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Investigation of charge carriers in poly(3,4-butylenedioxythiophene) (PBuDOT) by means of ESR spectroelectrochemistry

Abstract In situ ESR spectroelectrochemical studies of poly(3,4-butylenedioxythiophene) (PBuDOT) have been performed, in order to investigate more closely the species responsible for the conductivity of this polymer in the doped state. In the process of electrochemical doping of the polymer, ESR spectra at progressively changed potentials were recorded. Then the subsequent dedoping process was studied accordingly. The results reveal that PBuDOT's ESR spectroscopic properties are markedly different form its close relative, poly(3,4-etylenedioxythiophene) (PEDOT). Firstly, the potential dependence of the spin concentration displays a clear peak-shaped transient with a gradual decrease at higher oxidation potentials. Similar behaviour is seen for the ΔB_{pp} widths of the ESR signal, indicating that the type of interactions between paramagnetic centres is potential sensitive. The course of the reduction process of the polymer is more or less the reverse of the oxidation one, with only a slight hysteresis of the spin concentration and a barely discernible one of ΔB_{pp} widths being observed. In PBuDOT, as in PEDOT, distinct narrow ESR lines revealing a noteworthy spin concentration in the reduced state of the polymer have also been observed. The presence of these residual spins in the dedoped polymer may indicate that the dedoping process of this polymer is indeed a slow one. The presence of trace amounts of impurities or oxygen may hinder the dedoping process, especially for thicker films.

Introduction

The chemistry of cyclic alkylenedioxythiophenes began in the late 1980s with the synthesis of a pioneer compound, ethylenedioxythiophene (EDOT), by Bayer [1], the polymer of which has received unabated scientific interest in recent years in research groups throughout the world [2]. The reason for this are its much desired electrochemical and spectroscopic properties, such as low band-gap, high conductivity, and stability of both the oxidized and reduced forms, as well as electrochromic and antistatic properties, all of which have paved this polymer a way into numerous applications [3, 4, 5]. Two of the few drawbacks (or advantages, depending on one's point of view) of PEDOT, however, are its insolubility and infusibility. These properties are a consequence of the high regularity of this polymer's backbone, which is solely α–α′ coupled, accompanied by the cyclic character of the ethylenedioxy substituent which minimizes the disorder in the relative arrangement of the polymer chains through a curbed freedom of movement. Disruption of this regularity could be brought about by incorporation of a more flexible alkyl chain. One of the concepts of modification of the parent monomer structure was to graft pendant groups on to the 3,4-ethylenedioxy ring, while the other is to enlarge the size of the 3,4-alkylenedioxy ring itself. These efforts constitute two of the many pathways of modification of PEDOT aimed at development of new derivatives or relatives with enhanced properties, fine-tuned for specific applications. The first concept was realized through the synthesis of pendant alkyl-substituted PEDOT [6, 7]

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with different length alkyl groups, followed later by a synthesis of hydroxymethylated EDOT [8, 9] to which different alkyl chains were attached [10, 11]. To date, however, these modifications were unsuccessful in preparing a soluble PEDOT polymer. The second mentioned pathway of modification of EDOT has, to date, received limited attention. One of the first reports was the study of poly(3,4-propylenedioxythiophene) (PProDOT) by Dietrich et al. [12]. Later, the group of Reynolds reported the first systematic study of the electro- and spectrochemical properties of a number of different 3,4-alkylenedioxythiophenes [13, 14]. In one of their papers [13], they presented the results of electrochromic studies of poly(3,4-butylenedioxythiophene) (PBuDOT). Although the conductivity of this polymer is substantially impaired relative to PEDOT, it displays one of the fastest switching times together with one of the highest optical contrasts (ΔT amounting to 63%) in the alkylenedioxythiophene family. Although these preliminary studies seemed promising, to date and to the best of our knowledge there have been no further studies concerning this polymer. Recently, our group has reported on the basic cyclic voltammetry of PBuDOT [15].

Electrooptical applications of electrochromic polymers rely on precise control of the doping state of the polymer, since its electrochemical state determines its absorption spectrum. Of practical importance also is the issue of conductivity of the material. The mechanism of doping of organic conjugated polymers assumes the existence of two different charged species, namely polarons and bipolarons, which are also responsible for the propagation of the electrical current along the polymer chain [16, 17, 18]. Both species, however, carry a different contribution in the overall transferred current, with bipolarons being more mobile [18]. Since polarons carry a magnetic moment, they can be observed by means of ESR spectroscopy. Depending on the doping level of the polymer, it is possible for polarons to coexist together with diamagnetic bipolarons and interact [19], which makes it possible to observe both, though bipolarons indirectly. Recent studies looked at the influence of the doping level on such properties of PEDOT as conductivity and carrier mobility [20] and our group has followed on with ESR spectroelectrochemical studies of PEDOT [21]. Since these revealed some interesting findings relating to the doping and dedoping process of this polymer, we have decided to undertake similar studies on PBuDOT (a close analogue of PEDOT), to investigate its doping process. Since the spectroscopic properties are closely related to the electronic ones, these studies could help understand the differences in spectroscopic properties of PEDOT and its relatives.

Experimental

Cyclic voltammetry experiments were performed on an AUTOLAB potentiostat-galvanostat model PGSTAT20 (EcoChemie) driven by a computer. Platinum wire ($\phi = 1$ mm) was used as the working electrode. Its geometric area was ca. 0.10 cm^2; the excess area was sealed off with Teflon tape. Ag wire was used as a pseudoreference electrode. The potential of the ferrocene couple versus this electrode was $+0.59$ V. All potentials, however, are given versus the silver electrode used. Platinum coil wound around the two electrodes served as an auxiliary electrode. Before experiments, the whole cell was deaerated with argon.

The monomer 2,3,4,5-tetrahydrothieno[3,4-*b*][1,4]dioxocine
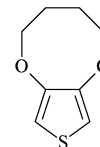
2,3,4,5-tetrahydrothieno[3,4-b][1,4]dioxocine
BuDOT

(BuDOT, **1**) was synthesized by our group in a multi-step synthesis, described by Kumar et al. [14]. Poly(3,4-butylenedioxythiophene) (PBuDOT) was obtained by electropolymerization on a platinum electrode from a 0.01 M solution of the monomer in 0.1 M Bu$_4$NPF$_6$ in CH$_3$CN using cyclic voltammetry with maximum oxidation current control.
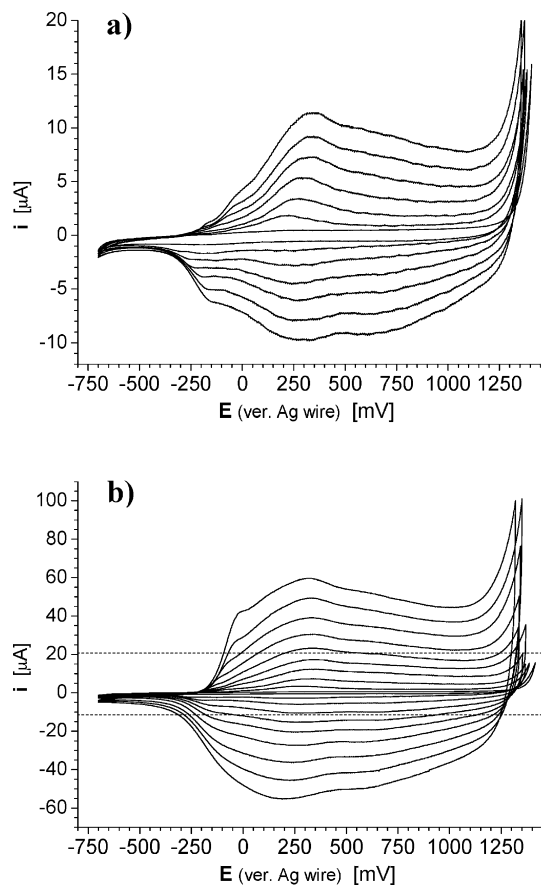
ESR spectroelectrochemical measurements were done on an ELPAN SE/X-2543 series, X-band (9.3 GHz) reflective-type ESR spectrometer (RadioPAN, Poland) with magnetic modulation of 100 kHz, coupled together with an ELPAN EP-21 type potentiostat driven by an ELPAN EG-20 potential generator. The spectroelectrochemical cell was a thin cylindrical glass tube narrowed at the bottom (3 mm in diameter). The reference and auxiliary electrodes were the same as described above. The electrolyte was 0.1 M Bu$_4$NPF$_6$ in CH$_3$CN, the same as for the polymerization. PBuDOT films were studied directly on the electrode on which they were synthesized.

First-derivative ESR spectra were recorded with attenuation of the microwave power of 3 dB ($\sim$15 mW). At this power level, saturation of the signal was not observed. Simultaneously, the microwave resonance frequency was also recorded.

The dependence of relative concentrations of paramagnetic centres in the studied polymers upon the potential applied to the polymer film was determined. The concentration of paramagnetic centres in the sample is proportional to the area under the absorption curve, so double integration of the first-derivative ESR spectra was performed.
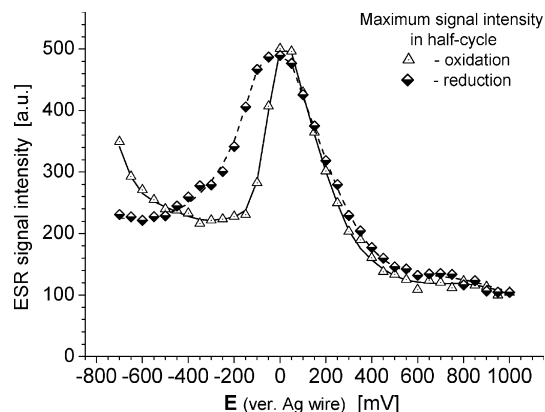
Results and discussion

Cyclic voltammograms (CVs) showing the process of electropolymerization of BuDOT upon successive cycling are shown in Fig. 1. What is interesting at first sight is that the CVs of the thin PBuDOT film at the beginning of the polymerization process differ from those observed for a much thicker film (Fig. 1a). The main oxidation peak appears at ca. 0.35 V, preceded by two small pre-peaks around -0.05 V. The main oxidation peak at 0.35 V can be attributed to the first oxidation step of the polymer in which polarons are generated. In the reduction half-cycle, three reduction peaks can be seen (Fig. 1b): a dominant one at 0.3 V and two smaller ones at -0.15 V and 0.6 V. This may be an indication that the reduction of the polymer is a stepwise process. Taking into consideration only the CV responses of very thin PBuDOT films first, we see that at this stage of the polymerization only two reduction peaks appear, at 0.25 V and -0.2 V. The dominant peak

Fig. 2 Maximum ESR signal intensity as a function of potential in both oxidation and reduction half-cycles

Fig. 1a, b Electropolymerization of BuDOT from 0.01 M solution in 0.1 M Bu_4NPF_6 in CH_3CN at a Pt electrode at 100 mV s^{-1}. Progressive CVs of growing PBuDOT film: (**a**) initial, (**b**) intermediate and final stages. For clarity, only selected cycles are shown

at 0.25 V may represent the process of reduction of polarons, while the peak at −0.2 V may represent the final disappearance of polarons from the polymer. Later, during polymer film growth, these two peaks coalesce into a broad and diffused one. The third reduction peak may have to do with reduction of bipolarons that could be expected at high oxidation potentials. Later in the polymerization process, a pre-peak of the main oxidation peak starts to separate from its rising shoulder at ca. 0 V. We have observed that if the polymerization process is allowed to continue, this peak grows further, eventually surpassing even the main oxidation peak. Such peaks were observed before for other derivatives of PEDOT, namely PEDOT-Ph to which PBuDOT's CV shows strong similarity [14]. Numerous electropolymerizations that were performed indicate that this peak may depend upon the absolute thickness of the polymer film, as it appears in further stages of the electropolymerization process regardless of the area of the electrode employed. Appearance and growth of this peak have been also observed upon electrochemical degradation of PBuDOT. It is unclear what it represents. Its sharpness may indicate that it is of non-faradic origin, representing, for example, conformation changes taking place in

the polymer upon transition from a non-conducting to a conducting state. However, further systematic studies are needed in order to elucidate the origin and meaning of this peak. It is also worth noting that the electropolymerization process of BuDOT is self-accelerating, i.e. upon consecutive polymer growth the oxidation of the monomer comes about at lower potentials. After synthesis, the CV in monomer-free electrolyte does not differ much from the one at the end of the polymerization. Apart from the peaks observed during polymerization, in the oxidized state the polymer displays a high background current. It should be also noted that by controlling the maximum monomer oxidation current it is possible to fabricate films with very reproducible CV responses each time.

In situ ESR spectra of PBuDOT film at progressively changed potentials for both oxidation and reduction half-cycles have been recorded. The potential dependence of their maximum amplitudes in both oxidation and reduction half-cycles is presented in Fig. 2. Starting from the minimum reduction potential, we observe a notable amplitude of the ESR signal, indicating unpaired spins in the polymer even at such low potentials as −0.7 V, where on the CV the current is flat and low. With increasing potential, we observe at first a sharp drop in the intensity of the signal between −0.7 V and −0.2 V, followed by a sharp rise up to a potential of 0.0 V where a maximum is attained. Above 0.0 V, the signal intensity gradually decreases with increasing oxidation potential, slowly levelling out as it approaches the potential of 1.0 V. The intensity of the signal, however, does not drop to near-zero levels as observed in PEDOT [21]. In the reverse reduction half-cycle, the shape of the potential dependence of the ESR signal amplitude resembles the oxidation half-cycle up to a potential of 0.1 V. Upon decreasing the potential, a gradual increase of the signal amplitude takes place, reaching a peak at 0.0 V, after which it decreases again. From then on, the course of the dependence is different than in the oxidation half-cycle. The intensity decreases more slowly yet monotonously, and the growth of the ESR signal when heading for the minimum reduction potential is absent.

Owing to this, the amplitude of the ESR signal at −0.7 V is lower than of its oxidation half-cycle counterpart. The intensity alone, however, cannot be taken as a direct measure of any property of the system studied and, as such, it can only serve as an indication of the experimental behaviour of the system.
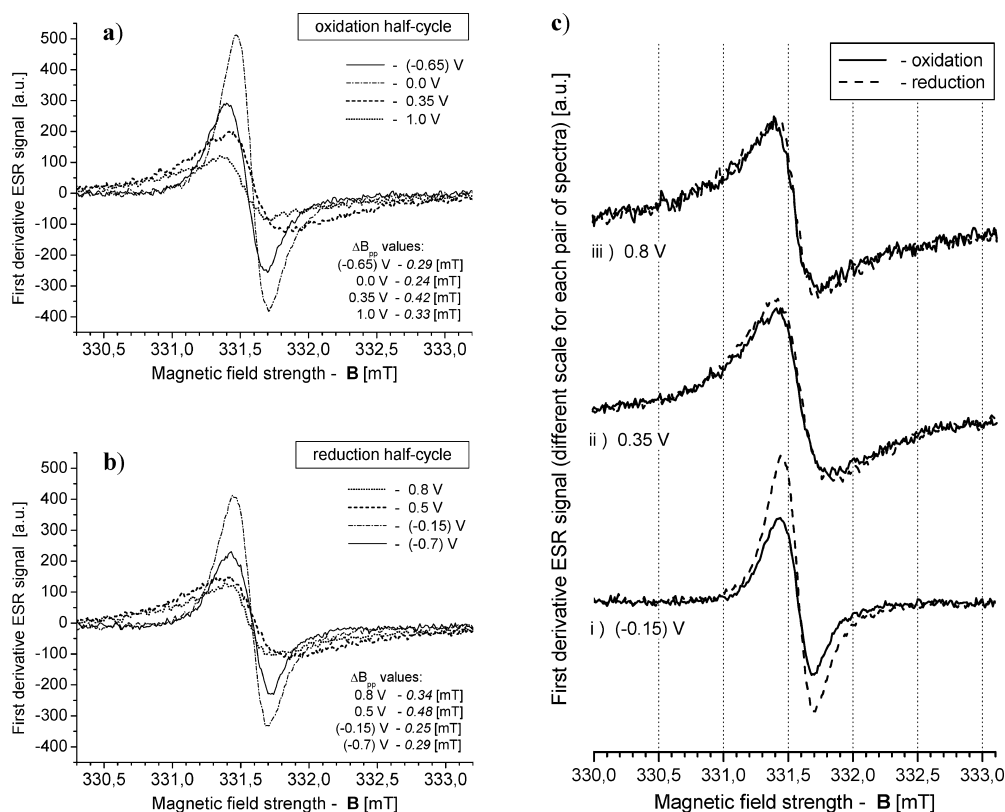
In Fig. 3, selected ESR spectra from both oxidation and reduction half-cycles are gathered together to enable more quantitative comparisons of the changes of both the signal intensities and linewidths of the spectra at different potentials. It follows that the signals are widest at potentials past the maximum height spectra in the oxidation, and before in the reduction half-cycles, and later decrease back again. Detailed discussion of the potential dependency of the widths (ΔB_{pp}) will be given below.
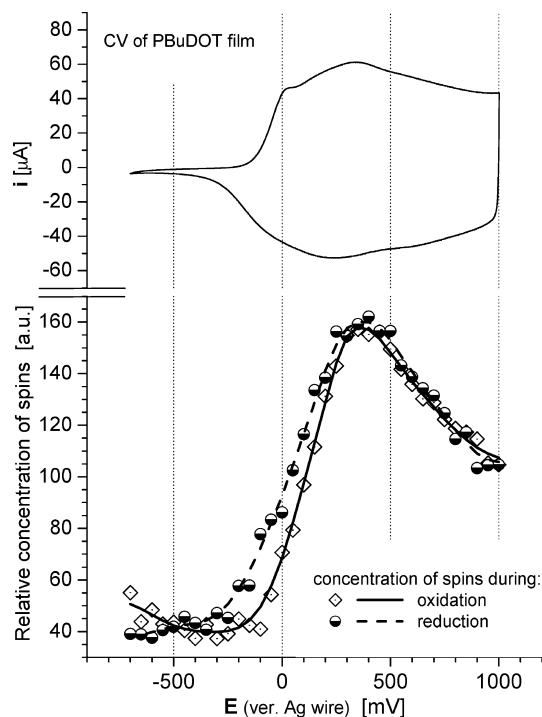
The presence of the ESR signal in PBuDOT over the whole potential range studied indicates that, at all times, paramagnetic centres are present in the film. Their relative concentration, given by the double integral of the ESR line, is presented in Fig. 4. In the oxidation half-cycle, three distinct regions may be distinguished on the plot. In the first one between −0.7 V and −0.3 V, the spin concentration decreases. Then, in the second region, it starts to increase, slowly at first but quickly later, reaching a well-defined maximum at 0.35 V. In the third region, at higher potentials, a clear (linear-like) diminution of the number of spins is observed. Relating these changes to the CV of the polymer, we can see that the rapid increase in the number of spins agrees with the evolution of the dominant oxidation peak of the polymer. Interestingly, however, the first oxidation peak of the polymer, the so-called pre-peak, is not reflected in the spin concentration curve. This may strengthen the supposition presented earlier that the process behind this peak is of non-faradic origin. At the potentials of this peak the spin concentration just begins to increase. The oxidation of the polymer brings about a conformational change of the polymeric units, which are required to flatten out the polymer. The change of polymer chains contacting the metal electrode can be especially important, as it can have an effect on the electrode's double layer capacity. This is a similar effect as in the case of molecules adsorbed on the electrode surface. At this point, the polymer is only lightly doped; however, it may well have already traversed the percolation threshold [22] and the whole film has become conductive. When this happens, the area of the electrode increases suddenly and markedly, as now the electrode area comprises the metal and a highly porous conductive polymer film. This sudden increase of electrode area, together with the above-discussed conformational change, cause an increase in the capacity of the double layer, which manifests itself in the form of a sharp CV peak. The decrease of the number of spins at high positive oxidation potentials may be an indication of pairing of polarons to spinless bipolarons or formation of diamagnetic polaron pairs: π-dimers [23, 24].

In the reduction half-cycle, the changes in the spin concentration follow a similar but reverse trend as in the oxidation half-cycle. The apex of the concentration curve appears again at around 0.35 V, slightly earlier

Fig. 3 Selected ESR spectra of PBuDOT at selected potentials in the (a) oxidation and (b) reduction half-cycles and (c) a comparison of the ESR spectra at the same potential in both oxidation and reduction half-cycles

Fig. 4 Relative concentration of paramagnetic centres in PBuDOT film as a function of the potential during oxidation and reduction half-cycles. *Above*: a CV of PBuDOT in monomer-free electrolyte (0.1 M Bu$_4$NPF$_6$ in CH$_3$CN recorded at 100 mV s^{-1})

paired electrons are present in it. Interpreting these results, it should be pointed out first that these spins can only originate from the polymer. Since the polymer was synthesized through electropolymerization, then no residual initiator molecules are left in it. Radicals appearing upon degradation of either the polymer or the electrolyte–solvent system are also highly improbable, since the studied potential range is well within the stability potential window of both the electrolyte and polymer. One possibility is that these spins represent pinned defects in the polymer backbone that are a result of the polymerization method employed. These could be conjugation defects or radicals trapped at chain ends. Since electropolymerization is in fact a radical polymerization, then side reactions are inevitable, especially at later stages of the polymerization when monomer radical cations can react with already deposited film.

Another possibility is that at least some of the PBuDOT chains exist in a quinoid form in the dedoped state, with one delocalized unpaired electron occupying both HOMO and LUMO orbitals of the undoped polymer. This interpretation has been already proposed for PBuDOT's parent relative PEDOT to explain its Raman spectra in an undoped state [22]. However, recent theoretical calculations presented by Brédas and co-workers [25] point to an opposite conclusion, providing numerical evidence for a benzenoid character of the PEDOT chain in the reduced state. Finally, a third explanation can be proposed. It is known that PEDOT is very easily oxidized and that it is stable in this form. Open circuit potential measurements carried out by Kvarnström et al. [26] indicate that PEDOT films, dedoped electrochemically by keeping them at sufficiently low reduction potentials, within 200 s can self-attain potentials at which the polymer is in its oxidized form. PBuDOT, being a close relative, may exhibit similar properties since the potential of the main oxidation peak in both polymers is similar. Upon reduction, the polymer layers close to the electrode become insulating and slow down the process of reduction of layers further away. Some time may be needed to fully dedope the whole of the polymer film. On the other hand, these outermost layers are directly exposed the electrolyte medium. Any impurities present in it, as well as trace amounts of water and most importantly oxygen, can therefore reoxidize these layers, creating a situation where a dynamic equilibrium between electrochemical reduction of the film and its reoxidization is set up. If this is the case, then it may not be possible to fully dedope PBuDOT at all, especially thicker polymer films. In this way, part of the polymer film may be lightly doped at all times, giving the observed ESR signal.

Another result that showed up during the determination of the spin concentration was the Dysonian character of the spectra at potentials where the slope of the spin concentration dependence is steepest, i.e. up to 0.3 V in both the oxidation and reduction half-cycles. This is interesting since it could suggest metallic-type properties, and these, at an intermediate doping level

than the main broad reduction peak for PBuDOT. Afterwards the spin concentration decreases quickly, but slightly slower compared to a corresponding increase in the oxidation half-cycle, leading to a narrow hysteresis. This similarity between the oxidation and reduction half-cycle transients may imply that the doping and dedoping processes of PBuDOT follow similar mechanisms. This behaviour differs compared to PEDOT, for which during the reduction half-cycle (dedoping) a clear hysteresis of the spin concentration and of ΔB_{pp} widths was observed [21]. The observed narrow hysteresis indicates, however, that some factors retarding the reduction process of the polymer do exist in PBuDOT as well. One of these could be the movement of counterbalancing anions out of the film. On the other hand, the more bulky butylenedioxy cyclic substituent may enhance the movement of anions to and from the polymer by spacing the polymer chains further apart.

The difference in the spin concentration at the beginning and at the end of the experiment is a puzzling phenomenon. Before the proper ESR spectroelectrochemical measurements, the polymer was always subjected to two or three voltammetric cycles so that its electrochemical response could stabilize. After that, the polymer was held at a potential of −0.7 V. If, during such pre-treatment, the polymer did not become fully dedoped, then some charge carriers could still be left in it, giving an abnormally high ESR signal.

The fact that a small spin concentration exists in the reduced (dedoped) state of PBuDOT suggests that un-

when polarons start to emerge, are rather unexpected. Studies of poly(3-methylthiophene) revealed that metallic-type conductivity emerges only at high doping levels [18], but in the case of PBuDOT at highest oxidation potentials the Dysonian character of the ESR line disappears. To elucidate this phenomenon, however, further studies concerning especially the temperature dependence of PBuDOT conductivity would be necessary.

Analysing the peak-to-peak widths (ΔB_{pp}) dependence on potential (Fig. 5), we can also distinguish different regions on the plot. In the oxidation half-cycle, ΔB_{pp} at first stays constant up to ca. -0.5 V, after which it starts to decrease, traversing a shallow trough at -0.1 V. After that, a rapid rise is observed until 0.4 V. Afterwards, ΔB_{pp} values decrease up to 0.75 V, after which they appear to stabilize. The shape of this ΔB_{pp} transient shows some similarities to the spin concentration transient. Changes in the widths of the signals are in part a reflection of the changes in the number of spins in the sample. With an increase in the concentration of polarons, observed between -0.2 V and 0.35 V, dipolar interactions of their unpaired magnetic moments in their increasing population grow stronger, causing the ESR lines to broaden as observed. Above 0.35 V, the concentration of polarons starts to decrease and so does ΔB_{pp}. Correlation of these two parameters can be explained in terms of a process of pairing of the polarons, in which bipolarons or π-dimers are formed, the decrease of ΔB_{pp} being due to weakening dipolar interactions [27] between ever more separated unpaired polaronic spins. The stabilization of the widths' magnitude, however, may imply that at these potentials the spins are far enough from each other that their mutual interactions do not change further. In the reverse reduction cycle, up to 0.75 V the ΔB_{pp} widths remain constant, although the spin concentration increases. Next, a sharp rise is observed, reaching a maximum at 0.5 V. The magnitude of this peak is larger than in the oxidation half-cycle. A decrease of the widths up to -0.05 V follows on, postponed relative to their rise in the oxidation half-cycle by 50 mV. Next, up to -0.5 V,
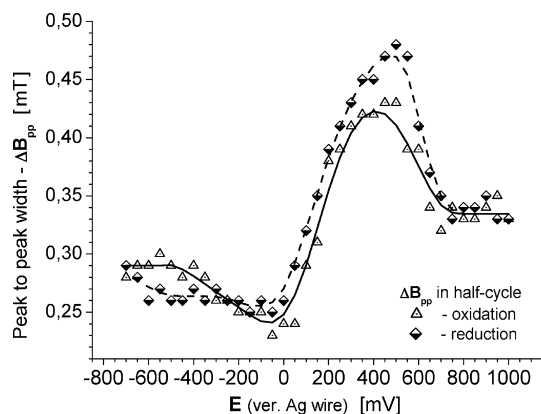
the widths do not change and only near the end of the cycle increase a little. Comparing the shape of this dependence with the one for the spin concentration, we see that the two are less interconnected with each other. Nevertheless, it should be concluded that the mutual interactions between the charge carriers in the polymer strongly depend upon their concentration. Analysing the form of the ESR spectra of PBuDOT, especially in the oxidized state, we have noted their asymmetric-like shape, leading to a supposition that they can comprise more than one component. This issue is currently under investigation.

Linewidths of ESR lines depend on the types of magnetic interaction between paramagnetic centres in the sample [28]. In PBuDOT, we see that the absolute magnitude of their variation across the whole potential range is moderately large. However, simultaneous analysis of the changes in the spin concentration and ΔB_{pp} widths points to additional conclusions. When broadening of ESR lines takes place and, at the same time, the spin population increases, this effect could point to statistical distribution of their magnetic fields. Such statistical distribution of magnetic moments is characteristic for less mobile unpaired electrons. Lines which could be attributed to this type of spin were observed at the beginning of doping of PBuDOT when polarons predominate. If later, however, the linewidths of the signals decrease, then this may either further corroborate the supposition that these spins no longer see each other. This could be possible if they are homogeneously distributed in the polymer. Alternatively, they could cluster together and the drop in ΔB_{pp} could be a result of the emergence of exchange interactions. Exchange or superexchange interactions of mobile unpaired electrons average the statistical distribution of magnetic fields in the sample and the ESR lines become narrowed. On the other side of the potential range, we also observe narrow ESR lines. Narrow lines are characteristic of paramagnetic centres with averaged magnetic fields. This group of paramagnetic centres may be formed by highly mobile spins. In light of the earlier discussion of the problems with dedoping of PBuDOT, these lines may originate from the residual polarons present in the lightly doped film layers exposed to oxidation by species present in the electrolyte. The high mobility of these sparse spins could be responsible for the small linewidths of the ESR lines. Exchange interactions, however, would require that these spins form groups or packets, which would require them to take some preferred positions along the polymer chain, possibly near the spins localized on neighbouring chains.

Fig. 5 Changes in signal linewidths (ΔB_{pp}) of PBuDOT in the course of the oxidation and reduction half-cycles

Conclusions

The results of ESR spectroelectrochemical studies of PBuDOT show that different members of the poly(3,4-alkylenedioxythiophene) family behave differently upon doping and dedoping. In the process of electrochemical

oxidation, the concentration of paramagnetic species in PBuDOT increases markedly, indicative of the formation of polarons. Together with the increase in the polaron concentration, the types of interaction between paramagnetic species change. An increase in the ΔB_{pp} of ESR lines observed upon doping may indicate a transition from highly mobile groups of spins to less mobile and weaker interacting ones. At higher oxidation potentials, however, a decrease of spin concentration and ΔB_{pp} widths is observed which may be a sign of the formation of bipolarons. The reduction process of the polymer is generally similar to oxidation. During reduction of polarons, a narrow hysteresis on the spin concentration and ΔB_{pp} curves is observed, indicating that some factors retarding the reduction process do exist. These factors could be associated with the movement of counterbalancing anions out of the polymer film upon dedoping. In the reduced state of the polymer, a non-zero spin concentration holds up, which may indicate the presence of residual spins. Their presence in the dedoped polymer may suggest that the dedoping process of PBuDOT is slow. Considering the low oxidation potential of PBuDOT, the slow dedoping process of the polymer may be further slowed down by the presence of trace amounts of water or oxygen that could reoxidize the polymer.

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