Formation of color centers and paramagnetic species by alkaline hydrolysis of polydiphenylenesulfophthalide

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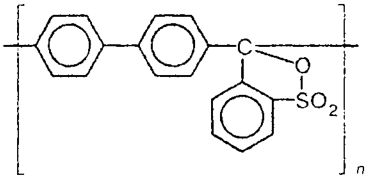
Blue color centers (CC) (an intense absorption band (AB) at 566 nm and a weaker AB at 350 nm) and paramagnetic species (PMS) that give an ESR singlet with $g = 2.0028$ and $\Delta H = 10$ Oe are formed by the treatment of a DMSO solution of polydiphenylenesulfophthalide with an excess of LiOH. The formation of blue CC is accompanied by a decrease in the intensity of the absorption band of the phenyl groups of the polymer at 270 nm. The blue CC were attributed to quinoid structures like the Chichibabin hydrocarbon. The long-wave absorption at 650—800 nm was assigned to the regions of quinoid-benzoid conjugation. The color centers and PMS were also observed when the polymer was hydrolyzed in cyclohexanone; however, in this case, the reaction was accompanied by polymer aggregation. The electronic spectrum of the Chichibabin hydrocarbon was calculated by the PM3 method. The identity of CC formed by alkaline hydrolysis and appearing in the polymer—aniline—cyclohexanone system was shown. The absence of "quinoid" CC for polyterphenyl sulfophthalide was explained by the energetically unfavorable singlet state for structures similar to the Müller hydrocarbon.

Key words: polyarylenesulfophthalides, alkaline hydrolysis, triarylmethyl radicals, the Chichibabin hydrocarbon, the Müller hydrocarbon, electronic spectra, ESR spectra.

We have previously found[1] the formation of paramagnetic species (PMS) and color centers (CC) in the polydiphenylenesulfophthalide (**1**)—aniline—cyclohexanone system (**A**) and shown[2] that the sulfophthalide cycle opens in **1** under the action of aniline. The interaction of **1** with alkalis is also accompanied by the disclosure of the sulfophthalide cycle and results in the formation of the corresponding polytriphenylcarbinol salt.[3] In this work, we studied the reaction of **1** with LiOH in DMSO and cyclohexanone (CyH) by electron and ESR spectroscopy.



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When an aqueous 5 *M* solution of LiOH is added to a DMSO solution of **1** and the resulting mixture is intensely stirred, it (polydiphenylenesulfophthalide (**1**)—LiOH—DMSO system (**B**)) almost immediately gains a blue color, increasing in time. Two absorption bands (AB) appear and increase in the electronic spectrum: a more intense band with λ_{max} = 566 nm and a less intense band at 340—360 nm (Figs. 1 and 2). The parallel changes in these bands are shown in Fig. 3. A decrease in the intensity of AB of the polymer is observed at 270 nm (see Figs. 1 and 3) simultaneously with the accumulation of CC, *i.e.*, some portion of compound **1** is transformed into the colored form. It is difficult to study the CC observed and the mechanism of their formation because the "tail" of the band at 566 nm is stretched to nearly 800 nm, which is the result, most likely, of the formation of CC with longer-wave AB. In the case of system **A**, the band at 580 nm has a resembling complicated shape with an extended long-wave tail (Figs. 4 and 5). In addition, in system **A** when thin (~0.04 mm) CaF_2 cells are used, we detected a

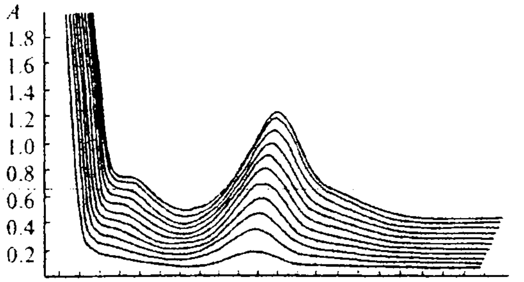

Fig. 1. Change in time of the electronic absorption spectra of system **B** {**1** [$3 \cdot 10^{-4}$ mol L^{-1}] + LiOH [0.2 mol L^{-1}] + H_2O [4 vol.%] + DMSO}. Cell thickness $d = 0.2$ cm. Recording of the first spectrum was started 40 s after adding alkali; time of recording of one spectrum is 140 s.

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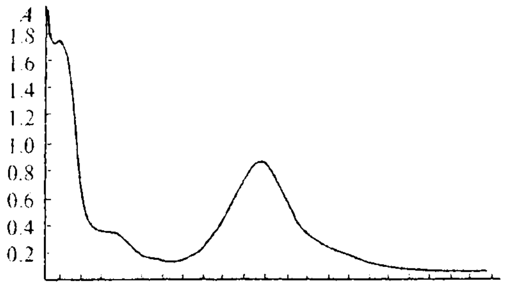


Fig. 2. Electronic absorption spectrum of system **B** 46 min after mixing of the reactants; *d* = 0.2 cm.

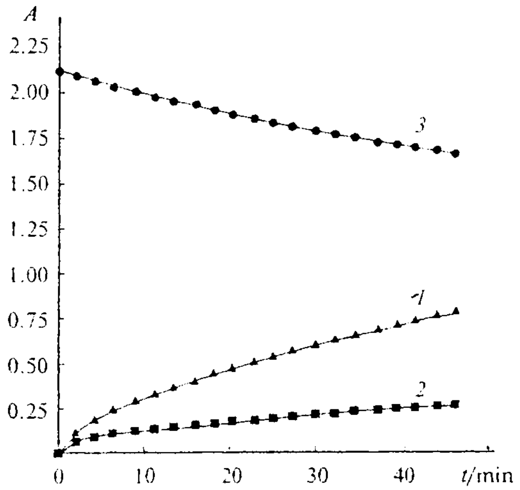


Fig. 3. Change in time of the optical density of system **B** at three wavelengths: *1*, 566 nm; *2*, 350 nm; and *3*, 270 nm.

relatively weak AB in the 380—390 nm region, which changes in parallel with the AB at 580 nm.

Since the electronic spectra have a complicated character, we expanded them into Gaussian components. This expansion is rather conventional and restricted because the shape of absorption bands in electronic spectra is often not Gaussian: in fact, the most intense bands in the spectra observed at 566 and 580 nm are asymmetrical. The result of expansion of the spectrum of system **B** in energy units (eV) is presented in Fig. 6, and the separated bands have the following positions of maxima in nm (eV) in the order of increasing wavelength: for system **A**, 354 (3.50), 379 (3.27), 403 (3.08), 498 (2.48), 542 (2.28), 558 (2.11), 680 (1.82), and 757 (1.64); for system **B**, 327 (3.79), 355 (3.49), 415 (2.99), 481 (2.58), 519 (2.39), 571 (2.17), 667 (1.86), and 725 (1.71). Comparison of the data of expansion for systems **A** and **B** shows that (1) for both spectra, the electronic spectra in the 1.5—4.0 eV energy region can be presented as eight Gaussian components of the bands, and each band of one system corresponds to a similar band in another system; (2) almost all bands of system **A** have a bathochromic shift with respect to the corresponding bands of system **B**. The expansion of the most intense AB in both systems into two components (at 542 and 588 nm for system **A** and at 519 and 571 nm for system **B**) is due, most likely, to the asymmetrical shape of this band rather than two-electron transitions in this spectral region.

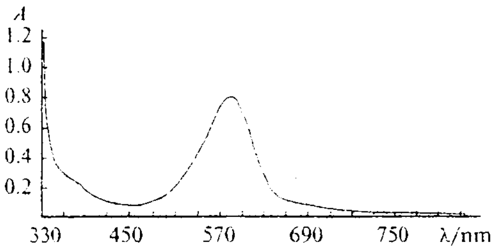


Fig. 4. Optical spectrum of system **A**′ {**1** [0.05 mol L^{-1}] + CyH [50 vol.%] + AN [50 vol.%]} 46 min after mixing of the reactants; *d* = 0.04 mm.

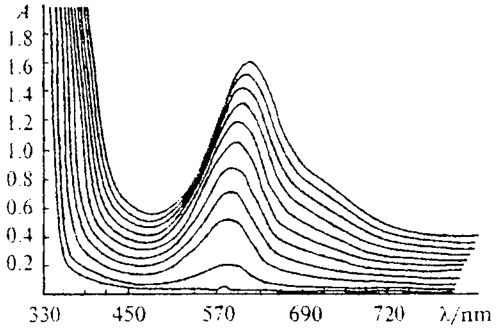


Fig. 5. Change in time of the electronic spectra of system **A**″ {**1** [3 · 10^{-4}] + CyH [50 vol.%] + AN [50 vol.%]}; for conditions of spectra recording, see Fig. 1.

Transition of the polymer to the colored form in an alkaline medium occurs rather slowly: the maximum yield of CC that is proportional to the polymer concentration is achieved within 20—120 min for the studied concentrations of the polymer 3 · 10^{-3}—3 · 10^{-4} mol L^{-1} and alkali 10^{-1}—10^{-2} mol L^{-1}. The kinetic curves of CC accumulation often have additional inflections, gradually achieving a plateau, unlike the curves presented in Fig. 3.

When low concentrations of **1** (~10^{-4} mol L^{-1}) were used, a very weak ESR signal was detected and the absorption band at 410 nm, which is directly related to the ESR signal, was virtually not observed. This spectral region exhibits only a weak shoulder (see Fig. 2), and the expansion of the spectrum gives a band at 415 nm, which is assigned in part to radical species. At the polymer concentration of ~10^{-2} mol L^{-1}, immediately after the addition of alkali, we observed the ESR singlet (ΔH = 10 Oe, g = 2.0028) corresponding to a PMS concentration of ~10^{-5} mol L^{-1} and a pronounced shoulder at ~410 nm in the electronic spectrum. The intensities of the ESR signal and the shoulder at 410 nm remained almost unchanged during the reaction under specified conditions and time.

A stronger ESR signal was recorded when alkali was added to a solution of **1** in CyH. The reaction is accompanied by a noticeable aggregation of the polymer, which results in a strong light scattering in the electronic spectra of the mixture (see Fig. 4) and a nonuniform PMS distribution over the sample height. The intensity of the

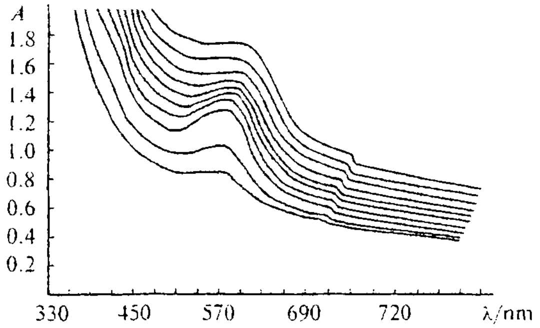


Fig. 6. Expansion of the electronic spectrum of system **B** (see Fig. 2) into Gaussian components.

ESR singlet (ΔH = 10 Oe, g = 2.0028) (Fig. 8) smoothly increases in time and 2 h after mixing corresponds to a PMS concentration of ~10^{-3} mol L^{-1}. For DMSO, the achieved concentration of PMS is ~100-fold lower at the same concentrations of the reactants. We attribute the shoulder at 410 nm in the electronic spectrum of a CyH solution to PMS.[1] The AB at 580 nm is observed in a CyH solution, *i.e.*, CC characteristic of both mixture **A** and the reaction of the polymer with alkali in DMSO are also formed.

The results obtained suggest that the PMS detected by us are attributed to radicals of the triarylmethyl type (Ar_3Me).[1] The formation of radicals of this type by the alkaline treatment of triarylmethane dyes has been observed previously (see, *e.g.*, Ref. 4). The formation of triphenylmethyl radicals through carbanions by the combined action of alkalis and oxidants on triphenylmethane compounds is also known.[5] In our case, the air oxygen could be the oxidant. However, we did not observe AB of carbanions and special experiments showed that blowing with argon and evacuation (to 10^{-4} Torr) of systems **A** and **B** did not prevent the formation of radicals and blue CC. The presence of radicals of the triarylmethyl type in the system suggests that the blue CC can be due to quinoid structures similar to the Chichibabin hydrocarbon, whose formation has been postulated for the thermolysis of polytriphenylcarbinol.[7] The Chichibabin hydrocarbon, has an intense absorption band at 570 nm and weaker absorption band at 310 nm.[6] The basic ionic forms of sulfophthalein dyes also absorb in the 500—600 nm region.[8,9] For example, the electronic spectrum (ES) obtained by us for Phenol red dye in DMSO with an alkali additive has an intense band at 570 nm and a weak band at 350 nm. Either the quinoid structure involving the oxygen atom[8,9] or the zwitterionic structure are also assigned to these forms.[10] In our case, we cannot *a priori* rule out the possibility of formation of similar forms from some defect polymer structures, for example, terminal structures. Triarylmethyl carbanions with biphenyl substituents also exhibit intense (ε ~10^5 L $mol^{-1}cm^{-1}$) AB in the 550—580 nm region,[11] but their spectra additionally contain higher-intensity bands at 260 nm, which were not observed in our case.

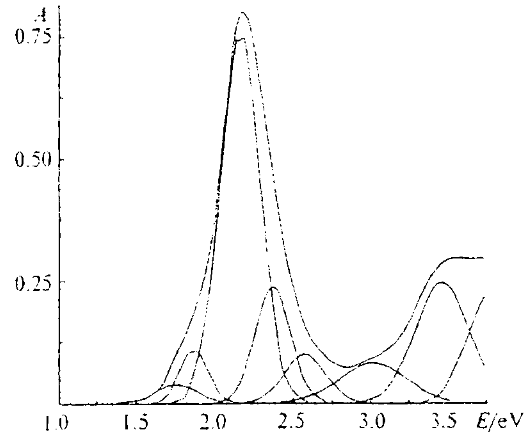


Fig. 7. Change in time of the electronic absorption spectra of system **B′** {**1** [$3 \cdot 10^{-4}$ mol L^{-1}] + LiOH [0.2 mol L^{-1}] + H_2O [4 vol.%] + CyH}; for conditions of spectra recording, see Fig. 1.

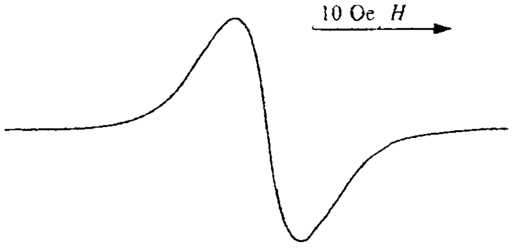


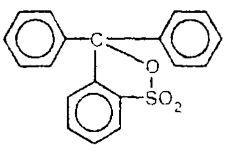
Fig. 8. ESR spectrum of system **B′** 4 h after mixing of the reactants.

It is noteworthy that the shapes of the asymmetrical intense AB at 566 nm in the polymer and the corresponding AB in the Chichibabin hydrocarbon are similar.[12] At the same time, the band at 570 nm in the ES of Phenol red is also asymmetrical. It is impossible to choose between the two structures on the basis of the position and shape of AB.

However, the following experimental facts favor the quinoid structure of blue CC similar to the Chichibabin hydrocarbon.

(1) Sensitivity of these CC toward oxygen. On prolonged storage of systems **A** and **B** in air, blue CC gradually disappear and red CC with AB at 480 nm appear. It is known that the Chichibabin hydrocarbon reacts with the air oxygen to form red peroxides.[13]

(2) Under similar conditions, triphenylmethyl radicals[14] are formed in a high yield (to 70%) by the alkaline hydrolysis of model compound **3**.[1] In the polymer, the formation of radicals on the adjacent quaternary C atoms can give the desired quinoid structures.[7,15] The alkaline hydrolysis of polyterphenyl sulfophthalide (**4**) and its dissolution in an aniline—CyH mixture[1] give only radicals of the triarylmethyl type, which agrees with the absence of the quinoid form of the Müller hydrocarbon (**5**).[16,17] In addition, the PM3 quantum-chemical calculations show that the triplet state of the Müller hydrocarbon is by 0.78 eV energetically more favorable than the singlet state.



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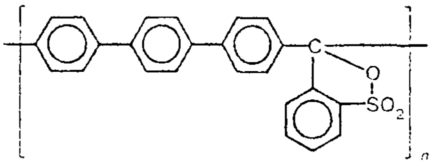

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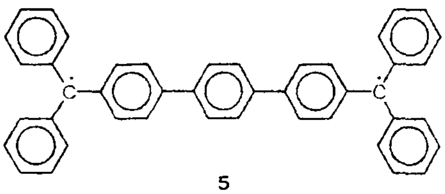

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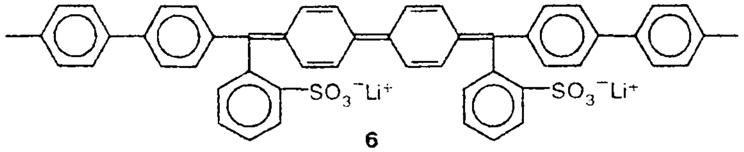
The electronic spectrum of the classical Chichibabin hydrocarbon, which we calculated by the PM3 method taking into account the configurational interaction, presents an intense AB (oscillation strength 2.26) of the singlet transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied MO (LUMO) at 474 nm, a low-intensity (oscillation strength 0.001) band at 288 nm, and a medium-intensity band (oscillation strength 0.122) at 265 nm. The transition at 474 nm corresponds to the AB at 570 nm in the experimental spectrum of the Chichibabin hydrocarbon. The second band at 310 nm cannot be assigned so unambiguously. Since the PM3 method is not specially parametrized for the calculation of optical spectra, it noticeably overestimates the energies of transitions. Calculation also gives the completely forbidden triplet transitions at 428 and 1017 nm. Taking into account the energy shift, we may expect the appearance of phosphorescence and chemiluminescence in the region of ~1500 nm for both the Chichibabin hydrocarbon and similar quinoid structures. The results of quantum-chemical calculations of several quinoid structures will be presented in more detail and discussed elsewhere.

The assumption on the quinoid structure of CC makes it possible to assign, first, the Gaussian band in the expansion of ES in the region of 480 nm to red peroxides, which are most likely slowly formed during the oxidation of quinoid structures of the type of the Chichibabin hydrocarbon in air; second, the long-wave Gaussian bands in the 660—680 and 720—750 nm regions can be attributed to CC with adjacent quinoid structures linked by biphenyl bridges. The quinoid-benzoid conjugation in these systems should result in a red shift of AB in ES relative to those of isolated quinoid structures similarly to the situation observed when the number of conjugated double bonds increases.[18] Based on the known[6] molar absorption coefficient of the Chichibabin hydrocarbon, $\varepsilon_{max} = 1.05 \cdot 10^5$ L mol^{-1}cm^{-1} at 574 nm, we can estimate the maximum concentrations of the quinoid Chichibabin hydrocarbon type structures (see Figs. 2, 4 and 5). For example, for the case presented in the last (in time) spectrum (Fig. 5), we obtain for system **B**, $[CC] \approx 3.7 \cdot 10^{-5}$ mol L^{-1}; for system **A'**, $[CC] \approx 1.9 \cdot 10^{-3}$ mol L^{-1}; and for system **A''**, $[CC] \approx 5.7 \cdot 10^{-5}$ mol L^{-1}. From these, taking into account the initial concentrations of monomeric units, we found that in the first case, ~12% of the units are transformed into the quinoid form; in the second case, ~4%; and in the third case, ~19% are transformed. These rough estimations explain why the strongest relative absorption in the 650—850 nm region was observed precisely in the third case: the higher fraction of the quinoid structures increases the probability of quinoid-benzoid conjugation. According to these estimations, the assignment of CC to defect structures is highly improbable, because $\varepsilon \approx 10^6$ L mol^{-1}cm^{-1} should be assumed for CC in the opposite case. For a more rigid estimation of the content of the quinoid structure, we should take into account a transfer of the optical density to a longer-wave spectral region in the quinoid-benzoid conjugation. This consideration should give a higher content of the quinoid structure in the polymer. Note that the estimation of the content of the quinoid structure for system **B** agrees, as a whole, with a decrease in the content of the benzene structures with AB at 270 nm (see Fig. 3).

In the case of alkaline hydrolysis, a specific form of the quinoid structure similar to the Chichibabin hydrocarbon can be presented as structure **6**, and the regions of quinoid-benzoid conjugation can be presented as structure **7**:



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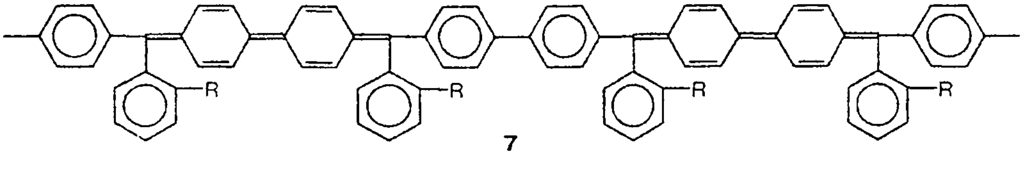

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Thus, the hypothesis about the quinoid structures similar to the Chichibabin hydrocarbon qualitatively explains all observed facts from the single point of view.

Only general assumptions based on the published data can be advanced for the mechanism of the appearance of radicals and biradicals in the systems under study. At first glance the formation of radicals of the triarylmethyl type by the alkaline hydrolysis of compounds containing the sulfophthalide center is somewhat unexpected, because sulfophthalides are usually considered to react with bases by the S_N2 mechanism,[19] which does not involve radical formation. However, heterolytic reactions are often accompanied by one-electron transfer to form radicals (see Ref. 20 and literature cited therein). The reactions of one-electron transfer involving the OH^- ion were observed as early as 1964[21] and have been further multiply confirmed.[22,23] In our case, it remains unclear in which stage of hydrolysis PMS appear, which can be treated as distonic radical anions with an unpaired electron on the quaternary carbon atom and a negative charge on the sulfo group. Note that an increase in the donating ability of the OH^- ion in aprotic solvents, in particular, DMSO, is known.[21,22]

The mechanism of radical formation during the dissolution of sulfophthalide-containing polymers in the aniline—CyH system is also unknown. This system is known to possess reductive properties. It follows from our experimental data that the reaction with an alkali affords CC and PMS, which are the same (or at least very close in structure) as those in system **A**. These data indirectly confirm the possibility of formation of CC and PMS in system **A** precisely from the polymer and indicate that these species can be studied more deeply in a simpler chemical system.

Experimental

The synthesis of the polymer (**1**—**7**) has been described in our previous work.[1] Electronic spectra were recorded on a Specord-M400 spectrophotometer in 2-mm quartz cells with standard caps (without sealing) at room temperature. Thin dismountable CaF_2 cells were used for system **A'**. ESR spectra were recorded on an SE/X-2544 Radiopan spectrometer in glass tubes (diameter 4 mm) with rubber caps at room temperature. LiOH (reagent grade), distilled water, and distilled solvents (DMSO, cyclohexanone, and aniline[1]) were used.

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