Some chemical reactions in the polydiphenylenesulfophthalide—aniline—cyclohexanone system

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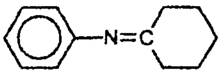
Two main reactions were observed in the polydiphenylenesulfophthalide—aniline—cyclohexanone ternary system by ^{13}C NMR and IR spectroscopy: (1) condensation of aniline and cyclohexanone to give the corresponding anil; (2) opening of the sulfophthalide ring in the polymer under the action of aniline. Both reactions also take place in the corresponding binary mixtures, and they should be taken into account in studies of the color and paramagnetic centers in this ternary system.

Key words: polydiphenylenesulfophthalide. aniline, cyclohexanone, ^{13}C NMR spectroscopy, IR spectroscopy.

Previously,[1] the formation of color centers and paramagnetic species in the polydiphenylenesulfophthalide (**1**) — cyclohexanone (**2**) — aniline (**3**) system in air at room temperature was reported. We found by ^{13}C NMR and IR spectroscopy that at least two main chemical reactions occur in this system under the conditions studied.

The first of them is the well-known[2] formation of anil (**4**). The ^{13}C NMR spectrum of compound **4** recorded in DMF-d_7 in the presence of 6—10 % (w/w) polymer **1** contains only three sharp signals (at 25.2, 27.9, and 175.6 ppm) of the ten signals described in a previous study.[3] The remaining seven signals are markedly broadened. The formation of **4** in the system in question is also accompanied by the appearance of an absorption band at 1652 cm^{-1} corresponding to the C=N stretching vibrations in the IR spectrum of the reaction mixture.[4] The yield of compound **4** in a mixture of compounds **2** and **3** (1 : 1) can reach ~10%,[2] and, judging from the intensity of the band at 1652 cm^{-1}, it does not change noticeably in the presence of the polymer.



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The second reaction occurring in this system is opening of the sulfophthalide ring in polymer **1** under the action of aniline, which has been assumed earlier[1] based on the published data.[5] The opening of the sulfophthalide ring proceeds to a noticeable extent in the presence of excess **3** (both with and without **2**) and is accompanied by a decrease in the intensity of the ν_s(S=O) and ν_{as}(S=O) absorption bands at 1194 and 1350 cm^{-1} and by an increase in the intensity of the band at 616 cm^{-1}. Note that the band at 616 cm^{-1} is typical of the ionic forms of polymer **1** described previously.[6] In the ^{13}C NMR spectrum recorded in a solution in DMF-d_7, the ring opening is manifested as the shift of the signal for the quaternary carbon atom from 96.5 to 72.6 ppm. Owing to the complexity of the system and to the broadening of many NMR signals, the products of the ring opening in **1** have not been unambiguously identified. However, it should be noted that the formation of ionic forms upon cleavage of the sulfophthalide ring could account for the increase in the electrical conductivity of the mixture, which we observed after the addition of compound **3** to a solution of **1** in **2**.

In any case, the reactions reported here should be taken into account both in the studies of the mechanism of formation of color centers and paramagnetic species in this system and in the interpretation of the thread-like structurization of this system and polymer aggregation observed at some ratios of the components.

Experimental

Synthesis and purification of the polymer were described previously.[1] Freshly distilled aniline and cyclohexanone were used. DMF-d_7 (with a degree of deuteration of 99%) was used as received.

IR spectra were recorded on a Specord M-80 spectrophotometer in 0.013—0.040 mm-thick KBr cells. NMR spectra were recorded on a Bruker AM 300 operating at 75 MHz with

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complete proton decoupling for ^{13}C. The chemical shifts were referred to the signal of the high-field methyl group of DMF-d_7, whose chemical shift was taken to be 30.11 ppm. Solutions of the polymer with a concentration of ~6—10% were used.

Electrical conductivity was measured by an E7-8 alternating current bridge at a frequency of 1 kHz in a 10 mL glass cell with flat platinum electrodes. The concentration of the polymer in the electric measurements was 0.2%.

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