Poly(methacrylic acid)-Bound Dihydroxybenzene Units: Redox Polymers

Saād Moulay, Razika Mehdaoui

Laboratoire de Chimie-Physique Moléculaire et Macromoléculaire, Faculté des Sciences de l'Ingénieur, Département de Chimie Industrielle, Université de Blida, Route de Soumāa, B. P. 270, Blida 09000, Algeria

ABSTRACT: Poly(methacrylic acid) (PMAA) was functionalized with a hydroquinone/catechol under the reaction conditions of Minisci. Optimum conditions for maximum functionalization (52%) were found to be as follows: [benzoquinone]/[PMAA] ratio, 0.75; reaction time, 3 h; temperature, 75°C; and a nitrogen atmosphere. Redox properties of hydroquinone/catechol-modified PMAA (PMAA-HQ) were evaluated by their midpotentials potentiometrically estimated to be 898 mV at 20°C. At 35°C, a two-stage oxidation was observed with a midpotential of 1000 mV. These midpotentials were found to be higher than those of hydroquinone, catechol, and a 1 : 1 hydroquinone-catechol mixture, under the same conditions of potentiometric titration. Under the modification reaction conditions, the modified PMAA underwent severe degradation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 954–961, 2006

Key words: modification; functionalization of polymers; redox polymers; PMAA; benzoquinone

INTRODUCTION

Acrylic polymers and their derivatives have gained special interest in laboratory and industry levels. Because of their intrinsic properties, they have been used in many applications. In fact, crosslinked polyacrylates are valuable items in the following: diapers, feminine hygiene products, hospital products, and condensation preventing agents.[1] Poly(acrylic acid) and its analogues stand by now as featuring polymers because of the existing carboxyl functionality through which the polymers can be easily modified. Indeed, they were considered polyligands in making heavy metal complexes.[2] These complexes were tested as ultrafiltration membranes for the removal of radionuclides.[3] Moreover, for water treatment study, poly(acrylic acid) was often used as a model for the complexation of humic acids[4] and as flocculant and sludge thickener.[5] Göbel et al. grafted *N*-dodecyl acrylamide groups onto poly(acrylic acid) matrix, affording hydrophobically modified polymer, which was subjected to adsorption study.[6]

However, the major drawback of the poly(acrylic acid) and poly(methacrylic acid) (PMAA) is their facile degradation by the anhydride formation, starting at a temperature of 150°C, and the decarboxylation is significant beyond 250°C.[7]

Polymers with redox properties have been the concern of many researchers since 1949.[8] They are known by the terms "oxidation–reduction polymers" and "electron-transfer polymers." These polymers are high-molecular-weight substances that can transfer electrons in contact with reactive ions or molecules. They are usually loaded with functional groups of the redox-type either as pendant groups from polymer matrix or being part of the polymer chain. Of the chemically incorporated redox moieties onto polymeric matrices are ferrocene, pyridinium, mercaptyl, hydroquinone, catechol, and their dialkoxylated precursors. Efficiently protected hydroquinone or catechol-containing monomers are polymerizable by conventional techniques and yield resins with redox properties.[9] New polymerization methods, such as atomic transfer radical polymerization and stable free radical polymerization, have emerged and have been applied for the preparation of controlled molecular weight polymers.[10–13] Redox properties can be estimated by either cyclic voltammetry[14] or potentiometric titration.[15,16] Wand et al. prepared polyhydroquinone with a molecular weight ranging between 1600 and 3200, and estimated its redox ability by cyclic voltammetry.[17] Yamamoto and Kimura synthesized poly(hydroquinone) with an intrinsic viscosity of 0.13 dL g^{-1} by polycondensation of 1,4-dibromo-2,5-diacetoxybenzene in the presence of a nickel complex, followed by removal of acetoxyl group with lithium aluminum hydride.[18] Chow et al. applied the ring opening metathesis polymerization to the hydroquinone- and catechol-fused norbornadiene derivatives.[19]

Besides the oxidation–reduction capabilities, other important properties of the redox polymers with dihyroxybenzene moieties were reported.[9] There are various applications of redox polymers, including antioxidants, electrical conductors, electrode coatings for sensors, and corrosion inhibitors.[9]

In the present article, we wish to report results on the chemical modification of PMAA by hydroquinone/catechol moieties to afford redox polymers (PMAA-HQ), using the conditions of Minisci,[20] that is, a homolytic modification by an oxidative decarboxylation. The midpotentials, E_m, of the modified PMAA at 20°C and 35°C were experimentally determined. We recently reported the results of the modification of poly(acrylic acid) by hydroquinone/catechol.[21]

EXPERIMENTAL

Materials

The chemicals were purchased from the following companies: Fluka AG (Buchs, Switzerland), Merck (France), Aldrich (France), and Prolabo (France). Methacrylic acid was purified by vacuum distillation. All the liquid reagents thus purified were characterized by their refractive indexes with Carl Zeiss Jena refractometer. Azobisisobutyronitrile and potassium persulfate were recrystallized from methanol and water, respectively.

Viscometric measurements

The viscometric measurements were performed in aqueous solution of hydrochloric acid ($2 \times 10^{-3}M$) at 30°C, using Cannon Ubbelohde capillary viscometer 532 10/I, Schott-Gerate CT 1650. The average molecular weights M_v were estimated by the relation of Mark–Houwink–Sakurada, $[\eta] = KM_v^a$, where $[\eta]$ is the intrinsic viscosity and K and a are the Mark–Houwink constants; the latter ones were taken as 6.6×10^{-4} dL g^{-1} and 0.5, respectively, for these conditions.[22] $[\eta]$ was deduced from the plot of $\eta_{red} = f(C)$ of the viscosity equation $\eta_{red} = [\eta] + K_H[\eta]^2C$ where η_{red} is the reduced viscosity, K_H is the Huggins constant, C is the concentration of the polymer solution in g dL^{-1}, and t and t_0 are the efflux times of the polymer solution and the solvent, respectively.

Spectroscopic analyses

UV–vis spectra were recorded using a UV–vis spectrophotometer Shimadzu 120; bidistilled water was employed for UV analyses. Infrared spectra were taken with a Genesis II FT-IR. The polymer samples for infrared analysis were in the form of cast films.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermograms were recorded on Setaram Labsys DSC 16 at a rate of 5°C min^{-1} under nitrogen atmosphere.

Potentiometric titrations

Potentiometric titrations were conducted under nitrogen atmosphere, using a platinum working electrode and a calomel reference electrode coupled to a pH-meter/millivoltmeter Peak Tech 6150 DM. The potential was calculated as $E = E_r + E_c$, where E_r is the reading potential against the calomel reference and E_c is the potential of the calomel against the hydrogen electrode; E_c was taken as 248 and 238 mV for 20°C and 35°C, respectively.[23]

Synthesis of PMAA

PMAA was synthesized via a radical polymerization in methanolic solution of methacrylic acid, using AIBN as a radical initiator under nitrogen atmosphere. The polymerization reaction was carried out at 60°C for 2 h. PMAA was precipitated from the methanolic solution into toluene as a nonsolvent. The polymer was purified by dissolution/precipitation cycle. The polymer was afterwards washed twice with toluene and dried at 45°C in vacuo for 2 days.

Chemical modification of PMAA

In a 500-mL round-bottomed flask equipped with a condenser, 1 g of PMAA was dissolved in 50 mL, followed by addition of 50 mL of an ethanolic solution containing 1.5 g of a 1 : 1 mixture of *o*- and *p*-benzoquinone. To this homogenous mixture, 0.079 g of silver nitrate was added, followed by addition of 150 mL of distilled water. The system was heated to 75°C under magnetic stirring. Once this temperature was reached, a saturated solution of potassium persulfate (3.76 g) was added dropwise within 90 min. The reaction was then stopped, and the flask content was allowed to cool down to room temperature. The modified PMAA was isolated by the following sequential steps: (1) evaporation of ethanol followed by addition of 50 mL of distilled water; (2) the mixture was allowed to stand for 1 day to assure the precipitation of the unreacted benzoquinone which was filtered; (3) the modified PMAA was obtained by casting from the solution within 4 days. The cast film was then dried in vacuo at 45°C for 4 days.

The degree of substitution S (%) was provided by the following eq. (1):

$$S(\%) = \frac{n_{VHQ}}{n_{MAA} + n_{VHQ}} \tag{1}$$
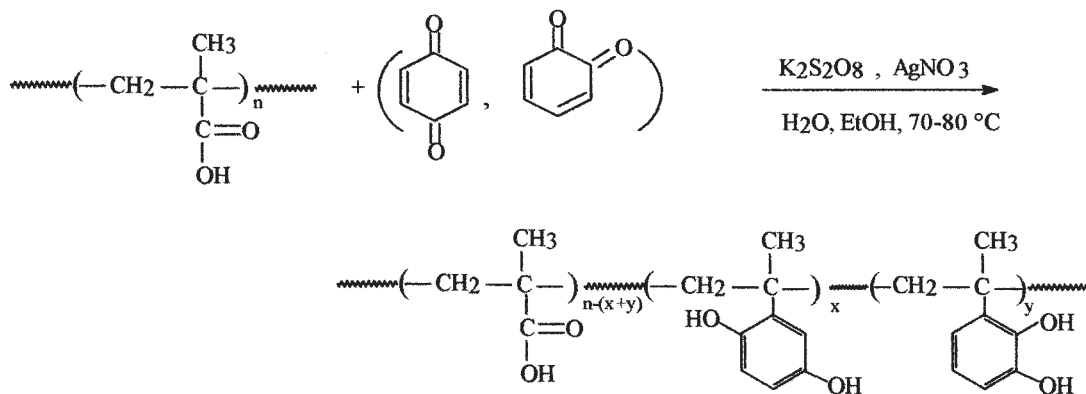
Scheme 1

$$n_{MAA} = \frac{m - n_{HQ}M_{VHQ}}{M_{MAA}} \quad (2)$$

where n_{VHQ} is the number of moles of hydroquinone and catechol (in the form of vinylhydroquinone and vinylcatechol) present in PMAA-HQ, estimated from the UV calibration curve; n_{MAA} is the number of moles of methacrylic acid present in PMAA-HQ, provided by eq. (2); m is the sample weight of PMAA-HQ used in the UV measurement; M_{MAA} and M_{VHQ} are the molecular weights of methacrylic acid and vinylhydroquinone (or vinylcatechol), respectively.

Potentiometric titration

About 0.03 g of PMAA-HQ of optimal degree of substitution (52%) was dissolved in 80 mL of glacial acetic acid (90%) in a thermostated electrolytic cell fitted with a magnetic stirrer and the two electrodes (the platinum working and the calomel reference ones). Prior to the titration, the solution was bubbled with a stream of nitrogen for 30 min to flush the dissolved

oxygen. The potentiometric titration was performed with $0.05M$ ceric ammonium nitrate (CAN) in acetic acid (90%) at a constant temperature and under nitrogen atmosphere. Readings of the potential were recorded in millivolts. A color change was observed throughout the titration.

RESULTS AND DISCUSSION

Modification of PMAA

PMAA was made by radical polymerization, using AIBN as the radical initiator and methanol as the reaction solvent. Under the polymerization conditions, the average molecular weight of PMAA was found to be 51600 ($[\eta] = 0.15$ dL g^{-1}). It is interesting to notice that the molecular weight of PAA obtained under identical conditions was found 5.5-fold that of PMAA, suggesting the methyl effect in the latter polymer.[21]

The oxidative decarboxylation conditions of Minisci[20] were applied to the chemical modification of PMAA by benzoquinone (a 1 : 1 mixture of o- and p-benzoquinone). The overall reaction is depicted in Scheme 1.
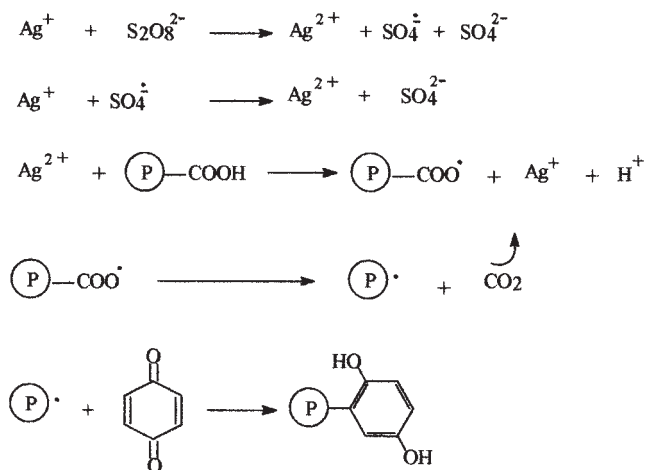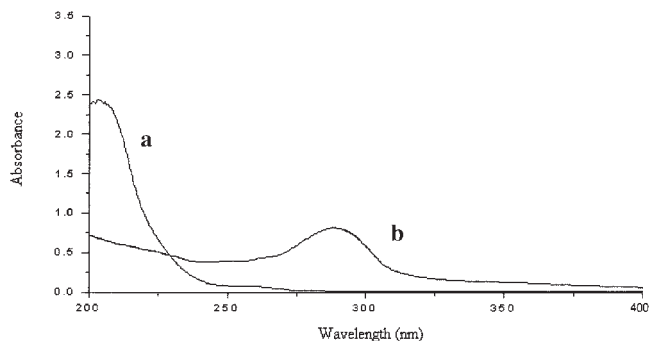

Scheme 2

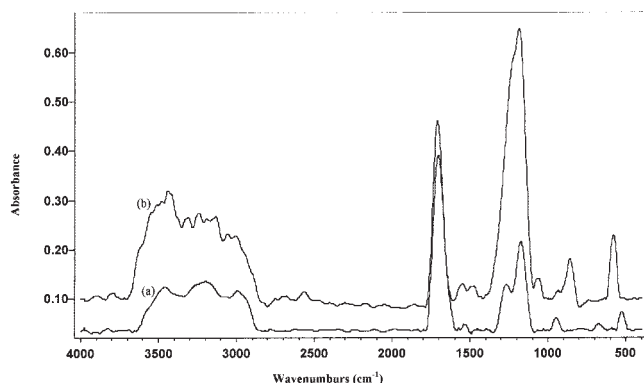**Figure 1** UV–vis spectra of PMAA (a) and PMAA-HQ (b) in distilled water.

Figure 2 Infrared spectra of PMAA (a) and PMAA-HQ (b).

As observed with the modified PAA,[21] the modified PMAA remained soluble in water and methanol and showed a strong resistance to air oxidation; polyvinylcatechols were reported to be sensitive to air, giving colored materials with defying solubility.[8,9] Indeed, while poly(3-vinylcatechol) could stand to air oxidation for a limited period of time and remained soluble, poly(4-vinylcatechol) was prone to oxidation upon exposure to air and became pink and insoluble. The solidity to air oxidation of PMAA-HQ can be ascribed to the lower degree of substitution and to the sparse distribution of hydroquinone/catechol groups over the polymer matrix. In addition, the film of the modified PMAA was mostly transparent with lightly dark regions.

The mechanistic pathway for the modification is likely the one shown in Scheme 2. The system $K_2S_2O_8/AgNO_3$ induces the oxidative decarboxylation, affording a polymeric radical. The latter radical behaving as a nucleophilic alkyl (an electron-rich site) readily reacts with benzoquinone, considered an electron-deficient species. Minisci advanced such a mechanistic explanation in the homolytic alkylation of pyridine and its derivatives.[24,25] Nucleophilic alkyl radicals were reported to preferentially attack the carbon atom of the benzoquinone.[25] In the absence of benzoquinone, an insoluble product immediately precipitated from the reaction medium, sug-

gesting a substantial crosslinking; benzoquinone is a well-known radical scavenger.[26]

PMAA-HQ was analyzed by UV–vis and infrared spectroscopy, and both analyses strongly indicated a successful substitution. Indeed, the UV–vis spectrum illustrated in Figure 1 shows a well-resolved band at λ_{max} = 288 nm attributable to hydroquinone or catechol entity. The infrared analysis (Fig. 2) revealed new bands for the modified PMAA (PMAA-HQ), compared to the spectrum of PMAA. The intensity of the O—H stretching band centered at 3500 cm^{-1} was enhanced due to the incorporation of dihydroxybenzene; two hydroxyl groups of the latter replaced one hydroxyl group of the carboxylic acid. A shoulder-looking band that appeared at 1360 cm^{-1} is assigned to O—H deformation vibration mode of the dihydroxybenzene. The bands which appeared at 1498 and 1595 cm^{-1} corresponded to C=C stretching. Also, the intensity of the bands between 1120 and 1380 cm^{-1} was enhanced.

The average molecular weight of PMAA-HQ was found to be 6200 ([η] = 0.052 dL g^{-1}), suggesting the occurrence of a severe degradation during the modification reaction; this molecular weight was about an eighth of that of the starting PMAA. This molecular weight lowering remains unexplained; the radical chain scission stemming from the decarboxylation process would not account for, as the benzoquinone would scavenge every possible radical formed by this kind of scission. As can be seen in Table I, similar degradation phenomenon with almost the same magnitude was observed with PAA under identical reaction conditions.[21]

The degree of substitution of carboxylic groups by hydroquinone (and catechol) was estimated by UV absorbances of the modified PMAA by means of a calibration curve; the latter was established by measuring absorbances of dilute hydroquinone solutions at λ = 288 nm.

A degree of substitution of 13% was obtained under the following conditions: reaction temperature of 75°C, reaction time of 90 min, and an equimolar ratio [benzoquinone]/[PMAA]. This low substitution may be due to the competitive degradation.

TABLE I
Comparative Results of the Modified PMAA-HQ and PAA-HQ[a]

Polymer	S (%)	t_{opt} (h)	R_{opt}	M	T_g (°C)	E_m (mV) 20°C	E_m (mV) 35°C
PMAA-HQ	52 (13[b])	3	0.75	6200[c]	70	898	971;1267
PAA-HQ[d]	30 (9[b])	6	1	38900[c]	96	863	911;1109

t_{opt}, optimal time; R_{opt}, optimal molar ratio[benzoquinone][polymer]; M, molecular weight.
[a] Temperature, 75°C; nitrogen atmosphere.
[b] Under aerobic conditions.
[c] The initial molecular weights were 51600 and 277000 for PMAA and PAA, respectively.
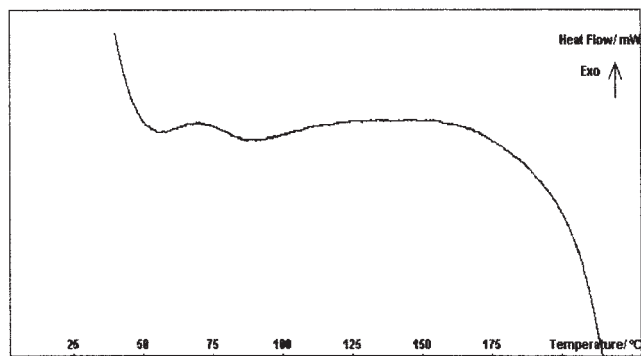[d] Results from Ref. 21.

Figure 3 DSC of PMAA at a rate 5°C min^{-1}, under nitrogen atmosphere.

Thermal behavior of PMAA-HQ was ascertained by DSC and compared to that of the unmodified PMAA. Figures 3 and 4 illustrate the DSC thermograms of both PMAA and PMAA-HQ, respectively. One transition occurred for PMAA at a temperature of 81°C, which was taken as the T_g of the polymer. However, for PMAA-HQ, two distinct transitions took place: the first transition appeared as a shoulder at 70°C, which can be imputed to the T_g of the polymer, and the second one is markedly shown at 195°C as a well-resolved endothermic peak, which corresponds to the melting point T_m of the polymer. The lower T_g measured for PMAA-HQ can be due to the relatively low molecular weight obtained. In fact, it is well known that the T_g is related to the molecular weight, by the famous Fox–Flory relation,[27,28] eq. (3):

$$T_g = T_g(\infty) - K'/M \qquad (3)$$

where T_g is the glass-transition temperature of the polymer of definite molecular weight M, $T_g(\infty)$ is the limiting high-molecular-weight value of T_g, and K' is a constant.

The application of this relation using $T_g(\infty) = 81°C$, $T_g = 70°C$, and M = 6200 gives a value of 7×10^5 for K', which is in a good agreement with the literature.[29]
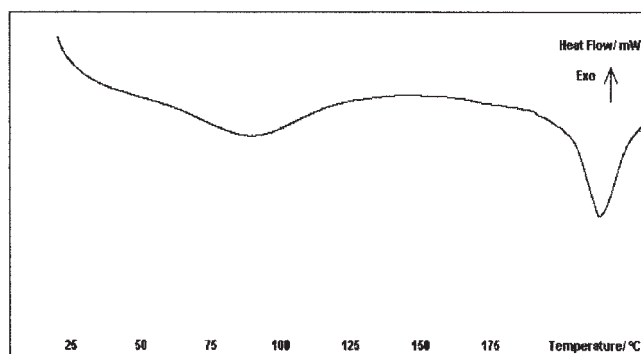

Figure 4 DSC of PMAA-HQ at a rate 5°C min^{-1}, under nitrogen atmosphere.

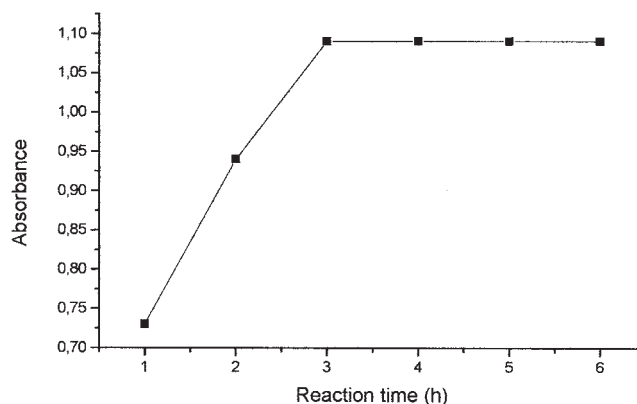**Figure 5** Plot of the variation of the absorbance of PMAA-HQ at $\lambda_{max} = 288$ nm in distilled water against the reaction time under the following conditions: [benzoquinone]/[PMAA] = 1; temperature = 75°C.

On the other hand, the observed endothermic peak may strongly suggest the formation of crystalline regions during the degradation. It is therefore featuring to note that a decrease in molecular weight facilitated the crystallization phenomenon of the polymer.

Effect of reaction time and benzoquinone concentration

By using a 1 : 1 [benzoquinone]/[PMAA] ratio and working at a temperature of 75°C and under ambient atmosphere, the absorbance, which reveals the extent of substitution, was found to increase with time and leveled off beyond 3 h (Fig. 5).

Figure 6 illustrates the variation of the degree of substitution with the benzoquinone concentration (taken as the molar ratio [benzoquinone]/[PMAA], [PMAA] was constant at 1 mol under optimal time (3 h) and temperature of 75°C and under ambient atmosphere). The max-
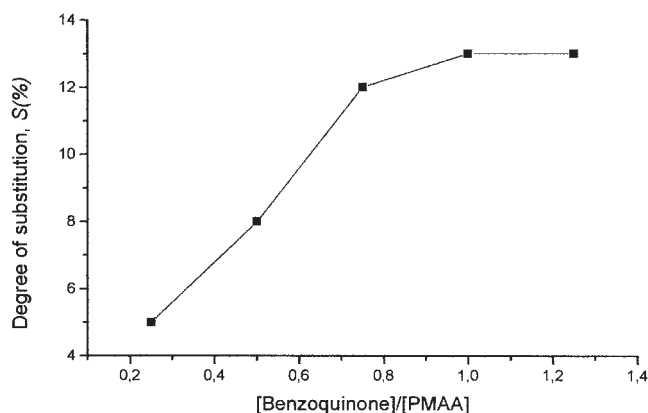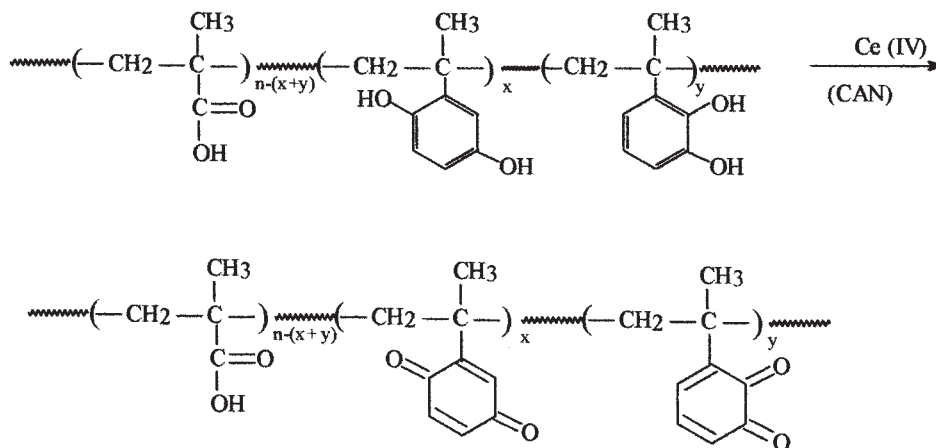

Figure 6 Plot of the variation of degree of substitution, S (%), of PMAA-HQ against the molar ratio [benzoquinone]/[PMAA] under the following conditions: temperature = 75°C; reaction time = 1.5 h.

Scheme 3

imum substitution 13% was reached for a molar ratio [benzoquinone]/[PMAA] of 0.75. However, the degree of substitution was found to be 52% when working under nitrogen atmosphere. As shown in Table I, the degree of substitution in PMAA-HQ was higher than that in PAA-HQ, suggesting a higher decarboxylation rate of PMAA giving rise to the more stable tertiary radical.

Potentiomteric study

Hydroquinone/catechol-containing polymers are usually characterized by their midpotentials, E_m, that is, potentials of half oxidation.[8] Customarily, polyvinylhydroquinone and polyvinylcatechol were potentiometrically titrated with CAN in 90–95% glacial acetic acid.[8,9]

The titration of PMAA-HQ of 52% substitution was undertaken under conditions cited in the liter-

ature[8,9] at 20°C and 35°C. Scheme 3 illustrates the oxidation reaction that took place during the potentiometric titration. The potentiometric study at 35°C was performed to gain an insight into the effect of an elevated temperature on the redox behavior of the polymer. Under the same conditions, and for the purpose of comparison, the titrations of the monomeric hydroquinone, catechol, and 1 : 1 hydroquinone/catechol were also made. As observed earlier,[15,21] a significant delay in the establishment of an equilibrium potential was noted in the initial stages of the titration of PMAA-HQ. It was necessary to wait for 30 min to observe a stable value, and at the end of titration, stable values were obtained within 5 min. However, for the monomeric substances, stable values were obtained within <5 min throughout the titration.

From the plots in Figures 7 and 8 the midpotentials at 20°C can be deduced to be 702, 818, 744, and 898 mV for hydroquinone, catechol, 1 : 1 hydroquinone/cate-
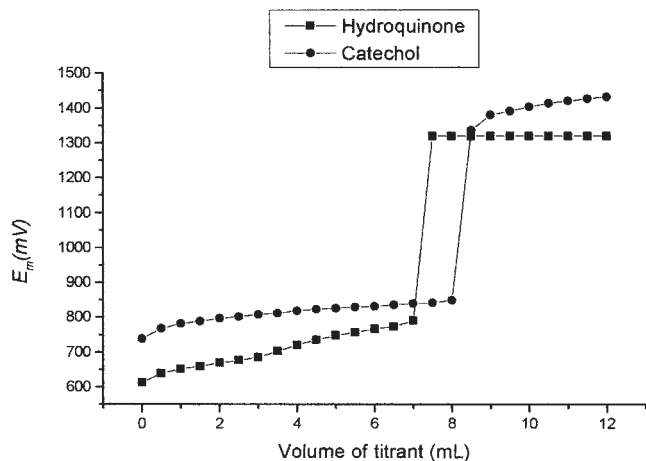

Figure 7 Plots of the potentiometric titration at 20°C with 0.05M CAN in 90% acetic acid: ■, hydroquinone; and ●, catechol.
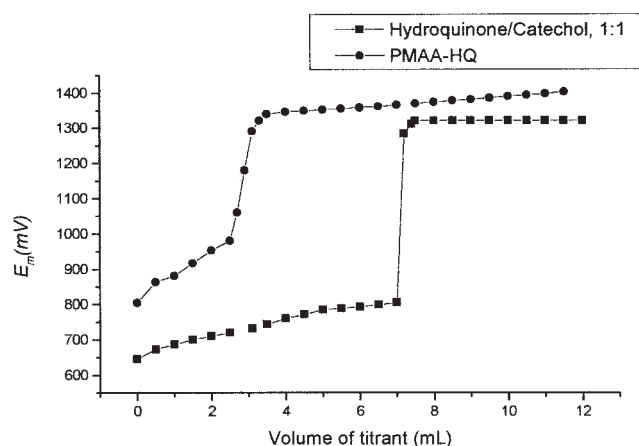

Figure 8 Plots of the potentiometric titration at 20°C with 0.05M CAN in 90% acetic acid: ■, 1 : 1 hydroquinone/catechol; and ●, PMAA-HQ.
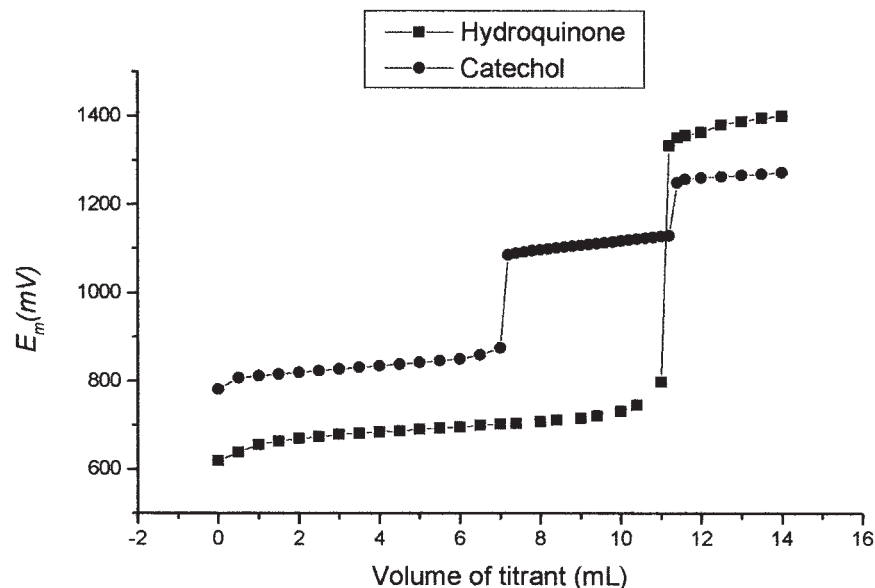
Figure 9 Plots of the potentiometric titration at 35°C with 0.05M CAN in 90% acetic acid: ■, hydroquinone; ●, catechol.

chol, and PMAA-HQ, respectively. That is, an 80–196 mV rise in the midpotential for the polymer based on those of the monomeric compounds. It is indeed a substantial rise. That the E_m of the polymer was higher than those of the monomeric entities owes to a "polymer effect" as proposed by Nakabayashi et al.[30] The potential rise was believed to be the result of a plausible adherence of the oxidized form of the polymer to the indicator electrode (platinum electrode). On the opposite, poly(3-vinylcatechol) was earlier shown to

possess midpotentials lower than those of catechol under the same titration conditions.[15,16]

Plots of the titrations at 35°C are given in Figures 9 and 10. The midpotentials were found to be 702, 840, 790, and 1000 mV for hydroquinone, catechol, 1 : 1 hydroquinone/catechol, and PMAA-HQ, respectively. The effect of an elevated temperature on the midpotential was observed to be significant mostly for the polymer. The other facet of such assessment was clearly the occurrence of a two-stage oxidation, that is,
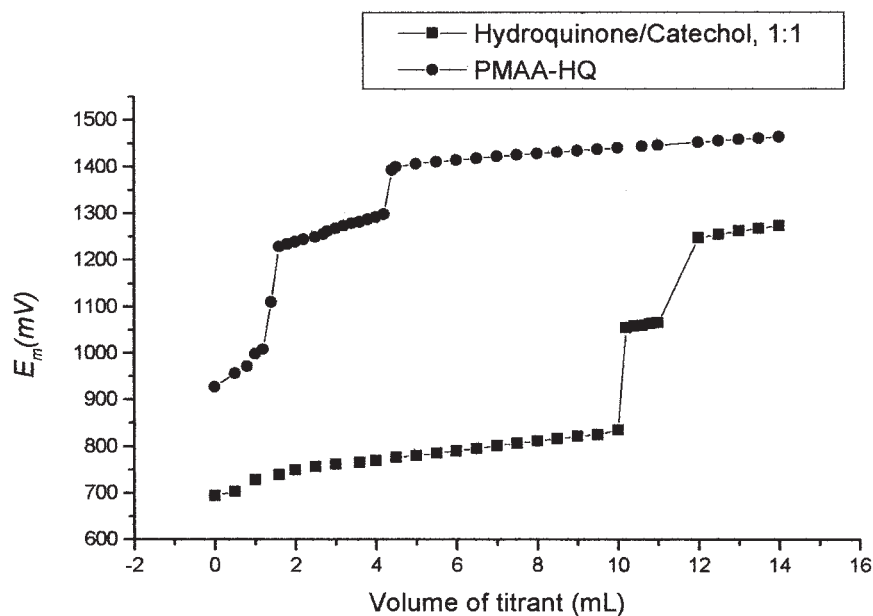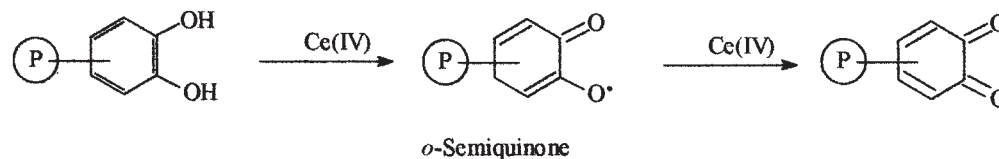

Figure 10 Plots of potentiometric titration at 35°C with 0.05M CAN in 90% acetic acid: ■, 1 : 1 hydroquinone/catechol; ●, PMAA-HQ.

Scheme 4

two equivalence points indicative of an intermediate semiquinone. The fact that this two-stage phenomenon did not occur for hydroquinone, can be therefore ascribed to an intrinsic oxidation property of the catechol, and consequently, the intermediate semiquinone would be rather the *o*-semiquinone as traced in Scheme 4. Stable semiquinone radical was detected earlier by ESR spectroscopy.[15,31] It is enlightening to recall that the titration of poly(3-vinylcatechol) at 35°C did not show this two-stage phenomenon as reported earlier.[15] In light of these findings, it can be deduced that the PMAA-HQ at 35°C potentiometrically responds in a way similar to that of catechol, probably because of the low degree of substitution and of the random distribution of the catechol units all over the PMAA matrix.

It is interesting to note that the E_m's for PMAA-HQ were somewhat higher than those for PAA-HQ (Table I), suggesting the methyl effect of PMAA-HQ.

Overall, the midpotentials obtained indicate that PMAA-bound hydroquinone/catechol should exhibit similar activity as a redox agent as monomeric catechol and hydroquinone.

CONCLUSIONS

The study shows the possibility to functionalize PMAA to afford materials with redox capacities. Indeed, the application of the conditions of Minisci to the modification of PMAA by benzoquinone is successful to a certain extent. The degree of modification depends on the reaction conditions. The hydroquinone/catechol-modified PMAA behaves as a redox polymer. The profile of the potentiometric titration of this redox polymer does not fit into that of monomeric analogue. The redox potential of the polymer is higher than that of the monomer. The polymer effect is manifested in this type of titration.

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