallium in the absence of a solvent or in aliphatic hydrocarbons.

Key words: galliumtrialkyls, alkyl iodides, magnesium, gallium, gallium arsenide.

Trimethylgallium and triethylgallium of high purity are used for the preparation of gallium arsenide semiconducting films by chemical vapor deposition of organometallic compounds.[1—3] The conventional methods by which they are synthesized, by the reaction of gallium trihalides with organolithium, organomagnesium, organo-

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