Electrosynthesis of a copolymer containing C₆₀ in the main chain

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Abstract
The electrochemical synthesis of a copolymer consisting of phenylene vinylene units and C₆₀ was studied. The starting materials were 3,4,7,8,11,12,15,16-octafluorotetraazaporphyrin and C₆₀. The fullerene is introduced into the polymer synthesis as a film on the working electrode. The C₆₀ film is dissolved upon reduction and the reduced fullerene species interacts with the simultaneously reduced precursor at the electrode surface resulting in a film on the substrate. The coupling reaction between the reduced species leads to a material where the fullerene units are incorporated into the main polymer chain. The film formed is characterized by cyclic voltammetry and by FTIR, Raman and UV–vis spectroscopy. The charging discharging reaction of the copolymer film was studied by in situ ATR-FTIR. The spectroscopic results indicate short chains of copolymeric structure. Fluorescence spectra were recorded from films of the copolymer and from PPV. The fluorescence of PPV was quenched to one tenth of its origin in the copolymer film.

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1. Introduction
Poly(paraphenylene vinylene), PPV and more recently oligo(paraphenylene vinylenes) have been extensively studied as donors in the combination with acceptor units [1–5]. Chemical copolymerization of different polymer material together with fullerenes has been the main approach to synthesizing efficient donor-acceptor systems [6–8]. To make use of the optical and electronic properties of conjugated polymers or oligomers but to avoid processing of the material for application, electrosynthesis utilizes an easy way to produce films directly on a conducting surface. Electrochemical derivatization of fullerenes has been reported earlier for example by Mangold et al. [9]. One demand for electrochemical polymerization is that the starting molecules or monomers are soluble either in water or in organic solvents. As this is not the case with C₆₀ instead the reduced highly soluble forms of C₆₀⁻ are used. Using cyclic voltammetry C₆₀ can be step-wise reduced in organic solvents to form first the monovalent anion and the multi charged anions and finally the hexa-anion [10]. The electrochemically formed di- and tri-anions of C₆₀ have been reported to be used for synthesizing covalent organofullerenes while the hexa-anion is reported to be highly reactive and therefore not suitable for electrosynthesis [9]. In a reductive polymerization coupling of radicals of both the fullerene and the monomer or precursor for a conjugated polymer can be achieved.

In this work PPV is electrosynthesized from a precursor on top of a drop cast C₆₀ fullerene film. A simplified scheme for the proposed reaction is drawn in Scheme 1. Upon reduction of the C₆₀ film soluble cations C₆₀⁺, C₆₀− and C₆₀−⁻ are formed simultaneously with reduction of the precursor at the electrode. As a result of these processes a film is deposited on the electrode substrate in which C₆₀ molecules are incorporated in the main chain of PPV.

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2. Experimental

2.1. Chemicals

The precursor used was 0.05 M \( \text{TPEB} \), dissolved in 0.1 M tetraethylammonium tetrafluoroborate (TEABF\(_4\)) in DMF (Lab-Scan). The salt was dried under vacuum before use. C\(_{60}\) was obtained from Acros (99.9% purity) and the dichloromethane used for dissolving C\(_{60}\) was obtained from J.T. Baker and was distilled before use.

2.2. Procedure

Electrosynthesis is made in a small volume electrochemical cell. A Teflon sealed Pt disk was used as working electrode (area \(0.07\ \text{cm}^2\)). The counter electrode was a GC-rod and as pseudo reference electrode a Ag/AgBr wire was used (+0.37 V versus SCE). Potential cycling is made between 0 and \(-2.3\ \text{V}\). C\(_{60}\) films are made by drop casting 100\% C\(_{60}\) saturated CH\(_2\)Cl\(_2\) solution on a Pt electrode in nitrogen atmosphere. In all cases the copolymer is synthesized on the Pt electrode covered with a film of C\(_{60}\). The electrochemical measurements were performed with an EG&G PAR potentiostat model 366 A. Raman spectra are recorded with a Renishaw Raman microscope system 1000B and the laser excitation wavelength used is \(\lambda = 780\ \text{nm}\). The spectra were recorded in the 180° configuration directly from the electrode surface. In situ FTIR measurements were made in an ATR spectroelectrochemical three-electrode cell using a ZnSe reflection element sputtered with a thin layer of platinum as working electrode. The electrochemical area of the working electrode was 0.5 cm\(^2\). A Pt foil served as counter electrode and a silver wire covered with AgBr served as pseudo reference electrode. The in situ ATR-FTIR technique and the cell set up have been described earlier [11,12]. Spectra were recorded with a Bruker IFS 66/S FTIR instrument equipped with an MCT detector. Every spectrum consists of 32 co-added interferograms covering a potential range of 70 mV. The resolution was 4 cm\(^{-1}\).

The spectra are differential spectra, i.e., each spectrum is related to a reference spectrum taken at a potential prior to the studied redox reaction. Absorption spectra of the films synthesized on ITO were recorded with a Shimadzu UV-2501PC spectrophotometer and Fluorescence spectra were measured using a Fluorolog-3 fluorometer (SPEX) and were corrected to the instrument wavelength sensitivity.

3. Results and discussion

3.1. Cyclic voltammetry

The reaction mechanism of the electrochemical reduction of the \( \text{TPEB} \) has previously been described in the literature [13,14]. The polymerization process of the precursor is performed by potential cycling at 50 mV/s between 0 and \(-2.3\ \text{V}\). As reported earlier the first reduction peak involves the splitting of bromine leading to the intermediate brominated quinodimethane. This intermediate is then further reduced at potentials below \(-1.5\ \text{V}\) and the remaining bromine is split away and paraphenylene vinylene oligomers are formed and deposited at the electrode [14]. Consecutive potential cycles give rise to small currents obviously due to the low conductivity of the adsorbed film. Characteristic cyclic voltammograms of p- and n-doping of the formed PPV film are shown in Fig. 2. The charging–discharging of the PPV films has been studied earlier with different techniques [15–17]. The structure of the electrochemically synthesized film was found to consist of short phenylene vinylene oligomers [16]. In order to simplify the comparison of the cyclic voltammetric response of the copolymer and the C\(_{60}\) film the cyclic voltammogram showing the five first cycles between 0 and \(-1.3\ \text{V}\) of the reduction of a C\(_{60}\) film (drop cast from dichloromethane) are shown in Fig. 3. Even if the film is...
cycled at a scan rate of 100 mV/s it is highly soluble upon reduction in TEABF₄–DMF. Therefore the currents radically decrease with the number of scan. In the first cycle only one broad peak at −0.95 V is obtained, slightly shifted to a more negative potential relative to the peaks seen in the consecutive scans at −0.9 and −0.55 V. This is due to the fact that the pristine C₆₀ film is non-conducting after drop casting and the ion transfer through the film is slightly hindered during the first cycle thus causing a small overpotential in the system.

The copolymerization is performed at an electrode that is covered with a film of C₆₀. This polymerization is made in the same way as for PPV shown in Fig. 4. Again the first scan differs remarkably from the consecutive scans. The reduction currents observed are twice as high as for the reduction of the precursor, α,α′,α′′-tetrabromo-p-xylene, this is mainly due to the reduction of C₆₀ species. The broad reduction at −1.0 V is assigned to the reaction where the C₆₀ film is reduced to C₆₀⁻ⁿ (where n can be 1–3). The first step of the reduction of the α,α′,α′′-tetrabromo-p-xylene leading to the intermediate brominated quinodimethane and the second step involving formation of PPV oligomers containing C₆₀ cannot be clearly separated in the voltammogram.

Fig. 2. The second cycle showing (a) n-doping and (b) p-doping of a PPV film. Scan rate 50 mV/s in 0.1 M TEABF₄–DMF solution.

Fig. 3. Five first cycles of a C₆₀ film drop casted on Pt. Scan rate 100 mV/s in 0.1 M TEABF₄–DMF.

Fig. 4. Electrosynthesis of the copolymer. Insert shows the first 5 cycles made at 50 mV/s in a solution containing 0.05 M α,α′,α′′-tetrabromo-p-xylene in 0.1 M TEABF₄–DMF. The scan are made with a Pt electrode which is covered by C₆₀ film. The main figure is an enlargement of the cyclic voltammograms excluding the first scan. Numbers indicate the order of scans.
Instead a broad reduction wave covering the potential range 
$-1.3$ to $-2.3$ V is seen. During consecutive scans (enlarge-
mint in Fig. 4) two reduction peaks are developed at $-1.2$ and 
$-1.9$ V, which currents grow with every cycle. The first peak 
is interpreted to be from the reduced C$_{60}$ species and the peak 
at more negative potential to PPV oligomers. A very small 
oxidation peak is observed on the reverse scan at $-0.8$ V from 
the reoxidation of the C$_{60}$ species. The C$_{60}$ radicals posses 
a relatively high stability [18–20] and the propagation of these 
species can be considered slow. This might lead to a low con-
centration of covalently attached C$_{60}$ in the polymer chain. 
In chemical synthesis of fullerene–styrene copolymer it was 
suggested that a star-like structure were several polystyrene 
arms are attached to the core of fullerene cages was formed 
[20]. During the electrochemical synthesis it can also be ex-
pected that not only linear chains are build up due to possible 
polyaddition of C$_{60}$ with free radicals and nucleophiles. 
The charging–discharging of the copolymer film takes 
place within a very broad potential range. The redox response 
is dependent on the scan rate and on the potential range. If 
the potential scan is limited to a range where only reduced 
fullerenes are active, i.e. from 0 to $-1.3$ V a reduction and 
oxidation response is obtained at $-1.15$ and $-0.9$ V, respec-
tively. When the scan is extended to more negative potentials 
multiple redox peaks are visible. Redox couples are seen at 
$-1.15$ V/$-0.8$ V, $-1.4$ V/$-1.3$ V, and at $-1.9$ V/$-1.8$ V. The 
peak potentials are independent of the scan rate but the CV 
shape gets more undefined and the currents are not growing 
linearly with increasing scan rate. This indicates that the film 
is not dependent on the diffusion rate of the counter ions, 
instead the donor–acceptor capacity of the film is influenced 
by the rate of the scan. The electrochemical reductions of the 
PPV–C$_{60}$ film takes place at more negative potentials than the 
corresponding reductions of a pure C$_{60}$ film. This has been 
observed earlier also for chemically synthesized PPV–C$_{60}$ 
dyads [21]. The reason for this has been explained by the inter-
vention between the PPV units and C$_{60}$ in the ground 
state, i.e. the ability of PPV to donate electrons to C$_{60}$. Oth-
wise neither the electronic nor the optical properties of the 
fullerene should change dramatically after functionalization. 
The cyclic voltammograms of the copolymer in a narrow and 
in a wide potential range are shown in Fig. 5.

3.2. Spectral characterization

3.2.1. Raman spectroscopy

The electrosynthesized copolymer films were character-
ized by Raman spectroscopy by measuring directly from the 
dry film surface. The spectra recorded were compared 
with spectra of films of PPV and C$_{60}$. The Raman spectra 
obtained are shown in Fig. 6. The characteristic vibrations of 
PPV in neutral form recorded with $\lambda_{exc} = 780$ nm are at 
1623 cm$^{-1}$ from the stretching mode of the C=C bond of the 
vinyl group, 1582 and 1552 cm$^{-1}$ from ring stretching C=C 
respectively C=C. The peak at 1170 cm$^{-1}$ has been assigned 
to both C=C stretching and to C-H bending of the phenyl
copolymer spectrum and might consist of several overlapping peaks. These peaks can be from C_{60} or from phenyl ring stretching C=C from very short oligomer units at 1573 cm\(^{-1}\). This is due to a shift to higher wavenumbers of the peak from monomeric species, peak at 1552 cm\(^{-1}\). A shift of the ring stretching mode to higher wavenumbers with increasing chain length in PPV oligomers has been reported earlier [25]. Upon charging of the PPV film the three bands in the region 1550–1630 cm\(^{-1}\) partly fuse together. The copolymer might partly be still in its charged form after polymerization and the band behavior in the spectrum in the above-mentioned wavenumber region could be caused by the remaining charges in the film.

### 3.2.2. FTIR spectroscopy

The FTIR spectra taken from films which are grinded into KBr pellets are shown in Fig. 7. The infrared spectrum of C\(_{60}\) contains four intramolecular modes F\(_{1u}\) at 526, 576, 1182 and 1429 cm\(^{-1}\) [26]. The strongest peak of C\(_{60}\) is the F\(_{1u}\) (4) mode at 1429 cm\(^{-1}\), its position is known to be sensitive to the number of charges on the C\(_{60}\) molecule [27]. The shift of the F\(_{1u}\) (4) mode upon reduction has been reported to be proportional to the amount of added electrons and is dependent on the counter ion present during reduction [27]. In the region of the spectrum shown in Fig. 7 also a peak at 1539 cm\(^{-1}\) is present which has been reported for C\(_{60}\) in solid state [28].

In the spectrum of the copolymer the strong F\(_{1u}\) mode from C\(_{60}\) has disappeared and instead a peak at 1397 cm\(^{-1}\) is seen. This is taken as an evidence for that the C\(_{60}\) core has accepted at least one electron and undergoes then further reaction with the reduced PPV precursor. Additional peaks are seen at 1575 and 1360 cm\(^{-1}\) indicating that more highly charged C\(_{60}\) might be present in the film [27]. The band at 1459 cm\(^{-1}\) has been assigned to the photopolymerized structure of C\(_{60}\) [29,30]. Weak bands at 1517 and 1424 cm\(^{-1}\) are assigned to the C=C ring stretching in the phenylene rings [16]. At this point we have not been able to point out a specific band that could be assigned to the covalent bond between the C\(_{60}\) core and the reacted precursor. The overall changes in the spectra, however, indicate that a reaction has taken place between the fullerene and the precursor during the reduction process.

In order to further study the formed copolymer film in situ FTIR spectra were recorded during charging of the film. Similar measurements have been made on PPV films [16] and on C\(_{60}\) films [27]. When \(\pi\)-conjugated polymers are excited by doping or by photo generation characteristic infrared active vibrations, so called IRAV bands appear. These bands differ completely from the IR-bands of the neutral polymer. The IRAV bands rise due to symmetry breaking which leads to that Raman active vibrational modes becomes infrared active. The characteristics of these bands in the doping spectra are dependent on the effective conjugation of the polymer, the de-localization of the doping induced excitations of the polymer backbone. Additionally to the IRAV bands some information on the electronic structure in the film can be obtained, i.e. free carriers or intraband excitations.

The in situ FTIR spectra recorded during a potential scan of a copolymer film in negative direction at a scan rate of 5 mV/s are shown in Fig. 8a. Every spectrum contains the changes taking place in the film during a potential interval of 70 mV. A continuous increase in the intensity with increasing applied negative potential of the upwards extending peaks can be seen in the frequency region of the polymer molecular vibrations. Strong downwards extending peaks in the spectrum are from solvent and from the neutral polymer as a result of spectra treatment.

The spectra recorded in the potential range \(-2.2\) to \(-2.3\) V from a PPV film and from a copolymer film are shown in Fig. 8b and c. These spectra represent the highest level of negative charging of the two films obtained in the medium used. In the case of PPV the characteristic IRAV band have risen upon charging and are listed in Table 1. Creation of free carriers in the film can be seen as the broad absorbance band extending from 2000 cm\(^{-1}\) to higher wavenumbers. In the case of the copolymer no distinct absorbance maximum is formed in the mid-IR field during charging. This would indicate that the effective conjugation length in the copolymer

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<th>Infrared active vibrations (cm(^{-1}))</th>
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![Fig. 7. FTIR spectra from KBr pellets of a C\(_{60}\) film and of the electrosynthesized PPV–C\(_{60}\) copolymer.](image-url)
Fig. 8. (a) FTIR spectra recorded in situ during a potential scan in negative direction at a scan rate of 5 mV/s of a copolymer film in (0.1 M) TEABF₄–DMF solution. The inset shows the cyclic voltammogram of the film. The lines mark the starting point of recording a spectrum that contains the potential induced changes in the film during 70 mV. (b) Spectra recorded in the potential range −2.2 to −2.3 V of the copolymer film and of the PPV film. (c) Enlargement of the low wavenumber region in the spectra of (b).

film would be very short. In Fig. 8c the lower wavenumber region containing the IRAV bands is expanded. In the copolymer film bands are rising due to charging. Even if the main pattern of the bands is rather close to PPV the bands, however, are not as distinct as in PPV. The main bands are listed in Table 1 together with the bands from PPV. C₆₀ is a stronger acceptor of negative charges than the phenylene vinylene units. This may lead to that charges are localized mainly on the fullerenes part of the copolymer therefore reducing the changes related to the conjugated structure in the segments between the fullerenes. During charging in positive direction (p-doping) of the copolymer identical IRAV bands were obtained as when only a PPV film is charged.

3.2.3. Fluorescence spectroscopy

Steady state fluorescence emission spectra were recorded from both copolymer films and from PPV films electrochemically deposited on ITO glass. The excitation wavelength was 380 nm and the spectra were recorded in the range 400–700 nm. In Fig. 9 the emission spectra of PPV and of the copolymer films are shown. The PPV emission band is very broad with maximum at approximately 500 nm. The emission bands of the copolymer have the same shape as PPV but the
intensity of the band is roughly one tenth of the emission of the pure PPV. The excitation spectra were measured with the monitoring wavelength 510 nm. The obtained excitation spectra resembled PPV absorption spectra. The absorbance maximum of the PPV film is at 370 nm and the copolymer film has its absorbance maximum at 360–370 nm. A possible reason for the PPV fluorescence quenching to one tenth of its original in the copolymer film is photoinduced electron transfer from excited PPV to fullerene [21].

4. Conclusions

The electrochemical synthesis of a copolymer of phenylene vinylene units and C60 cages was studied in this work. From earlier reported radical-initiated polymerization reactions between styrene and C60 it was known that the propagation of the C60 radical is slow due to its high stability [20]. It was also reported that C60 can act as a radical inhibitor in the copolymerization reaction [6]. In the case where a film of C60 is electrochemically reduced the population of the C60 radical close to the electrode should be high enough to reduce the influence of pristine C60. Due to that the material formed is insoluble in most common solvents many characterization techniques are excluded and therefore also the average number of C60 cage per polymer chain cannot be estimated. Both Raman measurements as well as FTIR measurements however show that the obtained structure should be of copolymer character; obviously chains with short chain length are formed. Until now only steady state emission spectra are measured from the films and therefore we cannot tell anything about the lifetime of the charge separated state.

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References