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Effect of Water on the Anionic Polymerization of α-Methyl-α-n-propyl-β-propiolactone

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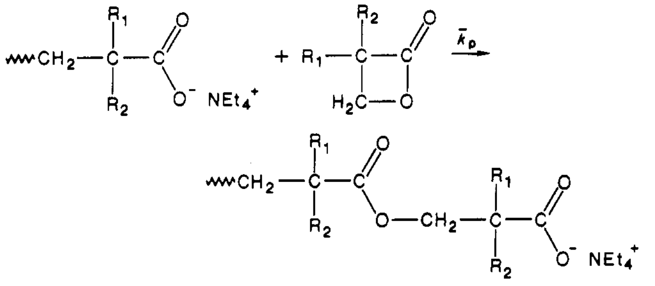
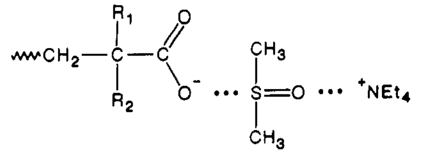
ABSTRACT: The effect of water on the anionic polymerization of α-methyl-α-n-propyl-β-propiolactone was studied by performing kinetic measurements in THF with different amounts of water, at 38.6 °C, with tetramethylammonium benzoate as the initiator. The data were treated by assuming that the propagation occurs through free ions, ion pairs, and the corresponding water-solvated species. Analysis of the results leads to the conclusion that the hydrated ion pairs do not contribute to propagation and that the free ions which are in small amounts are less reactive than the ion pairs. Thus the role of water introduced into the medium is to remove a large fraction of the ion pairs from the propagation reaction by hydration.

Introduction

The anionic polymerization reactions of α,α-disubstituted-β-propiolactones are known to be "living polymer" systems, and the kinetics and mechanisms of these polymerization reactions have been of interest to the authors for many years.[1-7] The basic reaction involved in propagation is an S_N2 attack by a carboxylate anion on the β-position of the lactone. The principal counterion of the initiators, which are generally used in our studies, has been the tetraethylammonium cation, as shown below:

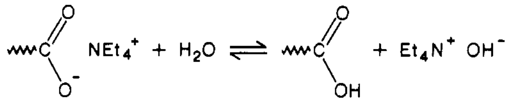


The global or average propagation rate constants, $\bar{k}_p$, have been determined in our previous investigations for a variety of ring substituents, R_1 and R_2, and for a range of solvents of varying polarity. Some unusual and unexpected substituent and solvent effects have been observed in these studies.[2,8] As an example of the latter, for several α,α-dialkyl-β-propiolactones, $\bar{k}_p$ was found to be higher in tetrahydrofuran, THF, than in dimethyl sulfoxide, DMSO, even though the latter is a much higher polarity solvent.[6,8] It was suggested in this case that the reduced reactivity in DMSO could be attributed to specific solvation of the carboxylate anion by this solvent with the formation of a less reactive solvated ion pair end group nucleophile, as represented schematically below:



In the present kinetic investigation our initial objective was to estimate the types and contributions of the ion pairs and/or free ion end groups which participate in the propagation reactions. For this purpose, we applied the kinetic treatment which has been successfully used to determine the rate and equilibrium constants in the anionic polymerization reactions of styrene and related monomers. With alkali-metal salts or organolithium initiators, styrene forms a "living polymer" system in THF.[9] From the global propagation rate constants obtained for these reactions in the absence and presence of an inactive salt with a common cation, at different concentrations of initiator ("living ends"), the rate constants for the free ions and ion pair end groups, and the dissociation constant for the equilibrium of these two end groups, can be readily calculated. However, the application of this kinetic analysis to our anionic polymerization and living polymer system gave meaningless results. We concluded that our reaction system was more complex and probably involved some additional reactive species and equilibria other than only free carboxylate anions and carboxylate tetraethylammonium ion pairs.

We suspected that trace amounts of water introduced into the system with either the solvent or the initiator, or both, may have played an important role in influencing the type and reactivities of the end groups, most likely through specific hydration of these end groups. The possibility that water could also neutralize and deactivate a significant proportion of the ions through the reaction



could be discarded because the equilibrium in such a system would be very strongly displaced to the left. That is, because ΔpK_a for salts of this type is around 5, even at a relatively high concentration of water the amount of neutralized carboxylic acid present would be less than 10^{-6} mol L^{-1}.

Therefore, to investigate in more detail the role of water and its effect on the state and reactivities of the end group nucleophiles, rate measurements were made on several series of polymerization reactions run at different initiator concentrations, to control the concentration of ion and ion pair end groups, in the presence of different amounts of added water.

Results and Discussion

The reaction system chosen for this study was the polymerization of α-methyl-α-n-propyl-β-propiolactone (R_1

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Table I
Molecular Weights and Molecular Weight Distributions Obtained from the Anionic Polymerization of α-Methyl-α-*n*-propyl-β-propiolactone[a]

$[H_2O]$,[b] mol L^{-1}	$\overline{M}_{n\,calcd}$[c]	$\overline{M}_{n\,exptl}$		$\overline{M}_w$[e]$/\overline{M}_n$
		osm[d]	GPC	
0.017	68 000	65 000	45 000	1.07
0.017	73 700	70 600	67 000	1.07
0.017	75 300	75 000	72 000	1.07
0.236	35 700	21 400	20 700	1.15
0.472	47 300	33 400	27 000	1.18

[a] In THF at 38.6 °C with tetraethylammonium benzoate as the initiator. [b] Concentration of water added to the system. [c] Calculated from the initial ratio of monomer to initiator and from the conversion of the monomer to polymer. [d] Osmometry in toluene at 37 °C. [e] Ratios of $\overline{M}_w$ to $\overline{M}_n$ were determined from the GPC diagrams in THF by using a polystyrene calibration curve.

$= CH_3$, $R_2 = CH_2CH_2CH_3$) in THF at 38.6 °C with tetraethylammonium benzoate as the initiator. Water was added to the reaction mixture to concentrations, $[H_2O]$, of 0.005, 0.047, 0.236, and 0.472 mol L^{-1}. The initial monomer concentration, $[M]_0$, was maintained at 0.270 mol L^{-1} in all experiments, but several different concentrations of initiator, [I], were used at each value of $[H_2O]$.

The polymerization reaction was shown to be a living polymer system, one without termination or chain transfer, by determining the molecular weights and molecular weight distributions of the polymer formed at different water and initiator concentrations. The data obtained are given in Table I, in which the calculated number-average molecular weight, $\overline{M}_n$, is based on the initial ratio of monomer to initiator and on the conversion of the monomer to polymer. The data show that there was good agreement between the calculated and observed values of $\overline{M}_n$, and reasonably narrow molecular weight distributions were obtained.

As indicated in the Introduction, the rate of the propagation can generally be represented by a single global, or average, rate constant, $\bar{k}_p$, and this constant presumably includes the contributions of both the free ion, $k_{(-)}$, and the ion pair $k_{(\pm)}$, end groups. For such a case, the rate expressions should be of the following simple form

$$-d[M]/dt = \bar{k}_p[M][I] \qquad (1)$$

in which $\bar{k}_p = \alpha k_{(-)} + (1 - \alpha)k_{(\pm)}$, and α is the fraction of free ion end groups. If so, the decrease in monomer concentration, [M], with reaction time, t, should be a linear function,

$$\ln [M]_0/[M] = \bar{k}_p[I]t = k_{exp}t \qquad (2)$$

where $k_{exp} = \bar{k}_p[I]$.

In the present case, however, $\bar{k}_p$ was found to increase with increasing initiator concentration, [I], at a given level of water concentration, $[H_2O]$, as shown by the data in Table II. A plot of these data in Figure 1 shows that $\bar{k}_p$ is a linear function of $[I]^{-1/2}$ at each value of $[H_2O]$. Apparently, therefore, the presence of small amounts of water plays a significant role in the mechanism of the propagation reaction, possibly again through hydration of the free ion, I, and ion pair, II, end groups, as represented schematically below

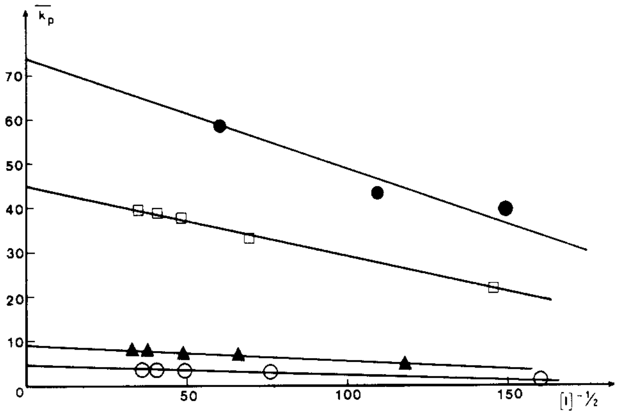
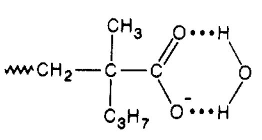
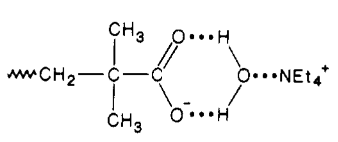


Figure 1. Dependence of $\bar{k}_p$ on $[I]^{-1/2}$ for different concentrations of H_2O in THF at 38.6 °C: (●) 0.005 mol L^{-1}; (□) 0.047 mol L^{-1}; (▲) 0.236 mol L^{-1}; (○) 0.472 mol^{-1} L^{-1} with $[\text{monomer}]_0 = 0.27$ mol L^{-1}.



I



II

where $^+NET_4$ is the tetraethylammonium counterion introduced into the reaction by the initiator.

This structure is supported by infrared studies of solutions of water with tetrabutylammonium halides in CCl_4. Depending on temperature and water concentration, 1:1 adducts or aggregates with OH···O bonded water molecules were detected.[10]

Indeed, the data in Table II show that for a given amount of initiator, $\bar{k}_p$ decreased considerably with increasing water concentration, but even at the highest concentration of water, the reaction was not severely inhibited.

As in the case of end group anion solvation by DMSO suggested above, it would be expected that the type of carboxylate ion hydration shown above for I and II would reduce the reactivity of the end groups. Thus it would be expected that four types of reactive end groups could participate in propagation, including both hydrated and nonhydrated free ions, P_n, and ion pairs, P_nNEt_4, each of which would propagate with its own rate constant.

$$P_n^-NEt_4^+ + M \xrightarrow{k_{(\pm)}} P_{n+1}^-NEt_4^+ \qquad (3)$$

$$P_n^- + M \xrightarrow{k_{(-)}} P_{n+1}^- \qquad (4)$$

$$P_n^-NEt_4^+{\cdot}W + M \xrightarrow{k_{(\pm)W}} P_{n+1}^-NEt_4^+{\cdot}W \qquad (5)$$

Table II
Global Rate Constants, $\bar{k}_p = k_{exp}[I]^{-1}$, Determined for Different Concentrations of Added Water, $[H_2O]$, at Different Initiator Concentrations, [I][a]

	$[H_2O]$[b]																		
	0.005			0.047					0.236						0.472				
$[I] \times 10^4$[b]	0.456	0.797	2.78	0.474	2.12	4.44	6.13	8.23	0.734	2.38	4.38	7.31	9.22	0.394	1.79	4.16	6.28	7.67
$[I]^{-1/2}$	148	112	60	145	68.6	47.4	40.4	34.9	117	64.8	47.8	37.0	32.9	159	75	49	39.9	36.1
$\bar{k}_p$[c]	40.1	42.9	58.7	22.0	33.2	38.0	39.0	39.7	5.00	6.82	7.06	7.98	7.92	0.83	2.92	3.12	3.23	3.36

[a] At an initial monomer concentration, $[M]_0$, of 0.27 ± 0.05 mol L^{-1} and a reaction temperature at 38.6 °C. [b] Concentrations in mol L^{-1}. [c] $\bar{k}_p$ in L mol^{-1} min^{-1}.

$$P_n^-{\cdot}W + M \xrightarrow{k_{(-)W}} P_n^-{\cdot}W \qquad (6)$$

In these equations W represent the presence of water of hydration which is intimately associated with the end group in some manner so as to decrease its reactivity, as illustrated in I and II. It would be expected, too, that for each type of end group, equilibria of the following types could exist:

$$P_n^-NEt_4^+ \overset{K_1}{\rightleftharpoons} P_n^- + NEt_4^+ \qquad (7)$$

$$P_n^-NEt_4^+ + H_2O \overset{K_2}{\rightleftharpoons} P_n^-NEt_4^+{\cdot}W \qquad (8)$$

$$P_n^- + H_2O \overset{K_3}{\rightleftharpoons} P_n^-{\cdot}W \qquad (9)$$

Hence, the global rate constant determined experimentally, k_{exp}, may include four component rate constants of reactions 3–6

$$k_{exp} = k_{(\pm)}[P^-NEt_4^+] + k_{(\pm)W}[P^-NEt_4^+{\cdot}W] + k_{(-)}[P^-] + k_{(-)W}[P^-{\cdot}W] \qquad (10)$$

and for the hydrated and nonhydrated free ions in equilibrium

$$[P^-] + [P^-{\cdot}W] = [NEt_4^+] = \alpha[I] \qquad (11)$$

If K_D is the dissociation constant of both types of ion pairs into both types of free ions

$$K_D = \frac{\alpha^2[I]}{1-\alpha} \qquad (12)$$

one finds

$$K_D = \frac{K_1(1 + K_3[H_2O])}{1 + K_2[H_2O]} \qquad (13)$$

Combining eq 10 and 13 gives an equation for $\bar{k}_p = k_{exp}[I]^{-1}$ which represents the possible contributions of the four different types of end groups and their equilibria

$$\bar{k}_p = \frac{1}{1 + K_2[H_2O]}k_{(\pm)} + k_{(\pm)W}K_2[H_2O] + \alpha\left(\frac{K_1}{K_D}k_{(-)} + \frac{K_1K_3}{K_D}k_{(-)W}[H_2O] - k_{(\pm)W}K_2[H_2O]\right) \qquad (14)$$

The form of eq 14 is $\bar{k}_p = A + \alpha B$, in which A and B are constants for fixed values of $[H_2O]$. If we assume that the fraction of free ions, α, is small in THF,[11] eq 12 can be simplified and rearranged into the form

$$\alpha \approx (K_D/[I])^{1/2} \qquad (15)$$

If so, then

$$\bar{k}_p = A + (K_D/[I])^{1/2}B \qquad (16)$$

Indeed, as discussed above, Figure 1 shows that $\bar{k}_p$ is a linear function of $[I]^{-1/2}$ at fixed values of $[H_2O]$. Moreover it must be pointed out that the negative slopes of these straight lines indicate that the free ions are less reactive than the ion pairs. Such a behavior has been shown in the case of the anionic polymerization of propylene sulfide[12] and of α-methyl-α-*n*-propyl-β-propiolactone,[7] in THF, with cryptates as the counterions.

The values of $\bar{k}_p$ extrapolated for $\alpha = 0$, k_p^{lim}, have been estimated for the four sets of experiments. According to eq 14

$$k_p^{lim} = \frac{1}{1 + K_2[H_2O]}(k_{(\pm)} + k_{(\pm)W}K_2[H_2O]) \qquad (17)$$

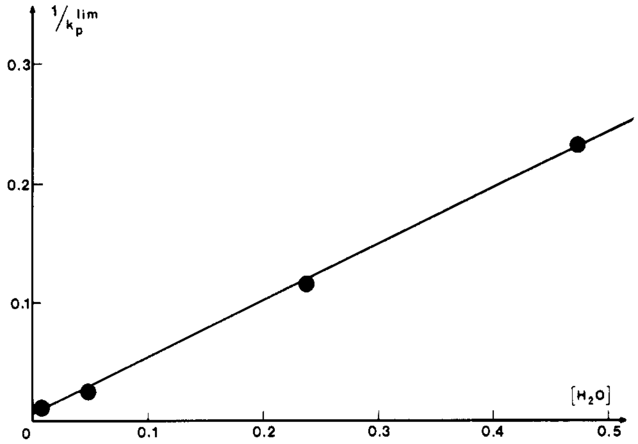


Figure 2. Dependence of $1/k_p^{lim}$ on concentration of $[H_2O]$ in THF at 38.6 °C.

Table III
Effect of Tetraethylammonium Tetraphenylborate, $Et_4N^+Ph_4B^-$, Added as an Unreactive Common Cation Source on the Rate of Propagation

$[H_2O]$, mol L^{-1}	[I] × 10^4, mol L^{-1}	$[Et_4N^+Ph_4B^-]$ × 10^4, mol L^{-1}	$\bar{k}_p$, L mol^{-1} min^{-1}
0.236	3.05 ± 0.01	0	7.10
		3.47	3.57
		3.62	2.94
0.005	0.92 ± 0.05	0	33.7
		1.96	18.8

It is also reasonable to assume, as a first approximation, that the reactivity of the hydrated ion pair end groups could be very much lower than that of the nonhydrated forms. Moreover, it we assume that the product $k_{(\pm)W}K_2[H_2O]$ is much smaller than $k_{(\pm)}$, eq 17 can be rearranged to the following form:

$$\frac{1}{k_p^{lim}} = \frac{1}{k_{(\pm)}} + \frac{K_2}{k_{(\pm)}}[H_2O] \qquad (18)$$

If this equation applies to the propagation reaction, a plot of $1/k_p^{lim}$ versus $[H_2O]$ should be linear. Such is the case shown in Figure 2, within the experimental error, thus verifying our assumptions. From the slope and the intercept of Figure 2, we obtain $K_2 \approx 50$ mol L^{-1} and $k_{(\pm)} \approx 100$ mol L^{-1} min^{-1}. However, the determination of these values is not very accurate.

Finally, some experiments have been performed in the presence of known amounts of tetraethylammonium tetraphenylborate, $Et_4N^+Ph_4B^-$. From the results shown in Table III, it can be seen that $\bar{k}_p$ decreases at constant water and initiator concentrations. This observation is in contradiction with the fact that ion pairs have been found to be more reactive than free ions. One can assume that the addition of $Et_4N^+Ph_4B^-$ leads probably to the formation of unreactive triple ions as already noticed in the case of the anionic polymerization of styrene in tetrahydropyran.[13]

Conclusion

The effect of water on the anionic polymerization of α-methyl-α-*n*-propyl-β-propiolactone has been studied by performing kinetic measurements in THF, with different amounts of water, at 38.6 °C, with tetraethylammonium benzoate as the initiator. It has been shown that the polymerization reaction has a living character and narrow moleular weight distributions have been obtained. The kinetic data have been treated by assuming that the propagation occurs through free ions, ion pairs, and the corresponding water-solvated species. Analysis of the data shows that the average rate constant $\bar{k}_p$ is a linear function of $[I]^{-1/2}$ at fixed values of $[H_2O]$, which means that the fraction of free ions is small in this system. The negative slopes observed on plotting $\bar{k}_p$ versus $[I]^{-1/2}$ indicate that free ions are less reactive than ion pairs. Moreover, the fit of the data to the equations derived on the basis of a negligible reactivity of the hydrated ion pairs shows that these species do not contribute to propagation. Thus the effect of water present in the reaction medium is to remove a large fraction of the ion pairs from the propagation reaction by hydration.

Preliminary studies by us on the Raman spectra of anhydrous and hydrated samples of tetraethylammonium benzoate in the solid state support these conclusions to the extent that two types of carboxylate ion pairs can be observed for the hydrated sample and only one for the anhydrous. On exposure of the latter sample to moist air, its spectrum develops a second peak. Further work in this field is in progress.

Experimental Section

The synthesis and purification of α-methyl-α-*n*-propyl-β-propiolactone were previously described. The initiator, tetraethylammonium benzoate, was obtained from Eastman Chemical Co. and recrystallized from a solution in THF containing 5% DMSO. The crystals were dried for 20 h under vacuum at 10^{-5} mmHg, at room temperature, and then sealed under vacuum. The tube was opened in a drybox. THF was of high-performance liquid chromatography grade. It was refluxed over KOH and then over $LiAlH_4$ and siphoned with a double-tipped needle into an apparatus for distillation containing $LiAlH_4$ and distilled in dry argon and collected in a storage bottle with a Teflon stopcock, ground glass joints, and two rubber septum stoppers.

Kinetics and Measurements. A standard solution of the tetraethylammonium benzoate initiator was prepared in a drybox in a volumetric flask stoppered with a rubber septum. The reactor was also stoppered with a rubber septum and kept under argon, and calculated quantities of the standard tetraethylammonium benzoate solution and THF were added with syringes. Monomer was added with a syringe with stirring while the reactor was maintained at a constant temperature. Samples were removed with a syringe and injected into a THF–methanol solution to terminate the polymerization. The clear solution so obtained was analyzed in an infrared spectrometer for monomer conversion as previously described.[2]

Registry No. H_2O, 7732-18-5; $Et_4N^+Ph_4B^-$, 12099-10-4; α-methyl-α-propyl-β-propiolactone, 16230-68-5; α-methyl-α-propyl-β-propiolactone (homopolymer), 25188-77-6; α-methyl-α-propyl-β-propiolactone (SRU), 25265-42-3.

References and Notes

(1) Cornibert, J.; Marchessault, R. H.; Allegrezza, A. F.; Lenz, R. W. *Macromolecules* **1973**, *6*, 676.
(2) Eisenbach, C. D.; Lenz, R. W. *Makromol. Chem.* **1976**, *177*, 2539.
(3) Bigdeli, E.; Lenz, R. W. *Macromolecules* **1978**, *11*, 493.
(4) Lenz, R. W.; D'Hondt, C. G.; Bigdeli, E. *ACS Symp. Ser.* **1977**, *No. 59*, 210.
(5) Spassky, N.; Leborgne, A.; Reix, M.; Prud'homme, R. E.; Bigdeli, E.; Lenz, R. W. *Macromolecules* **1978**, *11*, 716.
(6) Lenz, R. W. *Pure Appl. Chem.* **1981**, *53*, 1729.
(7) Haggiage, J.; Hêmery, P.; Boileau, S.; Lenz, R. W. *Polymer* **1983**, *24*, 578.
(8) Minter, E. M. Ph. D. Thesis, University of Massachusetts, 1983.
(9) Szwarc, M. *Carbanions Living Polymers and Electron Transfer Processes*; Interscience: New York, 1968; p 405.
(10) Wolff, M.; Hagedorn, W.; Mathias, D.; Rethel, R.; Millerman, E.; Leidner, L. *J. Phys. Chem.* **1978**, *82*, 2404.
(11) K_D is smaller than the value for potassium β-naphthoate compexed by [222] ($K_D = 10^{-6}$ in THF at 20 °C; see ref 7) due to the smaller size of the tetraethylammonium counterion compared to that of the cryptate K^+ + [222]. Thus the highest value of α is lower than 13% in the experiments.
(12) Sigwalt, P.; Boileau, S. *J. Polym. Sci., Polym. Symp.* **1978**, *52*, 51.
(13) Van Beylen, M.; Fisher, M.; Smid, J.; Szwarc, M. *Macromolecules* **1969**, *2*, 575.

Preparation of Thin Polymeric Films on Electrode Surfaces by Electropolymerization of *o*-Aminophenol

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ABSTRACT: Polymerization of *o*-aminophenol in acidic aqueous solutions was achieved electrochemically at basal-plane pyrolytic graphite and In–Sn oxide conducting glass electrodes by application of anodic potentials. The polymer poly(*o*-aminophenol) (PAP), which was prepared as a thin (0.2–0.5 μm) coating film on electrode surfaces, was electroactive in aqueous solutions and protic nonaqueous solutions and was semiconducting (conductivity 4.0×10^{-7} S cm^{-1} at 298 K). The characterization of the PAP film by IR spectroscopy, electrochemical and electrical methods, thermal gravimetric analysis, etc. suggested that the PAP is a ladder polymer with phenoxazine rings as electroactive sites.

Introduction

For the last several years electropolymerization of various aromatic compounds has been developed in our laboratory with the goal of obtaining thin polymer films and polymer film-modified electrodes for specific applications, such as electron-transfer catalyst (or mediator), sensors, and electrochromic materials and new conducting (or semiconducting or insulating) polymers.[1-22] This technique has been extensively applied to a great number of organic monomers by many investigators. In the case of the electropolymerization,[23] the polymerization reaction occurs at and/or in the vicinity of electrode surface and in some cases the resulting, insoluble polymers deposit on electrode surfaces as thin (typically ca. 100 Å–10^{-3} cm) organic layers, and consequently "polymer-coated electrodes" can be obtained in situ.

Recently, we[13] have reported the in situ preparation of the electrodes coated with conducting, electroactive, thin, ladder poly(*o*-phenylenediamine) (abbreviated as PPD (I)) films with phenazine rings by electropolymerization of the

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