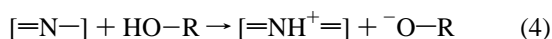


appropriate combination of primary (strong acid) and secondary (solvent) dopants can influence the conformational orientation of elementary units in the polymer conductive backbone such that the number of chain defects is reduced and conductivity increases up to 300 S/cm.

We have suggested that the molecules of the secondary dopant can serve not only to extend the chain conformation of the backbone of PANI-ES but also to work as dopants (through acid or charge transfer) of the base forms of PANI.⁸ This paper aims to provide further insight into the double role of the solvent molecules (dopant and agent promoting conformational changes in polymer chains). Here, we study the interaction of PANI-EB with several molecular complexes of hydroquinone (HQ). On the basis of the obtained experimental data, we discuss the intermolecular interaction of EB-PANI with hydroquinones.

The choice of hydroquinones is based on our recent finding that nonacid molecules that have OH groups are able to introduce (through H-bonding) proton-charged fragments into the EB backbone.⁸⁻¹¹ Scheme 4 illustrates the doping effect of hydroquinones according to the data of our electrochemical measurements:⁸

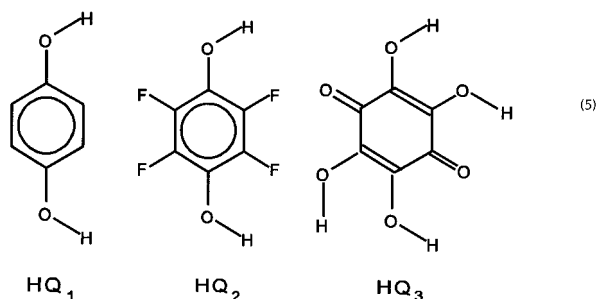


This doping process is similar to that of water or *m*-cresol. And what is more important, with hydroquinones possessing **two** OH groups, each molecule could react with two polymer chains. This creates the unique possibility of **bridging** two polymer chains simultaneously with their molecular doping, which can result in the formation of a highly conductive and ordered polymer network.

2. Experimental Setup

Thin PANI-EB films doped by different molecular forms of hydroquinone were prepared by their casting from solution of EB + HQ in *N*-methylpyrrolidinone (NMP) using the following method. Polyaniline powder substance was synthesized, according to the method in ref 13, in the form of PANI-ES, which was then converted into PANI-EB and dried in a vacuum chamber at 60 °C until the weight of the sample became stable. A 1–2% PANI-EB solution in NMP was then prepared.

As the molecular dopants of PANI-EB, the following derivatives of hydroquinone were used: hydroquinone (hereafter HQ₁), tetrafluorohydroquinone (HQ₂), and tetrahydroxy-1,4-quinone (HQ₃). Their structures are presented in scheme 5:



Solutions of 1–2 wt % of the dopants in NMP were prepared and then mixed with the PANI-EB also dissolved in NMP. In this way we have obtained a series of liquid samples corresponding to the different molecular ratios of active components: EB/HQ₁ = 8:1, 4:1, 2:1, 1:1, 1:2, 1:4; EB/HQ₂ = 8:1, 4:1, 2:1, 1:1; EB/HQ₃ = 2:1. The samples were homogenized by agitation in an oxygen-free atmosphere. Then a small

amount of each solution (two to five drops) was distributed over the surface of thin glass substrates (surface area of 3–4 cm²) and NMP was evaporated by vacuum-drying at 27–50 °C for 1 h.

Several series of the films were prepared to represent different times of storage of EB/HQ solutions before casting and drying. The first was made of freshly prepared solutions, the second by use of the solutions that were previously aged by storage (up to 1 month) in the environment, and the third by the casting of freshly prepared solution, the stabilization of the liquid film sample in the atmosphere saturated by NMP vapor over several days, and then its drying in a vacuum. It appeared that these details of sample preparation were very important in determining the resulting properties of the films.

Micrographs of the obtained films were made using a JENALAB-POL optical microscope in transmission mode with crossed-polarization filters (to detect possible macroscale crystallinity of the samples).

Optical absorption measurements were performed using UV–vis spectrometer (Lambda-6 by Perkin-Elmer) in the range 300–900 nm. No special correction of the absorption spectra was done to account for the absorption by the glass substrates, since they show 95% transparency at wavelengths above 320 nm. The chemical composition of the samples was examined using infrared spectrometry (FT-IR spectrophotometer System 2000 by Perkin-Elmer with a horizontal attenuated total reflectance accessory).

3. Results

3.1. Optical Microscopy and Chemical Stability Measurements. The first series of the films was made by the casting of freshly prepared EB/HQ₁ liquid substance and drying at 35–50 °C in a vacuum. All films were homogeneous, dark blue, and transparent. They show no evidence of crystallinity.

The second series of EB/HQ₁ films was obtained by casting the solutions subjected to a 30-day storage of the liquid substance in the environment and vacuum-drying at 27 °C. This procedure has resulted in the formation of large spherulite crystals in the cases when EB/HQ₁ = 2:1 and for higher HQ₁ concentrations (1:1; 1:2; 1:4). Some surface crystals were as large as 2 cm² and can be seen by the naked eye. Figure 1 shows the optical microphotographs corresponding to 2:1 (b) and 1:1 (c) ratios of PANI-EB to HQ₁. The substances with a lower content of HQ₁ (4:1 and 8:1) have not yielded formation of spherulite crystals and had an appearance of featureless homogeneous films (Figure 1a).

Prolonged contact between both reagents before casting and reduced temperature of drying was beneficial for crystallization of the EB/HQ₁ solution during its drying. Higher temperature (40 °C) hindered the formation of crystals.

We have tested the stability of the morphology of samples under the impact of different external factors. A heating of crystalline films up to 100 °C did not produce visible changes of their morphology. Placing the films into humid atmosphere or water was also not harmful to the crystalline state of the films. We expected that some hydroquinone will leak from the films during its storage in water. However, the analysis of the chemical composition of rinsing water (using the chemical oxidative analysis in acid media) has yielded no dissolved hydroquinone, thus showing its strong bonding in the film.

Immersion of crystalline EB/HQ₁ films in a 0.01 M solution of sulfuric acid results in the acid-doping of the polymer accompanied by a characteristic change of color (from blue to

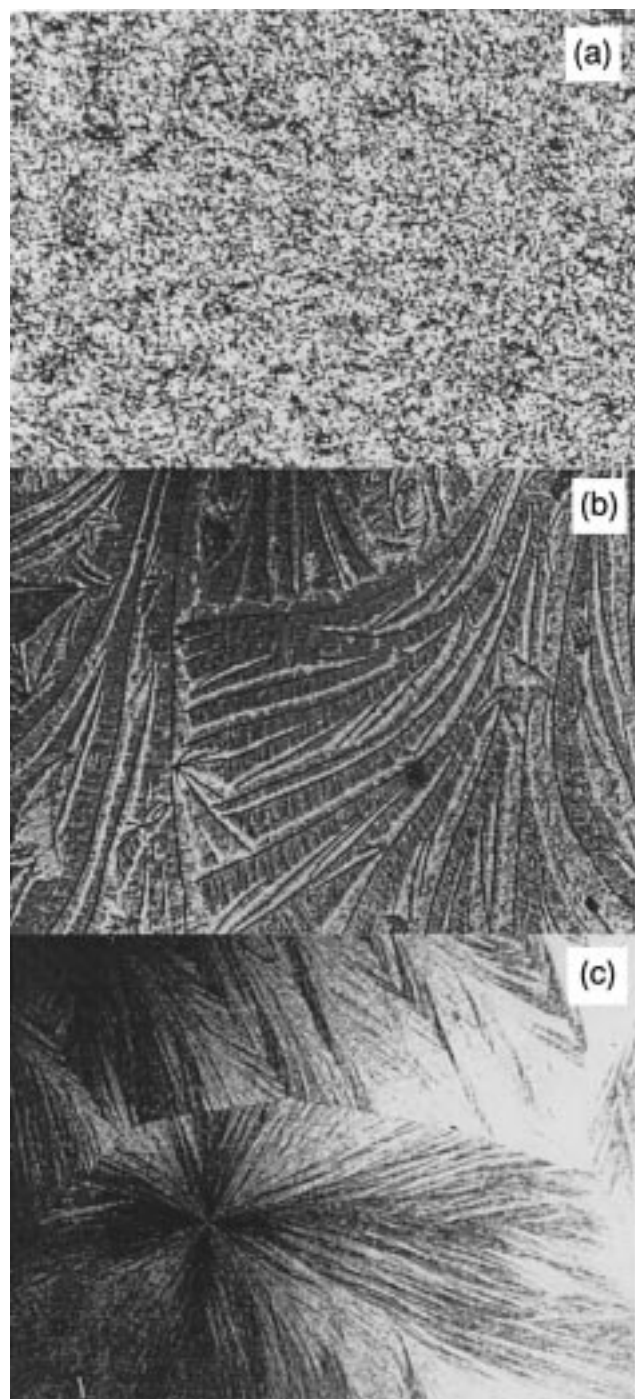


Figure 1. Optical micrographs of the EB/HQ₁ films corresponding to 4:1 (a), 2:1 (b), and 1:1 (c) ratios of the components. Liquid substances were stored for 30 days before the film casting. A length of 13 mm is equivalent to 100 μm in the figure.

green) and growth of electrical conductivity. This operation of acid doping does not alter the crystalline texture of the films (it is even enhanced sometimes). Table 1 shows characteristic values of the surface electrical resistance of undoped and doped films.

The films of EB/HQ₂ were prepared after a 1-week storage of the corresponding solution before film casting and drying. The samples were green (whereas the liquid substance was deep blue) and rather inhomogeneous. Their electrical conductivity was quit high. No crystalline texture was seen even at high concentration of HQ₂ (1:1). In this case we observed a spontaneous and irreversible sedimentation of the polymer in

TABLE 1: Surface Resistivity (Ω/\square) of the Films EB/HQ_{1,2,3} before and after Their Doping in 10^{-2} M Sulfuric Acid

film	ratio of the components					
	4:1		2:1		1:1	
	before	after	before	after	before	After
EB/HQ ₁	$> 10^6$	10^3	$> 10^6$	10^3	$> 10^6$	10^3
EB/HQ ₂	10^6	10^3	10^4	10^3	10^3	10^3
EB/HQ ₃			2×10^3	10^3		

the solution. On the basis of the color of the films and their increased electrical conductivity, we concluded that the polymer had transformed into its salt form that was not soluble in NMP.

The different colors of solution (blue) and film (green) show the possibility of different chemical mechanisms of the intermolecular reactions between components in both cases.

The EB/HQ₃ = 2:1 substance has yielded a pronounced spherulite crystallinity upon drying, as shown in Figure 2. Here again, we have noticed the importance of preliminary aging of the liquid substance before casting and drying. Although a 1-h storage results in formation of small crystals imbedded in the amorphous media (Figure 2a) the 24-h storage yields highly crystalline films (parts b and c of Figure 2). These last films are highly conductive even without subsequent acid doping.

The color of the liquid substance changes gradually during the first minutes after its preparation from red (the color of HQ₃ in NMP) to dark brown. Dry films are yellowish-brown.

3.2. UV-Visible Optical Absorption. More detailed characterization of optical properties of the obtained films was done using UV-vis absorption measurements. Figure 3 shows the optical absorption spectra of EB/HQ₁ films with varying ratio of the components.

We were not been able to observe the well-known^{14,15} optical absorption band at 300–320 nm of PANI-EB associated with $\pi-\pi^*$ transitions in the benzene ring because of limitations of our experimental setup, but the other band centered at 645 nm and ascribed to the $p-\pi^*$ transition in the quinoid imine rings is well seen both in the absorption spectrum of pure PANI-EB and in the composite films (Figure 3).

Increasing the concentration of hydroquinone results in the enhancement of the absorption band at 425 nm. This band is associated with the excitations of electrons into polaronic band of the PANI-ES form. Another band specific to PANI-ES is that at 900 nm (not seen in the spectra of Figure 4). The presence of a 425-nm absorption band in the spectra of the samples with a high content of HQ₁ indicates the protonation of the polymer chain by HQ₁ molecules through the mechanism of acid doping. Simultaneously, the absorption band at 645 nm decreases as a consequence of decreasing quantity of the imine centers. The dark blue color of PANI-EB is converted into the green-bluish color of the polymer film doped by HQ₁.

Figure 4 shows the absorption spectra of the EB/HQ₂ films. They do not possess crystallinity and are highly transparent. The tendency for a change in the absorption spectra from what corresponds to that of pure PANI-EB (curve 2) to that of PANI-ES (curve 1) with increasing concentration of HQ₂ is much more pronounced in comparison with the previous case of HQ₁ (Figure 3). Both characteristic absorption bands (at 425 and 900 nm) are emerging when the HQ₂ doping density increases. This effect is due to the much higher acidity of the hydroxyl groups in perfluorohydroquinone (HQ₂) than in hydroquinone (HQ₁) and their enhanced ability to cause the acidlike doping of the polymer. The band at 640 nm ($p-\pi^*$ transition) decreases several times while the doping level

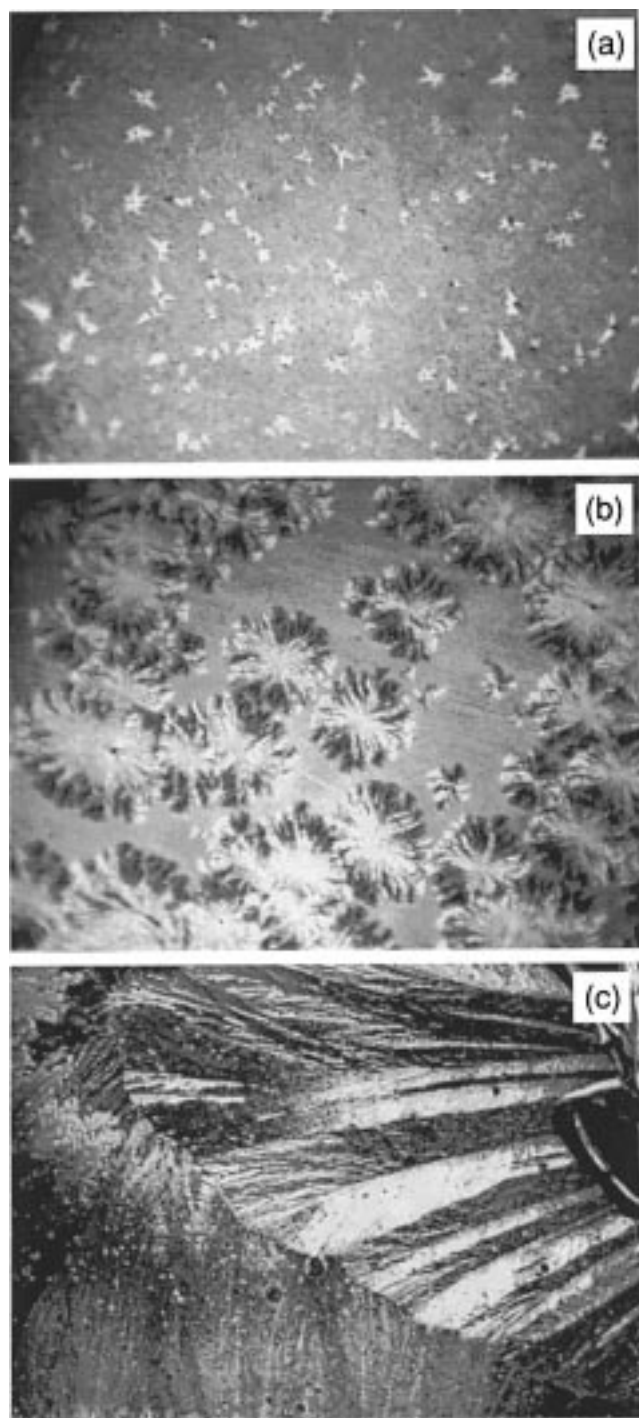


Figure 2. Optical micrographs of the EB/HQ₃ = 2:1 films corresponding to different times of the liquid-substance storage before casting: 1 h (a); 24 h (b); 96 h (c). A length of 13 mm is equivalent to 100 μm in the figure.

increases, thus indicating the gradual reduction of the concentration of quinone-imine groups in the film.

An interesting effect seen in Figure 4 is that the absorption spectra are influenced by the time of storage of the liquid substance in the environment before casting. Curves 5 and 6 of Figure 4 correspond to the film prepared from the same solution (EB/HQ₂ = 1:1) but stored for 1 h and 7 days, respectively. The spectrum of freshly prepared film is very similar to that of PANI-ES (the bands at 425 and 900 nm are very intensive), thus giving evidence of strong acidlike interaction between EB and HQ₂ according to eq 4.

Finally, Figure 5 resumes the absorption spectra of the films

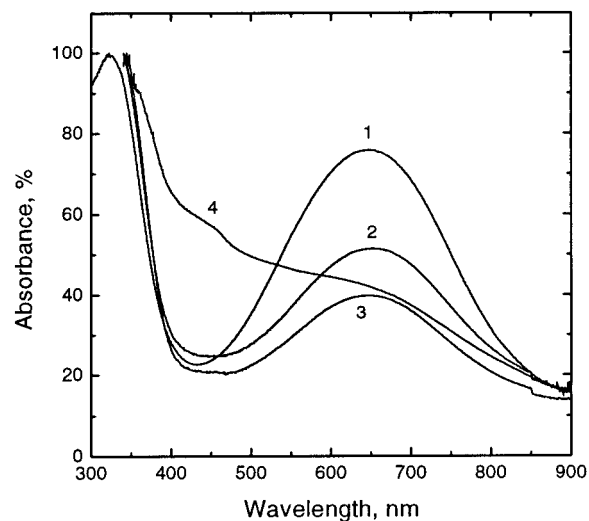


Figure 3. Optical absorbance spectra of EB (1) and EB/HQ₁ films corresponding to different molecular ratio of the components 4:1 (2), 1:1 (3), and 1:4 (4).

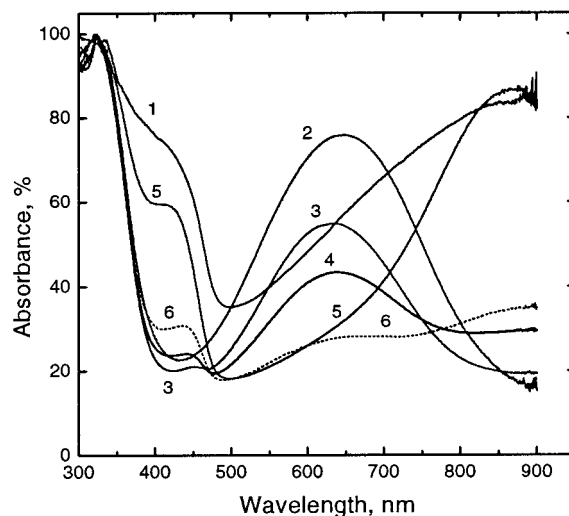


Figure 4. Optical absorbance spectra of ES (1), EB (2), and EB/HQ₂ films corresponding to different molecular ratios of the components: 8:1 (3); 2:1 (4); 1:1 (5, 6). Curves 5 and 6 correspond to the storage time (before film casting) of 1 h and 7 days, respectively.

of EB/HQ₃. It has been already mentioned above that this substance, while in the liquid form, undergoes a fast change of color immediately after its preparation, thus indicating the possibility of some transient chemical reactions. All film samples were prepared from the solution aged to a stable color. They were semitransparent, yellow-brownish with bright green specks and spherulite crystallinity. Absorption bands at 445 and 900 nm are present in the spectra of the samples, thus indicating the acidlike doping of the polymer backbone by HQ₃. The absorption band at 445 nm is obviously red-shifted with respect to that of PANI-ES (425 nm) as a result of reaction of the polymer with HQ₃. The small absorption shoulder at 500 nm is also present. Its intensity drops with the increasing time of the liquid-substance storage and is probably due to the excitation processes in HQ₃. Absorption at 645 nm is not present in the spectra of the films and only weakly seen in the spectrum of the sample stored in NMP vapor (curve 6 in Figure 5).

The observed absorption features indicate that the EB/HQ₃ films do not contain imine-quinone centers and that the backbone is constructed only from the benzene rings. We

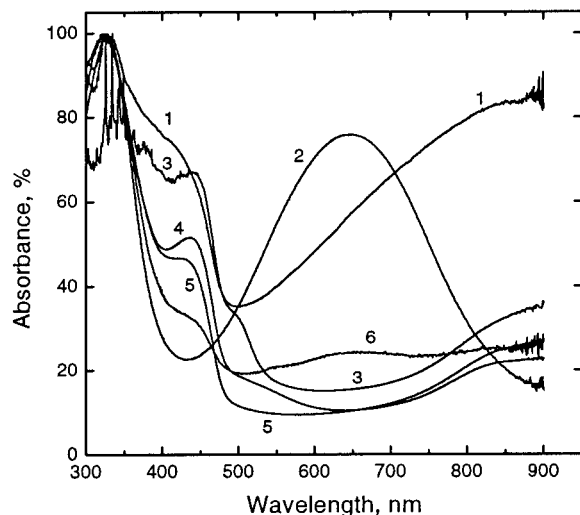
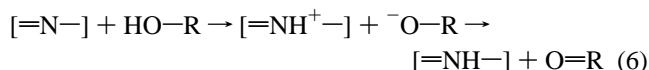


Figure 5. Optical absorbance spectra of ES (1), EB (2) and EB/HQ₃ = 1:1 films corresponding to different storage times before the film casting: 1 h (3); 12 h (4); 98 h (5). Curve 6 corresponds to the EB/HQ₃ film that was cast and kept in saturated NMP vapor for 4 h before drying.

assume that the polymer is in the oxidation state between those of EB and LEB.¹⁴ The reaction between PANI-EB and HQ₃ should be considered similar to the redox process when the polymer is reduced after the acidlike doping of the backbone (scheme 6):



Thus, the optical absorption spectra of the EB/HQ_{1,2,3} films show the presence of the intermolecular interaction between the imine centers of the polymer and hydroxyl groups of hydroquinones that causes the conversion of EB into the highly doped ES-like material. PANI-EB undergoes the acidlike doping by protons from the doping molecule (here, hydroquinone). The degree of conversion of EB into ES depends on the ability of the dopant molecule to hold the negative charge (transform to the anion). This ability is growing in the series HQ₁ → HQ₂ → HQ₃. Redox activity of the dopant could affect the process of EB → ES transformation and cause the conversion of EB into another redox form (here, into LEB as the result of the interaction of EB with HQ₃).

3.3. FTIR Measurements. We have used the FTIR technique to detect the possible presence of NMP solvent in the films, to evaluate the quantity of incorporated hydroquinone, and, finally, to analyze the changes of the chemical structure of the polymer as a result of its interaction with hydroquinones. Figure 6 shows spectra of different EB/HQ₁ films together with the spectra of each of the components of the liquid substance dried at the glass substrate.

The spectra in Figure 6 could be split into two major groups: one corresponding to pure EB and to EB/HQ₁ with a lower concentration of hydroquinone (curves 2–4 if numbered from top to bottom) and another representing the elevated HQ₁ concentrations (1:1 to 1:4, curves 5 and 6). The last group of curves shows the presence of HQ₁ (bands at 465, 510, 665, 754, 830, 1204, 1232, 1354, 1485, and 1725 cm⁻¹ are characteristic of hydroquinone and are not related to PANI-EB^{16–21}). The intensity of these bands is gradually increasing with growing concentration of hydroquinone. This observation gives clear-cut evidence of the incorporation of hydroquinone into the drying film.

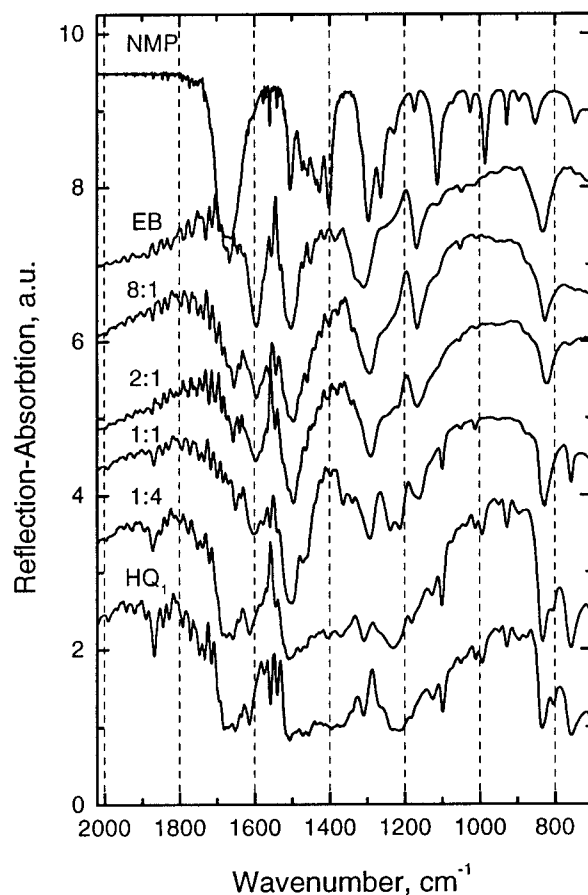


Figure 6. FT-IR spectra of the EB/HQ₁ films with different concentrations of hydroquinone in comparison with those corresponding to pure ingredients.

The possibility of the NMP presence in the films was evaluated based on the results reported earlier for EB films cast from NMP solutions.¹⁸ This solvent shows a strong absorption band at 1664–1682 cm⁻¹ due to the C=O bond vibration. This line is present in spectra 1–4 of Figure 6 although shifted to 1650 cm⁻¹ because of H-bonding between the C=O group of the solvent molecule and the N–H group of the polymer. The intensity of this band in the present case is much lower than that corresponding to the EB/NMP = 2:1 molecular ratio.¹⁸ This allows us to estimate the residual content of NMP in EB/HQ₁ films as not exceeding a few percent and to assume that this quantity does not affect reactions between PANI-EB and HQ₁.

The bands at 1680 and 1650 cm⁻¹ are very pronounced in the spectrum of pure hydroquinone (curve 7) and correspond to HQ₁ concentrations higher than EB/HQ₁ = 1:1 (curves 5 and 6). The most probable reason for the presence of this strong doublet is the vibration of the C=O bond in some resonant structures that are formed by HQ₁ interaction with NMP. This complication needs further detailed study to fully understand the vibrational behavior of EB/HQ₁ complexes.

Very informative seems to be the region 1400–1600 cm⁻¹ where the absorption by aromatic rings is contributing to the IR absorption spectra. There are two major bands at 1496 and 1594 cm⁻¹ representing the vibrations in the benzenoid (B) and quinoid (Q) types of aromatic rings respectively.^{17,18,21} Then the growth of the intensity of the band at 1496 cm⁻¹ with increasing concentration of HQ₁ indicates the change toward higher benzenoid-ring content. This fact confirms the H-bonding interaction between the polymer chain and hydroquinone molecules according to scheme 4. As a result of the reaction,

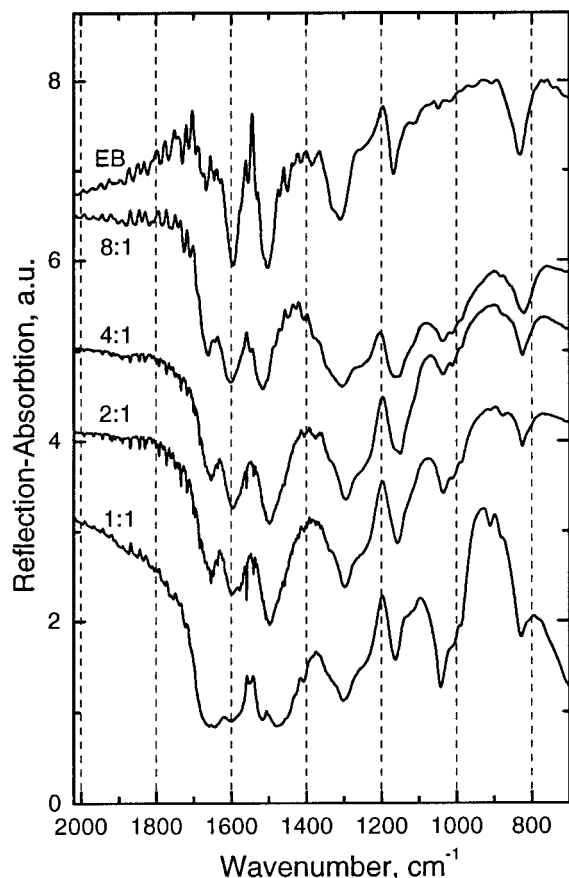
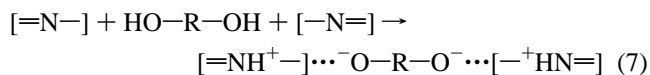


Figure 7. FT-IR spectra of the EB/HQ₂ films with different concentrations of HQ₂.

the Q rings of EB are transformed into the B rings with simultaneous introduction of the electric charge into the polymeric chain.

FT-IR spectra of dry EB/HQ₂ films are shown in Figure 7. The growth of the HQ₂ content results in the enhancement of the absorption band centered at 1050 cm⁻¹. We have assigned this band to the C–F vibration in 4*F*-hydroquinone. The relative intensities of the 1500 and 1600 cm⁻¹ bands are also changing, thus indicating the enhancement of the B-type aromatic-ring concentration with respect to that of the Q ring.

The intensive band at 1670 cm⁻¹ could be assigned to the C=O bond from residual NMP or appearing as the product of the proton transfer (scheme 4). Putting together all the observed data, we have assumed that in this case the reaction is not stopped at a stage shown in scheme 4 but goes deeper:



In this scheme two adjacent polymer chains interact with each other by forming H bonds with the same molecule of 4*F*-hydroquinone. The imine centers of both PANI fragments become protonated (doped), and simultaneously, the dopant molecule is converted into a doubly charged anion. The complex of two PANI chains and one doping molecular anion will have, additionally to the enhanced conductivity along the protonated backbones, the new property of interchain conductivity (because the HQ₂²⁻ anion works as an electronic bridge favoring the charge transfer between neighboring chains).

The FT-IR spectra of EB/HQ₃ are very similar to those presented in Figures 6 and 7, showing the changing relative intensities of the bands corresponding to B- and Q-type aromatic

rings and the presence of the band at 1670 cm⁻¹. So the interaction between the emeraldine polymer chain and different hydroquinones occurs in the same manner for all studied molecules and involves imine centers of the polymer and hydroxyl groups of HQ_{1,2,3}.

4. Discussion

4.1. Mechanism of Crystallization of EB/HQ_{1,2,3} Substance during its Drying. On the basis of the experimental data of section 3, we propose the following mechanism of the crystallization of the emeraldine base in contact with hydroquinones. HQ molecules interact with the polymer mainly through the H-bonding (similar to water or *m*-cresol^{10,22}) and π interaction with benzoic rings.⁷ Several OH groups present in hydroquinone dopant are interacting simultaneously with aniline cores belonging to different polymeric chains. This process causes the reorientation of conformational planes of units composing the polymer chain and mutual ordering of the neighboring chains. The polymer–dopant substance gains a cross-linked macrostructure with an order degree proportional to the concentration of the molecular dopant.

In the liquid EB/HQ substance, the ordering effects may be balanced by the factors causing a disorder (mechanical disturbances in drying liquid, temperature, etc.). Thus, the situation in liquid EB/HQ is quite similar to that found in the case of lyotropic liquid crystals.²³ In the present case the linearly extended polyaniline backbone acts as a mesogenic molecule. Upon drying and solvent removal, the ordered solution is converted into a spherulite crystal.

4.2. Factors Influencing the Formation of Spherulite Structures in EB/HQ_{1,2,3} Complexes. We have distinguished the following experimental variables influencing the process of the formation of spherulite structures.

(1) *Molecular Ratio between Aniline Units and HQ Dopant.* Only a ratio above 2:1 (with respect to HQ concentration) allows for the spherulite crystal morphology. The minimum value of this ratio for onset of the crystallization reaction depends on the chemical nature of the molecular dopant.

(2) *Time of Liquid EB/HQ Substance Aging before Film Casting and Drying.* Longer times probably promote the increase of oriented conformational structures in PANI–HQ complexes. The rate of the process depends on the molecular ratio EB/HQ_{1,2,3} and is higher for the solutions that are not stirred or shaken during the storage. This factor emphasizes the role of NMP (solvent) in conformational changes of the structure of PANI–HQ complexes. The presence of the solvent obviously benefits reorientation of the polymeric backbones, which is then fixed in dried film. It is logical to suppose that the liquid EB/HQ_{1,2,3} substance possesses a lyotropic crystallinity similar to those of other liquid crystals.²⁴

The ordered polymeric structure of the liquid substance may be destroyed as a result of mechanical perturbation (stirring, transfusion, shaking, etc.) especially when the concentration of hydroquinone is close to the minimum value allowing crystallization. To neutralize the effect produced by mechanical disturbance, an additional rest time would be necessary to allow reestablishment of the intermolecular ordering. This is why the films that were equilibrated in NMP vapor before complete drying (third series of the samples) exhibit crystalline order at quite a low content of hydroquinone dopant.

(3) *Temperature of the Equilibration of the Liquid Substance and Drying Temperature.* A lower temperature is favorable for the structural ordering. Its increase provokes the movement of the segments of the polymer–dopant macrostructures and

destroys the order. Other temperature-related factors are the rate of the solvent removal during drying and additional orientation in the PANI–dopant macroscopic network due to surface-tension gradients generated during its drying.

4.3. Impact of Ordering of Polymeric Network onto Its Physical Properties. The direct consequence of ordering in the macroscopic EB/HQ network is the increase of the electrical conductivity of the polymer. The effect of the hydroquinone molecular dopants on the conductivity value is as strong as the acid doping (Table 1).

We expect that the effect of quasi-crystalline ordering of polyaniline by its doping with molecular complexes possessing several OH groups may be a very useful supplement to other known methods of the formation of the supramolecular and conformational order of the polymeric chains^{25,26} such as mechanical stretching of PANI film deposited onto flexible substrate^{27,28} and interaction of PANI with solvent molecules^{6,29} or doped acid.³⁰

It has been discovered that PANI–ES chains are able to acquire a helical conformation with a clockwise or counter-clockwise screw direction depending on the type of optical-active anion.³¹ It seems very likely that in our case of EB/HQ_{1,2,3} the polymer chains could be oriented in a similar way through their H-bonding with the molecular dopant.

Molecular dopants of the polymer backbone enhance PANI solubility, change its conformational structure, induce orientation and liquid crystallinity in solutions, and produce molecular–polymeric crystals after the removal of solvent.

5. Conclusions

The effect of conformational reorientation and ordering of polymeric chains interacting with various molecular forms of hydroquinone has been discovered and studied. As a result of this study the following conclusions can be drawn.

(1) A molecular dopant undergoes an interaction with PANI through formation of hydrogen bonds between its hydroxyl group and imine center of the polymer. The presence of several OH groups at one dopant molecule results in its simultaneous reaction with several aniline cores belonging to different polymer chains.

(2) As a result of this multiple interaction, PANI backbones (coupled with dopant molecule and dissolved in NMP) obtain an ordered conformational structure and orientation typical of liquid crystals. After removal of the solvent the oriented polymer–dopant macronetwork is fixed in a quasi-crystalline spherulite structure.

(3) The mechanism of molecular doping of polyaniline seems to be rather universal, valid in the cases of strong acid doping, doping by solvent molecules, and in the present case. Depending on the chemical properties and structure of a molecular dopant, it could be involved in the charge exchange with the polymer backbone (proton and electron transfer) and thus could alter the optical and conductive properties of materials.

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