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Reversible redox behaviour of two electroactive polymethacrylates

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Summary

The radical melt polymerization of 2-[4-(6-methacryloyloxyhexa-1,6-diyloxy)phenylazo]-anthraquinone is described yielding the homopolymer $\mathbf{p_m}$ with the number average molecular weight (M_n) of M_n=74kg/mol determined by gel permeation chromatography (GPC) using polystyrene (PS) calibration. The redox properties of a thin film of $\mathbf{p_m}$ were investigated by cyclic voltammetry. Two reversible redox waves were found at all applied sweep rates indicating two reversible electron (**E**) transfer processes of the anthraquinone units according the **EE**-mechanism. A thin film of the randomlike copolymethacrylate $\mathbf{cp_r}$ with the molar mass of M_n=73kg/mol was investigated, too. The sidegroups of $\mathbf{cp_r}$ are substituted by 77mol% with benzyl, by 22mol% with phenylazoanthraquinone and by 1mol% with COOH groups. The redox properties of $\mathbf{cp_r}$ depend on the timescale of the cyclovoltammetric experiment. At high sweep rates two reversible redox waves are observable corresponding to the **EE**-mechanism. At low sweep rates an additional reversible redox wave appears, which is essentially smaller than the other two. The third wave is explained to be a result of hydrogen bonding between the COOH groups and anthraquinone mono- and dianions. The most anthraquinone units are reduced according the **EE**-mechanism without hydrogen bonding due to statistical reasons. The reversible redox properties of $\mathbf{p_m}$ and $\mathbf{cp_r}$ are closely connected to their molar masses (M_n≈75kg/mol), because both polymers have been previously obtained by radical solution polymerization yielding low molecular products with molar masses of M_n≈10kg/mol. The low molecular polymers have shown an irreversible redox behaviour. Therefore, it could be demonstrated that the molar mass of an electroactive polymer significantly affects its redox properties.

Introduction

In 1989, a new model of a chemical transducer based on molecular architecture has been published by *Shimidzu* (1). He has shown that the dye 2-(4-methoxyphenylazo)anthraquinone (**1**) meets all requirements of a chemical transducer, which can be switched between four discrete states applying two different stimulation modes. Similar transducer properties have been reported for a dihydroazulene-anthraquinone (2) and a stilbene-anthraquinone system (3). Furthermore, the switchability of a blend of **1** in polyacrylonitrile has been confirmed (4). But, polymer blends are not suitable materials for the use as memory devices, because low molecular compounds can diffuse in polymers (5-9). Due to the migration of transducer molecules, the molecular structure of the blend changes. As a result, the photo- and electrochromic properties of the material change, too, and the written information is lost. To overcome the problems of guest-host systems, the polymethacrylate **p** with phenylazoanthraquinone sidegroups has been synthesized by radical solution polymerization of the corresponding monomer yielding the product $\mathbf{p_s}$ with the molar mass of M_n=12kg/mol (GPC, PS-calibration) (10). The redox properties of

CH_3-R

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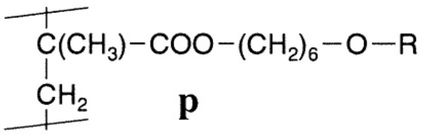
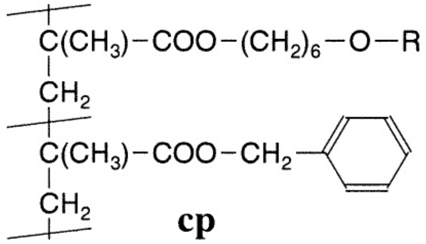
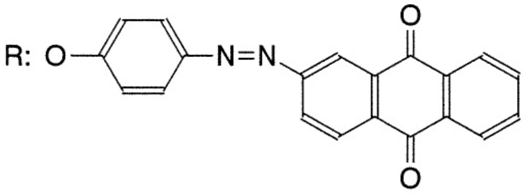


$$\begin{array}{l} C(CH_3)-COO-(CH_2)_6-O-R \\ | \\ CH_2 \end{array}$$

p



cp



p$_s$ have been investigated in CH_2Cl_2 by cyclic voltammetry. The voltammograms contain two reversible redox waves. They are typical for anthraquinone, which is reduced in aprotic solvents by two reversible electron (**E**) transfer processes according to the **EE**-mechanism in fig. 1 (11). In the electron transfer I, a quinone radicalanion is formed, which is reduced in the electron transfer II giving a quinone dianion.

The redox properties of thin films of **p**$_s$ are complex. Two different redoxmechanisms have been found depending on the timescale of the cyclovoltammetric experiment (12). Using high sweep rates, two reversible redox waves are observable according the **EE**-mechanism. At low sweep rates the second redox wave and the reoxidation peak of the first one disappear. This can be explained with an irreversible chemical (**C**) reaction following the electron (**E**) transfer I corresponding to the **EC**-mechanism in fig. 1. The product of the chemical reaction is unknown. One explanation for the kind of the reaction is the combination of neighboured quinone radicalanions, as it has been postulated by *Funt* for polyvinyl-*p*-benzoquinone, which shows the irreversible **EC**-mechanism (13). In contrast, a copolymer of 75mol% styrene and 25mol% vinyl-*p*-benzoquinone shows the reversible **EE**-mechanism. *Funt* draw the conclusion that the number of neighboured quinone radicalanions in the copolymer is too low for the appearance of the chemical reaction. The polymer **p**$_s$ is not a proper material for the application in a memory device due to the irreversible reaction occuring during the electrochemical switching. To overcome this, the dilution of the electroactive species has been approached to suppress the undesired reaction. Various copolymers containing the redoxactive group in low concentration have been synthesized (14-16). The copolymer **cp** containing phenylazoanthraquinone and benzyl sidegroups has been obtained by radical solution polymerization of the corresponding methacrylate monomers yielding the randomlike product **cp**$_s$ with a molar mass of M_n=9kg/mol (GPC, PS-calibration) (14). The content of the quinone sidegroup ($x_{quinone}$) is $x_{quinone}$= 5mol%. Thin

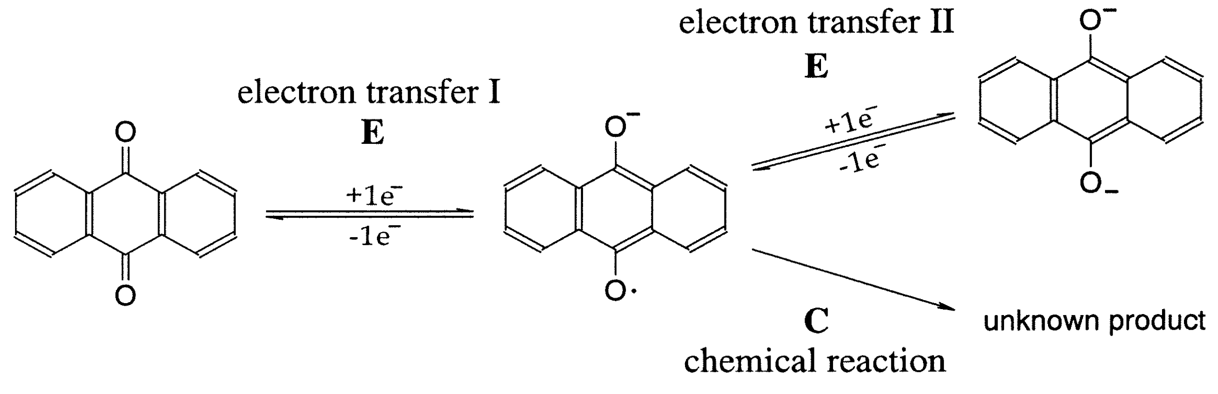


Figure 1: Redox scheme of anthraquinone with the **EE**- and **EC**-mechanism (11-12)

films of the copolymer $\mathbf{cp_s}$ show the same electrochemical behaviour, as it has been found for the homopolymer $\mathbf{p_s}$. At high sweep rates the reversible **EE**-mechanism and at low sweep rates the irreversible **EC**-mechanism have been observed (17). Thus, the suppression of the irreversible reaction has not been attained by the dilution of the redoxactive group. This result is astonishing reflecting the higher content of the redoxactive group in *Funt*'s copolymer ($x_{quinone}$=25mol%) than in $\mathbf{cp_s}$ ($x_{quinone}$=5mol%). The probability that quinone radicalanions are neighboured is essentially lower in $\mathbf{cp_s}$ than in *Funt*' s copolymer. Therefore, another reason than the dilution of the redoxactive species has to be responsible for the disappearance of the chemical reaction observed by *Funt*.

One important polymer feature is the molar mass. Many polymer properties like thermal, mechanical or electrical properties are known, which change as a function of the molar mass until a characteristic molar mass has been reached (18). Starting from this value the corresponding polymer property is independent of the molar mass. It can not be excluded a priori that the electrochemical behaviour of a redoxactive polymer coated on an electrode depends on the molar mass. The influence of the molar mass on the redoxmechanism has not been reported by *Funt*. To check the hypothesis of a correlation between the molar mass and the redoxmechanism of an redoxactive polymer, synthetical methods had to be found to obtain high molecular products for the homopolymer **p** and the copolymer **cp**.

The polymer-analogous esterification reaction of polymethacrylic acid with the corresponding alkylbromides in the presence of CsF has been successful to obtain the randomlike product $\mathbf{cp_r}$ with a molar mass of M_n=73kg/mol (GPC, PS-calibration) (14). The sidegroups of $\mathbf{cp_r}$ are substituted by 77mol% with benzyl, by 22mol% with phenylazoanthraquinone and by 1mol% with unconverted COOH groups. A high molecular product of the homopolymer **p** has not been available by this pathway (14). One method to obtain such material should be the radical melt polymerization of the corresponding monomer.

In this paper, the synthesis of the homopolymer **p** by radical melt polymerization of the corresponding methacrylate monomer yielding the product $\mathbf{p_m}$ is described. Furthermore, the redox properties of thin films of the homopolymer $\mathbf{p_m}$ and copolymer $\mathbf{cp_r}$ are outlined discussing the results of intensive cyclovoltammetric measurements.

Experimental Part

Materials

The synthesis of the monomer 2-[4-(6-methacryloyloxyhexa-1,6-diyloxy)phenylazo]anthraquirione is desribed in detail elsewhere (10). The initiator 2,5-bis(*tert*.-butylperoxy)-2,5-dimethylhexane was used as received from *Aldrich*. Propylenecarbonate and $N(C_4H_9)_4PF_6$ were received in the electrochemical grade quality from *Fluka* und used as received.

Polymerization

0.5g of 2-[4-(6-methacryloyloxyhexa-1,6-diyloxy)phenylazo]anthraquinone (1.0mmol) were heated in a glass tube, which has been flushed with N_2 before filling. After reaching 140°C, the monomer melt was degassed by passing N_2 for 30 minutes under stirring and keeping the temperature. 2.9mg of 2,5-bis(*tert*.-butylperoxy)-2,5-dimethylhexane (0.01mmol) were added to the melt. The polymerization mixture was stirred for 12 minutes at 140°C and afterwards cooled to room temperature. 20mL of $CHCl_3$ were given on the glassy solid to dissolve the reaction mixture, which was completed over night. The $CHCl_3$ solution was poured into 150mL of C_2H_5OH. The precipitated polymer $\mathbf{p_m}$ was filtered off, reprecipitated three times from $CHCl_3$ solution into C_2H_5OH and dried to constant weight at 40°C in vacuo. Yield: 0.15g (30%). IR (CH_2Cl_2): ν/cm^{-1} = 2945, 1724, 1676, 1593, 1501, 1474, 1326, 1146, 932, 841. ^{1}H-NMR ($CDCl_3$): δ = 0.7-2.0 (13H, m), 3.6-4.0 (4H, m), 6.6-6.9 (2H, m), 7.5-8.2 (9H, m). ^{13}C-NMR ($CDCl_3$): δ = 25.8, 26.0, 28.1, 29.1, 44.7, 44.8, 45.2, 64.8, 64.9, 65.0, 68.1, 114.5, 121.4, 125.5, 126.7, 127.0, 128.3, 133.2, 133.3, 133.8, 134.1, 146.4, 155.1, 162.3, 177.4, 177.5, 181.9, 182.1. UV/Vis ($CHCl_3$): $\varepsilon/10^3 cm^2 mol^{-1}$= $19 \cdot 10^3$ (388nm), $18 \cdot 10^3$ (341nm). Elemental analysis: $(C_{30}H_{28}N_2O5)_n$, calculated C72.56% H5.68% N5.64%, found C72.85% H5.64% N5.83%.

Cyclic voltammetry

Each polymer film was prepared by dropping 10µL of a 0.1wt% solution of the polymer in $CHCl_3$ on the cross-section plane of the glass-carbon working disc electrode with the diameters of 6mm for the total cross-section plane and of 3mm for the centered glass-carbon part. After evaporation of the solvent, the remaining polymer film was dried with hot air and the working electrode was ready to use. The film thickness was calculated to be 0.5µm using an estimated polymer density of 1.15g/cm^3 according to the polymer density of 1.1523g/cm^3 for a polymethacrylate, which is substituted in the sidegroup via the $(CH_2)_6$-spacer with a biphenylbenzoate mesogenic group (19). Cyclovoltammograms were recorded on a Bio Analytical System instrument. A three electrodes system was used consisting of the working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode. The solvent was propylenecarbonate containing 0.3mol/L $N(C_4H_9)_4PF_6$ as supporting electrolyte. The insolubility of the investigated polymers $\mathbf{p}_m$ and $\mathbf{cp}_r$ in the electrolytic system was verified. All experiments were carried out in N_2 atmosphere at room temperature. The sweep rate (v) was varied: v/Vs^{-1}=2, 0.6, 0.2, 0.08, 0.03. The formal potentials ($E^{0'}$) of the redox waves were obtained by averaging the cathodic (E_{pc}) and anodic peak potentials (E_{pa}). The separation of E_{pc} and E_{pa} was calculated (20): $\Delta E_p = E_{pa} - E_{pc}$. The reference electrode was calibrated by measuring the formal potential of the ferrocene (Fc) electrode: $E^{0'}(Fc/Fc^+)=+0.42V$. It was tested that the low molecular polymers $\mathbf{p}_s$ and $\mathbf{cp}_s$ showed the irreversible **EC**-mechanism using the described conditions.

Results and discussion

Polymer properties

The radical melt polymerization of 2-[4-(6-methacryloyloxyhexyloxy)phenylazo]anthraquinone was successful. The obtained polymer $\mathbf{p}_m$ was characterized by IR-, ^{1}H-NMR-, ^{13}C-NMR- and UV/Vis-spectroscopy. The spectroscopic data of $\mathbf{p}_m$ are in good agreement with $\mathbf{p}_s$ (10). The results of the GPC (PS-calibration) and differential scanning calorimetry (DSC) are given in table 1. The GPC-chromatogram of $\mathbf{p}_m$ shows monomodal distribution. Its molar mass (M_n=74kg/mol) is sixfold higher in relation to $\mathbf{p}_s$ (M_n=12kg/mol), which may be a result of branching during the melt polymerization. The degree of

Table 1: Properties of different samples of the homopolymer **p** and copolymer **cp**:

Polymer	Synthesis procedure	Reference	Yield / %	$x_{quinone}$ / mol%	M_n / kg·mol^{-1}	M_w / M_n	P_n	T_g / °C
$\mathbf{p}_m$	radical melt polym.	this work	30	100	74	2.4	149	89
$\mathbf{p}_s$	radical solution polym.	(10)	49	100	12	1.5	25	82
$\mathbf{cp}_r$	polymer reaction	(14)	64	22	73	2.4	290	69
$\mathbf{cp}_s$	radical solution polym.	(14)	59	5	9	2.1	45	71

branching could not be determined. Usually, branching is not significantly occuring for low monomer conversion degrees (18). Therefore, the low yield of $\mathbf{p}_m$ (30%) indicates not a high degree of branching. The glass transition temperature (T_g) of $\mathbf{p}_m$ (T_g=89°C) is 7°C higher in comparison to $\mathbf{p}_s$ (T_g=82°C), which can be explained with a molar mass effect. In addition to the glass transition, four peaks above the T_g are observable in the DSC-curves of $\mathbf{p}_m$. The peak temperatures are 115°C, 124°C, 154°C and 192°C. The four peaks can be explained with four liquid crystalline phase transitions in correlation to the liquid crystalline phase behaviour of $\mathbf{p}_s$ (17): g 82°C s_X 115°C s_B 125°C s_A 148°C n 186°C i.

Redox properties

The cyclic voltammograms of the high molecular polymers $\mathbf{p}_m$ and $\mathbf{cp}_r$ contain two reversible redox waves independently of the applied sweep rate (fig. 2). The variation of the sweep rate has only little effect on the formal potentials $E^{0'}$I and $E^{0'}$II determined for the waves I and II. The values for $\mathbf{p}_m$ are $E^{0'}$I=-0.80V, $E^{0'}$II=-1.15V and for $\mathbf{cp}_r$ $E_{0'}$I=-0.73V, $E^{0'}$II=-1.13V (table 2: v=0.2V/s). The curves of the homopolymer $\mathbf{p}_m$ show no peculiarities. But, two characteristics are noticable for the copolymer $\mathbf{cp}_r$. An additional peak III is observable at -0,93V for low sweep rates (v ≤0.08V/s) and the ratio of the reduction peaks I and II changes depending on the sweep rate. Using high sweep rates (v ≥0.6V/s), the peak II is higher than the peak I. At the lowest sweep rate (v=0.03V/s) this peak ratio is converted. Reduction peaks of similar magnitude are detectable with medium sweep rates (0.08V/s≤v≤0.2V/s). Thefore, a complex redoxmechanism is indicated for $\mathbf{cp}_r$.

The diagnostic parameter ΔE_p was determined for both polymers to distinguish between the adsorption and the diffusion redox mechanism and to investigate the reversibility of the electron transfer processes. A value of ΔE_p=0mV is expected for the adsorption mechanism, which is known for electrodes coated with thin redoxactice films with thicknesses of about 10nm. The shape of corresponding cyclovoltammograms is highly symmetrical and sharp. For thicker films an increase of ΔE_p and an altered shape of the curves are observable. The cyclovoltammograms look like those of solved redoxactive species, which are reversibly reduced by diffusion control. Both changes can be explained by the fact, that for relatively thick layers ΔE_p is governed by the rate of the electron transfer and by the rate of the diffusion of the electrolytic ions into the polymer film and out of it. The

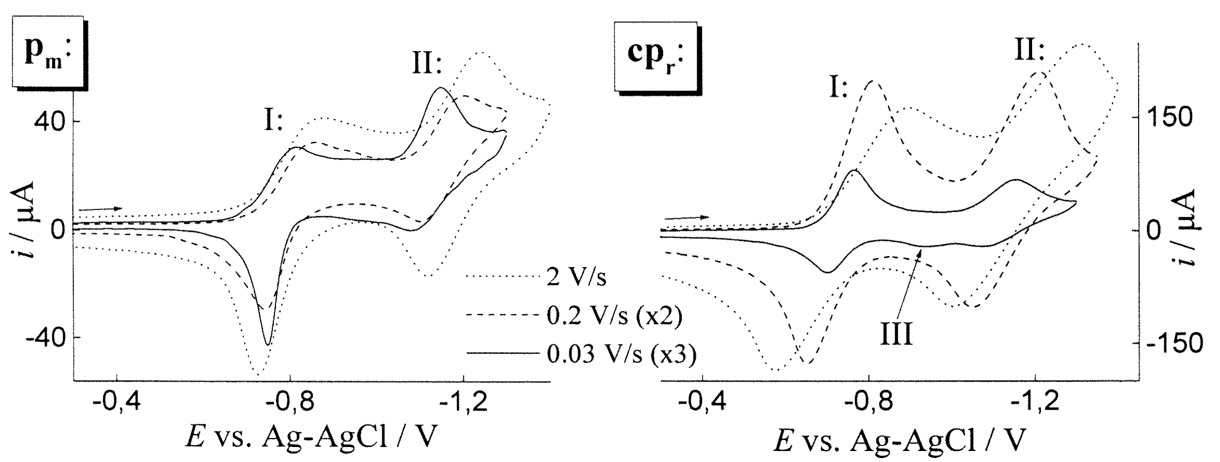


Figure 2: Cyclic voltammograms of thin films of $\mathbf{p}_m$ and $\mathbf{cp}_r$ scanning with the sweep rates of v=2V/s (dotted lines), v=0.2V/s (dashed lines, scaled up by the factor of 2) and v=0.03V/s (solid lines, scaled up by the factor of 3)

Table 2: Cyclovoltammetric data of the homopolymer $\mathbf{p_m}$ and copolymer $\mathbf{cp_r}$:

Polymer:	v / V·s^{-1}	$E^{0'}$I / V	$E^{0'}$II / V	ΔE_pI / mV	ΔE_pII / mV	i_{pc}I / µA	i_{pc}II / µA
$\mathbf{p_m}$	2.00	-0.80	-1.18	147	121	41.7	66.9
	0.60	-0.80	-1.16	114	88	24.4	36.4
	0.20	-0.80	-1.15	108	96	16.4	25.1
	0.08	-0.80	-1.14	92	86	12.7	22.0
	0.03	-0.78	-1.11	67	73	10.3	17.7
$\mathbf{cp_r}$	2.00	-0.74	-1.16	326	307	163.1	247.7
	0.60	-0.73	-1.15	259	251	156.5	190.8
	0.20	-0.73	-1.13	159	161	99.8	105.7
	0.08	-0.73	-1.12	98	102	55.4	51.7
	0.03	-0.73	-1.11	63	82	26.9	22.5

presence of the ions in the polymer film is necessary to maintain the electroneutrality during the redox cycling. The electrolytic ions act as counterions of the electrochemically formed ions in the polymer film. In the case of films with layer thicknesses of 1µm and more the value of ΔE_p =58mV for a reversible, diffusion controlled electron transfer of a solved species can be widely passed over (21). The ΔE_p -values of the polymers $\mathbf{p_m}$ and $\mathbf{cp_r}$ are in the range of 67-147mV for $\mathbf{p_m}$ and 63-326mV for $\mathbf{cp_r}$ (table 2). Due to the shapes of their curves and their ΔE_p -values the redox processes of the polymers are governed by diffusion control. This result is consistent with the polymer film thicknesses, which have been calculated to be 0.5µm. It can be stated that both redox processes of $\mathbf{p_m}$ are reversible, because its ΔE_p -values are smaller than 150mV even for the fastest sweep rate (v=2V/s). But, it can not be excluded that the redox processes of $\mathbf{cp_r}$ are only quasi-reversible, because its ΔE_p -values are greater than 150mV even for medium sweep rates (v ≥0.2V/s). This result for $\mathbf{cp_r}$ can be a solvent effect, becaus it is known that the electron transfer II of solved anthraquinone is only quasireversible in propylenecarbonate due to its value of ΔE_p>150mV using a low sweep rate (v=0.1mV/s) (22). Therefore, the larger ΔE_p-values of $\mathbf{cp_r}$ can be a result of a higher swelling degree of $\mathbf{cp_r}$ in propylenecarbonate compared with $\mathbf{p_m}$. This assumption is also indicated by the higher peak currents i_{pc}I and i_{pc}II of $\mathbf{cp_r}$ in relation to $\mathbf{p_m}$ (table 2), although the content of the redoxactice quinone group is essentially larger in $\mathbf{p_m}$ ($x_{quinone}$=100mol%) than in $\mathbf{cp_r}$ ($x_{quinone}$=22mol%).

A multi-sweep experiment was carried out at a newly made polymer film of $\mathbf{cp_r}$ to investigate the electrochemical behaviour of $\mathbf{cp_r}$ under steady state conditions using a low sweep rate (v=0.08V/s). 20 cycles were taken in series without a delay (fig. 3). The pattern of the curves change. With an increasing number of cycles the reduction waves I and II decline starting from cathodic peak currents of i_{pc}≈50µA until values of i_{pc}≈30µA are reached. Simultanously, an additional redox wave III with the formal potential of $E^{0'}$III=-0.97V grows up. With the 15th cycle, the pattern of the curves change not anymore. The cyclovoltammogram of the 20th cycle exhibits three reversible redox waves. The appearance of the wave III can be explained with the presence of COOH groups in $\mathbf{cp_r}$. Recently, an extensive investigation has been published on the reduction of quinones in aprotic electrolytic solvents in the presence of hydroxylic additives (23). Electrochemical effects have been found over the complete interaction range, from hydrogen bonding of reduced dianions to protonation of unreduced quinones. Three different types of electrochemical behaviour can be distinguished depending on the basicity of the quinone and the hydrogen bonding power or acidity of the hydroxylic agent. The

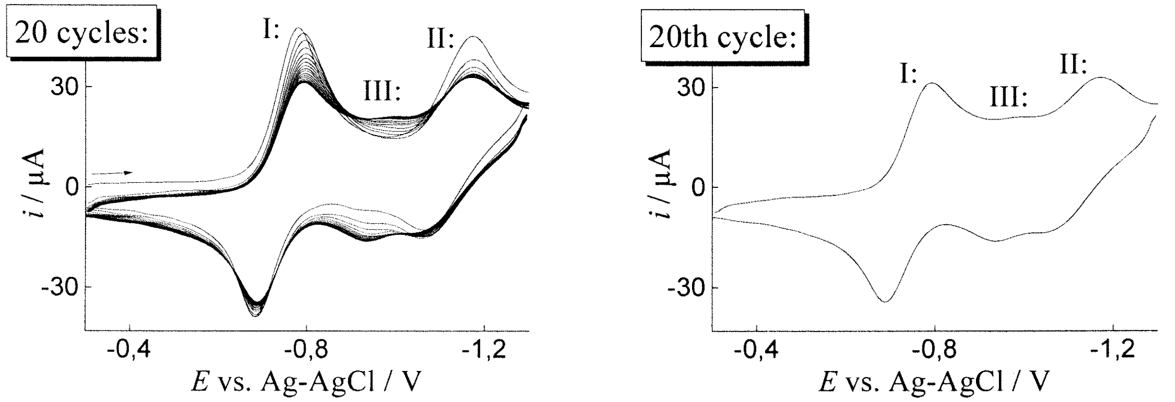


Figure 3: Multi-sweep experiment of a thin film of **cp$_r$** scanning 20 cycles in series without delay with the sweep rate of v=0.08V/s

investigated systems have been classified into weakly, moderately and strongly interacting quinone-additive pairs. For weakly interacting systems two seperated redox waves are observable. With increasing concentration of the hydroxylic agent the waves are shifted positively. Hereby, the second wave shifts more strongly. Finally, the second wave merges with the first. The positive shifts are caused by hydrogen bonding of the quinone mono- and dianion and not by protonation of the quinone. The copolymer **cp$_r$** can be classified as a weakly interacting system, because the basicity of phenylazoanthraquinone is low due to the strong electrons withdrawing effect of the conjugated phenylazo group. The COOH groups in **cp$_r$** are weak proton acids. Therefore, the wave III can be a result of hydrogen bonding between the COOH groups and the anthraquinone mono- and dianions formed during the redox cycling of **cp$_r$**. The redox wave III is essentially smaller than the redox waves I and II, because in **cp$_r$** the content of COOH groups (x_{COOH}=1mol%) is lower in relation to the content of anthraquinone groups ($x_{quinone}$=22mol%). Due to statistical reasons, only 4.5% of the anthraquinone mono- and dianions can undergo hydrogen bonding with the COOH groups.

Conclusion

It was possible to obtain the high molecular homopolymer **p$_m$** (M_n=74kg/mol) by radical melt polymerization of the corresponding methacrylate monomer. Thin films of **p$_m$** show reversible redox properties at all applied sweep rates during the cyclovoltammetric investigations according to the **EE**-mechanism. This electrochemical behaviour is remarkably different to the low molecular homopolymer **p$_s$** (M_n=12kg/mol) exhibiting the irreversible **EC**-mechanism. The electrochemical behaviour of the high molecular copolymer **cp$_r$** (M_n=73kg/mol) is complex due to the superposition of the **EE**-mechanism with a hydrogen bonding comprising redoxmechanism, which is caused by the presence of a small content of COOH groups in **cp$_r$**. But, **cp$_r$** shows not an irreversible redox behaviour as the low molecular copolymer **cp$_s$** (M_n=9kg/mol) exhibiting the **EC**-mechanism. It could be demonstrated in two cases that the molar mass of an redoxactive polymer significantly affects its redox properties. This can be explained by the different mobility of the polymer chains, which are swollen in the electrolytic solvent. For low molar masses, the chain mobility should be enlarged in relation to high molar masses due to the higher number of entanglements of the high molecular polymers, which act as physical cross links constraining the chain motion (24). Therefore, reactive species in the sidegroups have a higher reactivity for chemical reactions in the case of low molar masses. The possible reaction between quinone radicalanions can occur for the low molecular polymers $\mathbf{p}_s$ and $\mathbf{cp}_s$, but not for the high molecular polymers $\mathbf{p}_m$ and $\mathbf{cp}_r$.

Focus

The swelling properties of the low and high molecular polymers have to be investigated in the electrolytic solvent propylenecarbonate to check the hypothesis of the higher swelling degree of the polymers with low molar masses. Finally, the homopolymer $\mathbf{p}_m$ is a suitable material for further investigations verifying its electro- and photochromic properties due to its outstanding reversible redox behaviour and good film forming properties.

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References

1. Iyoda T, Saika T, Honda K, Shimidzu T (1989) Tetrahedron Lett 30:5429
2. Achatz J, Fischer C, Salbeck J, Daub J (1991) J Chem Soc Chem Commun :504
3. Newell AK, Utley JHP (1992) J Chem Soc Chem Commun :800
4. Saika T, Iyoda T, Honda K, Shimidzu T (1993) J Chem Soc Perkin Trans II : 1181
5. Knappe W (1954) Z Angew Phys 6:97
6. Moore RS, Ferry JD (1962) J Phys Chem 66:2699
7. Wong CP, Schrag JL, Ferry JD (1970) J Polym Sci Part A 8:991
8. Meerwall E, Antwerp RV (1982) Macromolecules 15:1115
9. Frisch HL, Stern SA (1983) Crit Revs Solid State Mat Sci 11: 123
10. Leitner MB, Ruhmann R, Springer J (1996) Macromol Chem Phys 197:237
11. Mann CK, Barnes KK (1979) Electrochemical Reactions in nonaqueous systems. Marcel Dekker, New York
12. Leitner MB, Ruhmann R, Springer J (1996) Polym Adv Technol 7:437
13. Funt BL, Hoang PM (1983) J Electroanal Chem 154:229
14. Leitner MB, Schinkel G, Springer J, Ruhmann R, Schulz G, Niesel FT (1997) React Funct Polymers 33:137
15. Leitner MB, Menner A, Schroeter M, Springer J (1998) Polym Adv Technol 9:624
16. Springer J, Leitner MB, Ruhmann R (1999) Polimery 44:13
17. Leitner MB (1997) Neue redoxaktive Polymethacrylate mit Phenylazoanthrachinonseitengruppen. Verlag Dr. Köster, Berlin
18. Elias HG (1990) Makromoleküle. Hüthig & Wepf, Basel Heidelberg New York
19. Wolff D (1994) Phasenstruktur von Azo-Gruppen enthaltenden flussigkristallinen Seitengruppen-Polymethacrylaten. Verlag Dr. Köster, Berlin
20. Bard AJ, Faulkner LR (1980) Electrochemical methods. John Wiley, New York
21. Merz A (1982) Nachr Chem Tech Lab 30:16
22. Sasaki K, Kashimura T, Ohura M, Ohsaki Y, Ohta N (1990) J Electrochem Soc 137:2437
23. Gupta N, Linschitz H (1997) J Am Chem Soc 119:6384
24. Strobl G (1996) The physics of polymers. Springer, Berlin Heidelberg NewYork