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Formation of mono-, bi-, and polyradicals upon reduction of poly(arylenesulfophthalides) by metallic lithium

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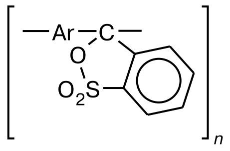
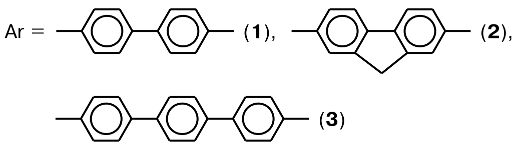
The reduction of poly(biphenylenesulfophthalide) (**1**), poly(fluorenylenesulfophthalide) (**2**), and poly(terphenylenesulfophthalide) (**3**) by metallic lithium in DMSO was studied using UV-visible and ESR spectroscopies. The reduction of compounds **1** and **2** affords blue diamagnetic color centers with absorption bands at 568 and 350 nm (shoulder) for **1** and at 576 and 360 nm (shoulder) for **2**. The color centers were attributed to quinoid structures of the Chichibabin´s hydrocarbon type, being biradicals in the ground singlet state. The spectra of compounds **1** and **2** also exhibit weak absorption bands at ~420 nm, which are assigned to monoradicals of the triarylmethyl type. The reduction of compound **3**, for which the formation of quinoid structures is energetically unfavorable, leads to polyradicals of the triarylmethyl type with a high content (~100%) of unpaired electrons in the main polymer chain. These radicals are characterized by absorption bands at 430 nm (allowed transition) and 638 nm (forbidden transition). The paramagnetic centers in all polymers under study give singlet lines with $g = 2.0028$ and $\Delta H \sim 10$ Oe in the ESR spectra. The color centers and radicals of the triarylmethyl type observed for the poly(arylenesulfophthalides) under study are assumed to be formed upon the dissociative electron transfer from lithium to the sulfophthalide cycles of the polymeric molecules. The PM3 calculations show a high electron affinity of the sulfophthalide cycle and a higher propensity of the fluorenyl bridge to form quinoid structures than that of the biphenyl bridge.

Key words: poly(arylenesulfophthalides), radicals of triarylmethyl type, polyradicals, UV-visible spectra, ESR spectra, quantum-chemical calculations, electron transfer.

Poly(arylenesulfophthalides) (PASP), *viz.*, film-forming polymers with the labile sulfophhthalide cycle in the main chain, are representatives of a wider class of cardo polymers and possess several interesting chemical and physical properties.[1] In particular, blue color centers and paramagnetic species were found upon dissolution of several PASP in a mixture of aniline with cyclohexanone[2] and during alkaline hydrolysis of these polymers.[3] It was assumed that the formation of the color centers and paramagnetic species in these systems is a consequence of electron transfer. However, the reduction of PASP by such electron donors as alkaline metals was not studied at all. Our attempt to study the electrochemical reduction of poly(biphenylenesulfophthalide) (**1**) in DMSO with $LiClO_4$ as a supporting electrolyte by cyclic voltammetry found the formation of an intense blue color both near the working electrode of the electrochemical cell during polarization and in the region of the auxiliary lithium electrode even in the absence of polarization. The absorption band with $\lambda_{max} = 575$ nm in the UV-visible spectrum of a polymer solution in the near-electrode region (Fig. 1) turned out to resemble much (in position and shape) the bands observed previously.[2,3] Reduction by metallic lithium is used for the generation of intermediate polyanions during polyradical formation,[4] and highly polar



1—3



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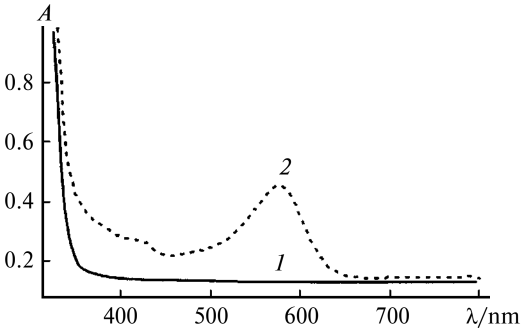


Fig. 1. UV-visible spectra of the DMSO + **1** (10^{-2} mol L^{-1}) + + $LiClO_4$ (1 mol L^{-1}) system: *1*, initial and *2*, for a solution in the region of the auxiliary lithium electrode in the electrochemical cell 12 h after the solution was loaded in the cell; optical path length l = 0.2 cm.

aprotic solvents, including DMSO,[5] are used for studying electron transfer reactions involving alkaline metals. The formation of colored products upon PASP reduction by lithium made it possible to study the reactions of poly(biphenylenesulfophthalide) (**1**), poly(fluorenylenesulfophthalide) (**2**), and poly(terphenylenesulfophthalide) (**3**) by metallic lithium in DMSO using UV-visible spectroscopy and ESR. In this work we report the main results of this study.

Experimental

Synthesis of polymers has been described previously.[1,2] In experiments, a solution of polymer in freshly distilled dehydrated DMSO was placed in a quartz cell 1 cm thick with a polished cap. Then freshly cut lithium in the form of fine pieces was placed in the cell in a dry box, argon was passed through the cell for 10 min, and the latter was closed with a polished cap. The cell with the solution was shaken on a shaker, and UV-visible spectra of the solution were recorded at certain time intervals on a Specord M-400 spectrophotometer. Portions of the solution were sampled in ESR tubes (~4 mm in diameter) under argon using a glass syringe. ESR spectra were recorded at 77 and ~293 K using an SE/X-2544 ESR spectrometer (Radiopan).

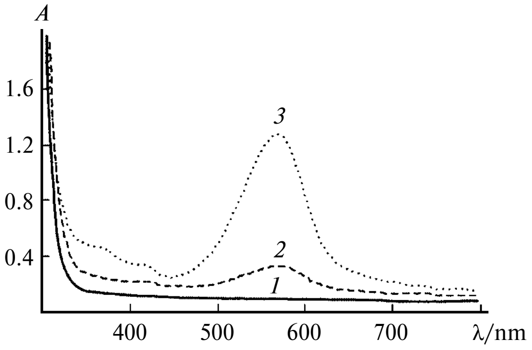


Fig. 2. UV-visible spectra of the DMSO + **1** (10^{-3} mol L^{-1}) + Li^0 system: *1*, initial (without Li^0); *2*, after loading Li^0 and passing argon for 10 min; and *3*, after 45-min shaking on a microshaker; l = 1 cm.

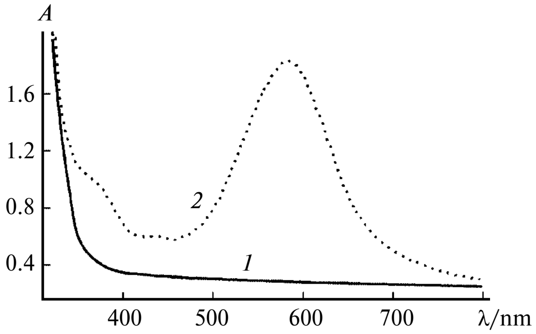


Fig. 3. UV-visible spectra of the DMSO + **2** (10^{-3} mol L^{-1}) + + Li^0 system: *1*, initial (without Li^0) and *2*, after loading Li^0 and passing argon for 10 min; l = 1 cm.

Results and Discussion

After loading lithium and passing argon through solutions of compounds **1** and **2**, we observed a blue color and absorption bands with λ_{max} = 568 and 576 nm responsible for this color for compounds **1** and **2**, respectively (Figs. 2 and 3). Shaking increased the intensity of the band at 570 nm and resulted in the appearance of new bands at 350 nm for compound **1** and 360 nm for **2**, with their intensity increasing in parallel with that of the band at 570 nm. For compound **2**, the intensity of the band at λ_{max} = 576 nm in the initial (after loading lithium) spectrum is much higher than that for **1** (and the rate with which the intensity of the band increases is also higher) (Fig. 4). In addition, the spectra of compounds **1** and **2** exhibit a weak absorption band at 420 nm (see Figs. 2 and 3), which changes slightly during shaking of solu-

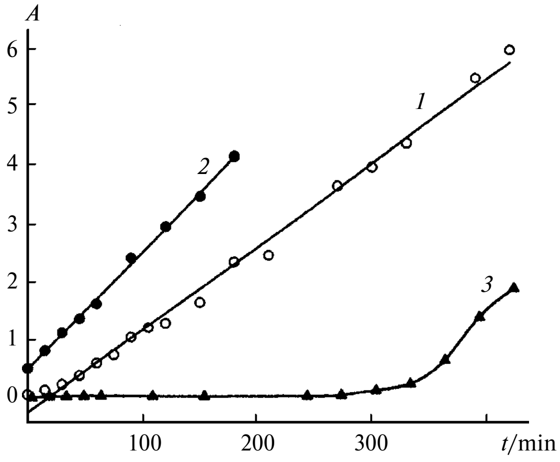


Fig. 4. Absorbance of the DMSO + polymer **1—3** (10^{-3} mol L^{-1}) + Li^0 systems at wavelengths of 568 nm (polymer **1**) (*1*), 576 nm (polymer **2**) (*2*), and 430 nm (polymer **3**) (*3*) *vs.* time of shaking.

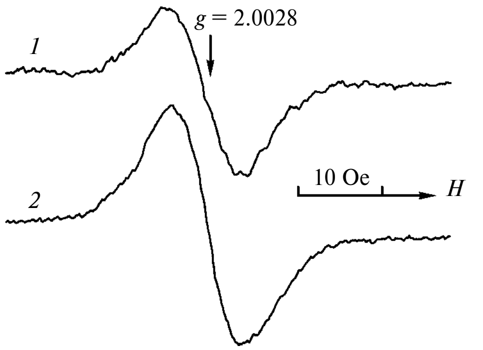


Fig. 5. ESR spectra of the DMSO + polymer **1** (0.2 mol L^{-1}) + + Li^0 system after 72-h shaking (*1*) and DMSO + polymer **3** (10^{-3} mol L^{-1}) + Li^0 system after 50-h shaking (*2*). The spectra were recorded at 77 K, and the signal shape is retained at room temperature.

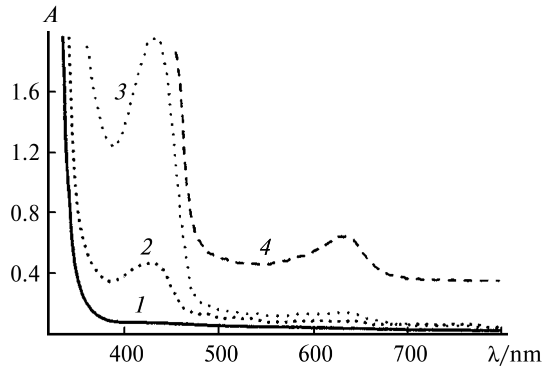


Fig. 6. UV-visible spectra of the DMSO + **3** (10^{-3} mol L^{-1}) + + Li^0 system: *1*, initial (without Li^0); *2*, after loading Li^0 and passing argon for 10 min; *3*, after 6.5-h shaking on a microshaker; and *4*, after 7-h shaking on a microshaker; l = 1 cm.

tions. It is very difficult to detect the band at 420 nm when the bands at 570 and 360 nm reach high intensity, but an insignificant intensity of the band at 420 nm is also observed in these cases. The width and asymmetry of the absorption band at 570 nm increase for both polymers with an increase in the color center concentration. The reason lies in the long-wave tailing. At low concentrations of polymers in colored solutions **1** and **2**, one observes a very weak ESR signal in the region of $g \approx 2$. At high concentrations of the polymers for colored solutions of **1** and **2**, a singlet line with $g = 2.0028 \pm 0.0001$ and $\Delta H \approx 10$ Oe is certainly detected (Fig. 5, spectrum *1*). Its intensity changes slightly during polymer reduction. Two points should be mentioned: (1) formation of the color centers for compounds **1** and **2** is also observed for the reaction with lithium in DMF and dimethylacetamide; however, the reaction is impeded by the interaction of the solvents with lithium (gas evolution occurs), and a high yield of the color centers is not achieved and (2) the UV-visible spectra observed by us differ significantly from the well-known spectra of the biphenyl radical anion and fluorene carbanion.[6]

After loading lithium and passing argon (before shaking), the absorption spectrum of a solution of polymer **3** contains a band with λ_{max} = 430 nm (Fig. 6). In the beginning of the process, the intensity of this band increases but its sharp growth begins only after shaking for ~5 h (see Fig. 4). This is also accompanied by the appearance of a weak band with λ_{max} = 638 nm, with its intensity increasing in parallel with the intensity of the band at 430 nm (see Fig. 6). The drastic increase in the band at 430 nm is reproduced satisfactorily only after prolonged shaking (4—5 h). The reduction of polymer **3** also results in the appearance of an ESR singlet signal with $g = 2.0028 \pm 0.0001$ and $\Delta H \approx 10$ Oe (see Fig. 5, spectrum *2*), which increases in parallel with the absorption bands at 430 and 638 nm.

We succeeded in monitoring the change in the intensity of the color centers for polymers **1—3** with time at a specified optical path length only when the concentration of the polymer as low as 10^{-4} mol L^{-1} was used (Fig. 7). The aforementioned change in the absorption band width at 576 nm for the color centers of polymer **2** is also shown in Fig. 7. Note that the use of such low concentrations of reducible reactants is not reasonable because of a significant influence of minor admixtures on the experimental results.

For all polymers considered, absorption bands at 420—430 nm were observed earlier in other systems and were attributed to allowed electronic transitions of radicals of the triarylmethyl type (RTAMT) (see Refs. 2 and 3 and literature cited therein). In the case of polymer **3**, the weak band at 638 nm is assigned to the forbidden transition of RTAMT,[2,7] which has a structure of distonic radical anion **4** and is formed by the sulfophthalide cycle

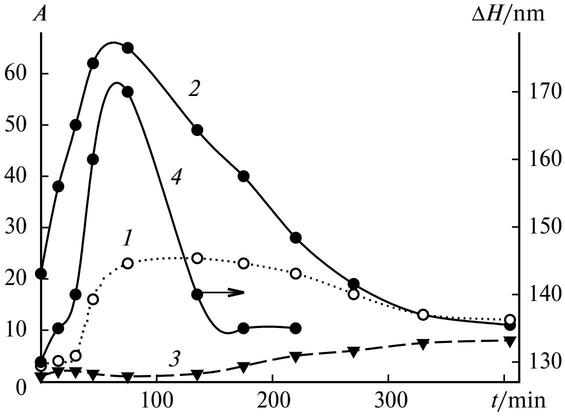
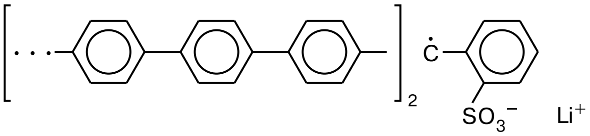


Fig. 7. Absorbance (*1—3*) of the DMSO + polymer **1—3** (10^{-4} mol L^{-1}) + Li^0 systems at wavelengths of 568 nm (polymer **1**) (*1*), 576 nm (polymer **2**) (*2*), and 430 nm (polymer **3**) (*3*) and absorption band width at 576 nm for the DMSO + polymer **2** + Li^0 system (*4*) *vs.* time of shaking.

opening due to the electron transfer from lithium to the polymer. The parameters of the observed ESR signals correspond to RTAMT [8—10] for all polymers studied. It is unclear yet why a sharp increase in the RTAMT concentration for the reaction of polymer **3** with Li^0 is observed only after prolonged shaking. Note that the long (≥24 h) reaction of **3** with Li^0 under these conditions, as shown by our approximation from the intensity of the absorption band at 430 nm, allows almost all quaternary carbon atoms in the polymer chain to be transformed into the radical state, *i.e.*, a polyradical with a high concentration of unpaired electrons was obtained. The following data were used for this estimate: for the reduction of polymer **3** (concentration 10^{-3} mol L^{-1}) in a 1-cm cell, the absorbance at 638 nm reaches 1.8; at low conversions A_{430}/A_{638} ~23; and for polyradicals $\varepsilon_{430} = 4 \cdot 10^4$ was accepted as for similar monomeric radicals.[7] The preparation of polyradicals and study of their properties is related to the problem of organic ferromagnetics and remains to be an urgent problem.[11,12]



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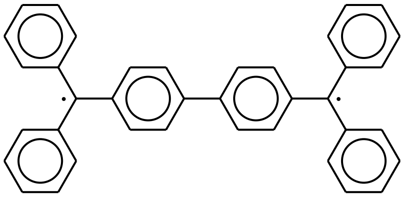
The color centers in polymers **1** and **2**, formed by the reaction of the latter with lithium, are similar to the centers observed in an aniline—cyclohexanone mixture and during alkaline hydrolysis.[2,3] They have previously been ascribed to quinoid structures of the Chichibabin´s hydrocarbon type.[3] The higher rate of color center formation for polymer **2** compared to polymer **1** results from the fact that the quinoidization of the fluorenyl bridge is more favorable than that of the biphenyl bridge.

For example, the PM3 quantum-chemical calculations give the singlet-triplet splitting equal to 0.08 eV for structure **5** and –0.01 eV for structure **6** (for calculation details, see Ref. 13). For polymer **3**, the formation of the quinoid structure is energetically unfavorable because Müller´s hydrocarbon, being its model system, has, most likely, the ground triplet state.[13]



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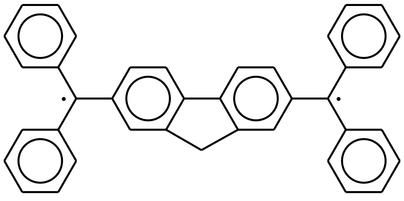

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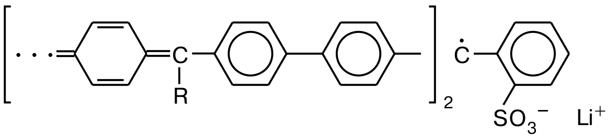
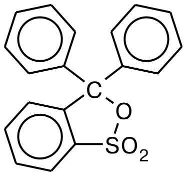
In our opinion, such an explicit dependence of the properties of the color centers (the appearance itself and the rate of formation) on the nature of the bridge in the chain of the polymers indirectly confirms their quinoid structure. The presence of the sulfur and oxygen atoms between the phenyl rings in the bridge also prevents color center formation upon dissolution of similar polymers in an aniline—cyclohexanone mixture.[2] An increase in the width and asymmetry of the bands at 570 nm with the concentration increase can be assigned, as in the case of alkaline hydrolysis,[3] to the appearance of quinoid-benzoid conjugation regions in the main polymer chain. Note that the creation of a continuous chain with such a conjugation should result in interesting electrophysical and physicochemical properties of the polymers.[14,15] However, it is clear that for the random character of cycle opening along the polymer chain, the conjugation should be interrupted by "stuck" RTAMT (structure **7**), *i.e.*, monoradicals of structure **7** are likely formed in polymers **1** and **2** at high degrees of conversion. In our opinion, a decrease in the energy of the forbidden transition due to the quinoid-benzoid conjugation should be a distinctive property of such radicals. Unfortunately, absorption bands of forbidden transitions of RTAMT at 500—700 nm for polymers **1** and **2** overlap with the strong absorption of the quinoid structures. The estimate of the monoradical concentration from the intensity of the absorption band at 420 nm and from the ESR data for polymers **1** and **2** shows that less than 0.5% polymer units are transformed into the radical state. The structure of monoradicals somewhat changes likely depending on the degree of polymer reduction, going from RTAMT with sulfophthalide cycles at the quaternary carbon atoms adjacent to the radical center to radicals of type **7**. The absence of a relation between the intensity of ESR signals and absorption band at 570 nm and dipole splitting of these signals for polymers **1** and **2** allows us to exclude the version that the observed paramagnetism originates from temperature-activated biradicals.



7

The PM3 calculations of a molecule of diphenylsulfophthalide **8** (model of PASP) and the corresponding radical anion show that the electron transfer to the sulfophthalide cycle is favored[16] by low-lying vacant orbitals in the molecule (the energies of three lowest vacant molecular orbitals are −0.76, −0.33, and −0.17 eV) and its comparatively high positive adiabatic electron affinity (EA = 1.76 eV).

Taking into account the relatively low concentration of RTAMT at all degrees of conversion of polymers **1** and **2**, we have to assume that the quinoid structures in these polymers appear due to the concerted reduction of the neighboring sulfophthalide cycles (Scheme 1).



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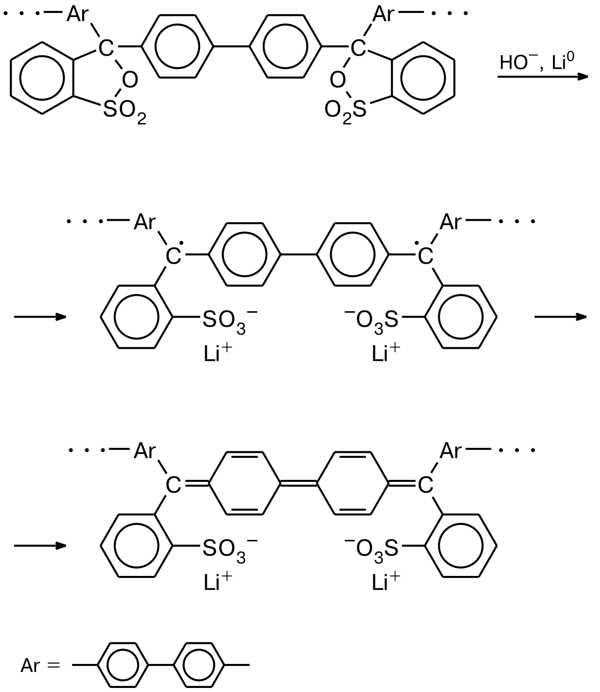
Scheme 1



In this case, we deal with the pronounced neighbor effect, which is well known for polymer-analogous reactions.[17] This effect should likely be manifested for polymers and also for any molecules containing two bound equivalent reaction centers, in particular, for syntheses of classical Thiele´s and Chichibabin´s hydrocarbons. The driving force of such reactions is the energetically favorable quinoid structure. However, details of these transformations are not always clear and worthy of additional investigation. For example, it is implied in the presented scheme that the appearance of the radical on one of the quaternary carbon atoms results in changes in the electronic structure of the adjacent sulfophthalide cycle favoring electron capture by this cycle. We cannot exclude that the second electron is immediately captured by the radical center and then is transferred to the adjacent sulfophthalide cycle according to the bridge mechanism characteristic of chemical and biological systems.[18] Collective phenomena in electron transfer reactions presently attract researchers´ attention (see, *e.g.*, the brief review of these phenomena[18]), and poly(arylenesulfophthalides) can be convenient for studying such phenomena.

Thus, PASP was found to be readily reduced by metallic lithium to form quinoid color centers and radicals. Reactions of electron transfer to the sulfophthalide cycle are favored by its high electron affinity. In fact, we deal with the formation of mono-, bi-, and polyradicals of the triarylmethyl type, and the monoradicals have the form of distonic radical anions, whereas the biradicals are formed in the ground singlet state, *i.e.*, as quinoid structures. The obtained experimental data confirm the involvement of electron transfer reactions in the generation of similar color centers and paramagnetic species upon alkaline hydrolysis of PASP and dissolution of PASP in an aniline—cyclohexanone mixture. The reduction of poly(terphenylenesulfophthalide) can produce polyradicals of the triarylmethyl type with a high content (~100%) of unpaired electrons in the main polymer chain. The quinoid-benzoid conjugation regions are formed in the polymers with the biphenyl and fluorenyl bridges. Our further work will be devoted to the study in more detail of the properties of polyradicals and polyconjugation in reduced PASP.

One should remember that quinoid structures in similar polymers can be formed in reactions different from electron transfer.[19]

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