Poly(Acrylic Acid)-Bound Piperonyl/3,4-Dihydroxybenzyl Units: Metallic Adsorption And pH-Metric Studies

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Received: 26th November, 2006
Accepted: 11th December, 2006

Web Publication Date : 25th February, 2007

ABSTRACT

Optimization of the esterification of poly (acrylic acid) (PAA) with piperonyl alcohol (PA) was undertaken in dioxane. Degrees of esterification (DE) were found higher in an open system than in a closed one, 28 versus 24%, under the following conditions: [PA] [PAA] molar ratio of 1, temperature of 110°C and time of 3h. A degree of esterification of 72% was obtained for the former system at a time of 5.5 h, but only 32% was reached for the latter system, for [PA]/[PAA] of 4. Treatment of the piperonyl-modified PAA with PCl_5 followed by hydrolysis afforded a copolymer of 3,4-dihydroxybenzyl acrylate and acrylic acid. pH-metric studies of PAA and modified PAA, and their corresponding systems containing Cu^{2+} and Cd^{2+} were performed using 0.1N NaOH. The adsorption extents of these two heavy metallic ions by PAA and PA-modified PAA were experimentally estimated.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

The use of chemically modified polymers is being increasingly widespread because they can display properties as desired. Acrylic polymers stand among the well-known polymers capable of undergoing chemical transformations, mainly the functionalization. The design and synthesis of polymeric architectures with acrylic segments have been surveyed[1]. The applications of poly(acrylic acid)(PAA) and other

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acrylic polymers, in their bare and modified forms, are obviously expected, chiefly because of the intrinsic properties of the carboxylic groups. Indeed, of the best applications of PAA is its adsorbing capability of heavy metallic ions via the chelating propensity of the carboxylic groups[2]. A good example is the use of the complexes formed by the reaction of PAA and heavy metals as ultrafiltration membranes for the removal of radionuclides[3]. Low molecular weight PAA was found very efficient as a salt scaling inhibitor in oil field operations[4]. Global et al. grafted N-dodecyl acrylamide groups onto PAA backbone, affording hydrophobically modified polymer, which was subjected to adsorption study[5]. On the other hand, cross-linked polyacrylates are valuable items in the following: diapers, feminine, hygiene products, hospital products, and condensation preventing agents[6].

Recently, we reported the anchoring of catechol and hydroquinone moieties onto PAA and poly (methacrylic acid) (PMAA) via an oxidative decarboxylation by means of the conditions of Minisci[7,8]; The polymers thus transformed were evaluated as valuable redox polymers. Moreover, catechol-bearing polymers were also subjected to the elimination of heavy metallic ions. For example, Iwabuchi showed earlier that macroreticular redox resins with catechol units prepared by deblocking the dimethoxyl groups of the 3,4-dimethoxybenzyl entities incorporated onto a styrene/divinylbenzene copolymer, could adsorb Hg^{2+} more efficiently than Al^{3+}, Co^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}[9].

Other properties of catechol-containing polymers were surveyed in the literature[10].

It is relevant to recall the importance of metal-catechol complexes *in vivo*. For example, an iron-catechol complex seems to occur in the biological oxidation of aromatic natural products, including lignin, catalyzed by dioxygenase enzymes[11].

We report in this paper the results of our work on the esterification of PAA with piperonyl alcohol (PA) and the metallic adsorption and pH-metry studies of the corresponding catechol-containing PAA (PAACa).

EXPERIMENTAL

Chemicals and solvents used in this work were purchased from one of the following chemicals sup-

pliers: Aldrich, Merck, Prolabo, Acros Organics, BDH chemicals, Riedel-deHaen, and Fluka. Acrylic acid (AA), ethyl acetate, chloroform, cyclohexane, dioxane, tetrahydrofuran (THF), methanol, and ethanol were purified by distillation before use. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Benzyl alcohol (BA) and piperonyl alcohol (PA) were used as supplied.

The viscometric measurements were performed in dioxane 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, $[\eta]=K M_v^a$ where $[\eta]$ is the intrinsic viscosity, K and a are the Mark-Houwink constants; the latter ones are taken as $7.6\times10^{-4} dL.g^{-1}$ and 0.5 respectively for these conditions[12]. $[\eta]$ 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, t and t_0 are the efflux times of the polymer solution and the solvent, respectively. UV-Visible spectra were recorded using a UV-visible spectrophotometer Shimadzu 120; dioxane and methanol of analytical purity were employed in UV analyses. Infrared spectra were taken with a FT-IR Paragon 1000PC. The polymer samples for infrared analysis were in form of cast films.

The potentiometric titrations were performed using a pH-meter Inolab pH level L.

Synthesis of polyacrylic acid(PAA)

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

Esterification of PAA with piperonyl alcohol (PA)

1. Open system

In a 500 mL three-necked round-bottomed flask equipped with a Dean-Stark trap, a thermometer, a

magnetic stirrer, and a condenser, 5.3 g of PAA (0.073 mole) were dissolved in 200 mL of dioxane, followed by addition of a stoichiometric quantity of PA (11.42 g, 0.073 mole). After homogenization of the mixture and the addition of 0.1 mL of concentrated H_2SO_4, the system was heated at 110°C for 3 h under magnetic stirring. The reaction was then stopped and the flask content was cooled down to room temperature. The modified PAA was isolated by precipitation in an appropriate non-solvent, and purified by dissolution/precipitation cycles. Afterwards, the product was filtered, washed twice with the non-solvent, and then dried *in vacuo* at 45°C for 4 days.

2. Closed system

The esterification of PAA with PA was carried out in a closed system by following the same procedure, but in the absence of a Dean-Stark trap.

The degree of esterification (DE) was estimated by means of a UV calibration curve using piperonyl alcohol or benzodioxole (λ_{max}= 284nm) for PA-esterified PAA, and benzyl alcohol (BA) (λ_{max}= 254nm) for BA-esterified PAA.

Removal of the methylenedioxyl group, PAACa

a. Reaction with PCl_5

In a 250 mL three-necked round-bottomed flask fitted with a thermometer, a magnetic stirrer, and a condenser, 4g of esterified PAA(DE=71.44%) were dissolved in 25 mL of dioxane, followed by addition of 21.6g of phosphorus pentachloride in 75 mL of dioxane. The system was heated at 60°C for 16 h under magnetic stirring. The mixture was then poured into 400 mL of ice-water. The product, the carbonate derivative, was purified by a dissolution/precipitation process, filtered and washed with the non solvent, and finally dried *in vacuo* at 45°C for 4 days.

b. Hydrolysis

In a 250 mL round-bottomed flask equipped with a condenser, 2.3 g of the corresponding carbonate were charged and 160 mL of water were added. The mixture was refluxed for 48 h under a continuous magnetic stirring. The system became homogenous throughout the hydrolysis reaction. After cooling the mixture to room temperature, the product was precipitated into a NaCl-saturated aqueous solution, fil-

tered, washed with THF, and finally dried *in vacuo* at 45°C for 4 days.

pH-metric titrations

Solutions(2.78×10^{-4} M) of PAA and PA-modified PAA(DE=71.44%) in 10 mL of water were titrated with 0.1 N NaOH at 17°C. The same procedure was applied to these materials but in the presence of $CuSO_4 \cdot 5H_2O$(0.1 M, 10 mL) and $CdCl_2 \cdot 2H_2O$ (0.1 M, 10 mL).

Estimation of adsorption extent

To an aqueous solution of 2.78×10^{-4} M of PAA (PAACa), were added 10 mL of 0.1 M $CuSO_4 \cdot 5H_2O$ (or $CdCl_2 \cdot 2H_2O$) and the mixture was allowed to stir for 1 h at room temperature; a precipitate was formed in the course of the reaction. The insoluble PAA complex was filtered; the filtrate contained the non adsorbed metallic ion. In a 250 mL dropping funnel, were charged the following: 10 mL of the above filtrate, 20 mL of 2.5 N NaOH, 5 mL of a solution of 10 wt.% potassium sodium tartrate, and 20 mL of 7.8×10^{-4} M chloroform solution of dithizone. After a vigorous shaking, the mixture was allowed to stand until the separation of the water and chloroform layers. The organic layer was then drawn and subjected to UV analysis. The absorption for Cu^{2+} and Cd^{2+} was measured at λ_{max} = 450 nm, and λ_{max} = 515 nm, respectively. The adsorption extent was then computed from a calibration curve, set for each metallic ion.

RESULTS AND DISCUSSION

Poly(acrylic acid-co-piperonyl acrylate)

Polyacrylic acid 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 PAA was found to increase with reaction time: 190000 ($[\eta]$=0.3325 dL·g^{-1}), and 298000($[\eta]$=0.415 dL·g^{-1}) for 45 min and 2 h, respectively.

The esterification of PAA($[\eta]$=0.3325 dL·g^{-1}) with PA was carried out in water and dioxane, eq. (1). With the latter solvent, the reaction was performed in open and closed systems. The PA-esterified PAA was characterized by a UV absorption band at λ_{max} =284-286

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nm, a characteristic band of benzodioxole(Figure 1b), and an IR absorption bands at 1732 cm^{-1}(attributed to the ester group) and 1037 cm^{-1}(assigned to the methylene of the methylenedioxyl group)(Figure 2b).

In order to assess the polymeric effect on the esterification reaction on polymers, the esterification of PAA with PA was attempted in water; water is usually not used as solvent in esterification reactions for they are equilibrated ones, and obviously the esterification yield would be but nil. This is wholly true at the molecular level, but at the macromolecular one, the assertion may be otherwise to a certain extent. In this attempt, the intent was to what extent the esterification of PAA with PA may occur. Figures 3 and 4 illustrate the degrees of esterification (DE) in water as a function of [PA]/[PAA] molar ratio and time, respectively. As can be seen, the ester was formed but in lower extents, not exceeding 4%. The fact that the esterification did take place could be ascribed to a polymeric effect, that is, some

ester groups formed could be embedded in the core of the polymeric chains and were thus not accessible to hydrolysis. Interesting is that the degree of substitution dropped drastically beyond a [PA]/[PAA] molar ratio of 2.

The results of the esterification in dioxane in an open system (removal of produced water by azeotropy with dioxane) are shown in figures 5. A degree of esterification was relatively substantial; about 72% was reached after a reaction time of 5.5 h. The rate was about 4.40% /h within the first four hours of reaction, but it increased abruptly to 19%/h beyond 4 h. Another finding was that the esterified PAA were unexpectedly of higher intrinsic viscosity, that is 0.6592 dL.g^{-1} for a DE of 20.32% and 0.7253 dL.g^{-1} for 61.57%, compared to that of PAA, 0.3325 dL.g^{-1}. The intrinsic viscosity was found to rise with DE as shown in figure 5. The high viscosity measured could not be due only to the extent of esterification, because a molecular weight of 550 000 was expected
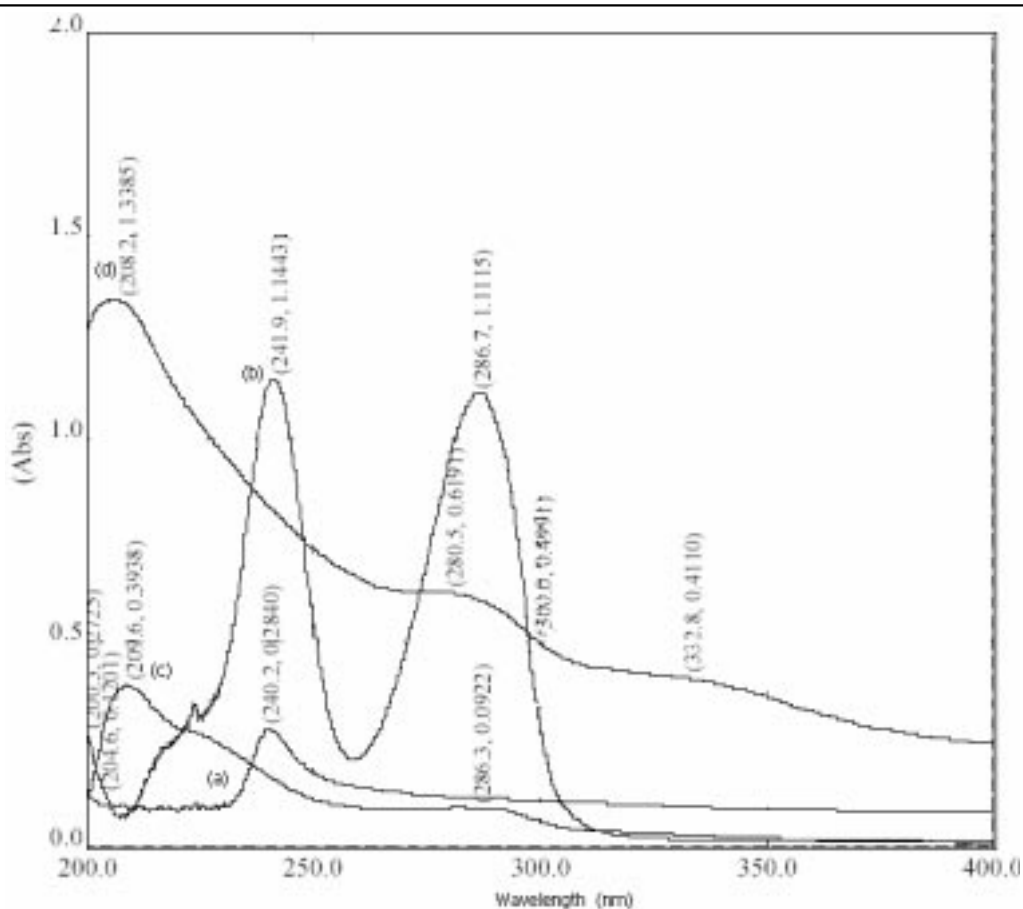

Figure 1: UV spectra: (a) PAA in dioxane (C=1 g/L), (b) PA-esterified PAA in dioxane (C=0.13 g/L), (c) Carbonate derivative in methanol, (d) PAACa in bidistilled water (C=2.44.10^{-2} g/L)

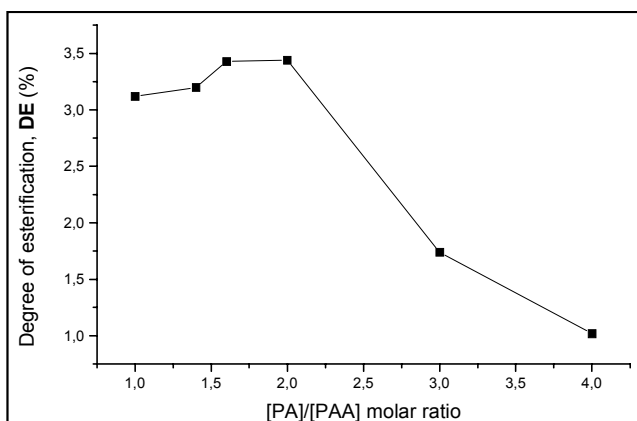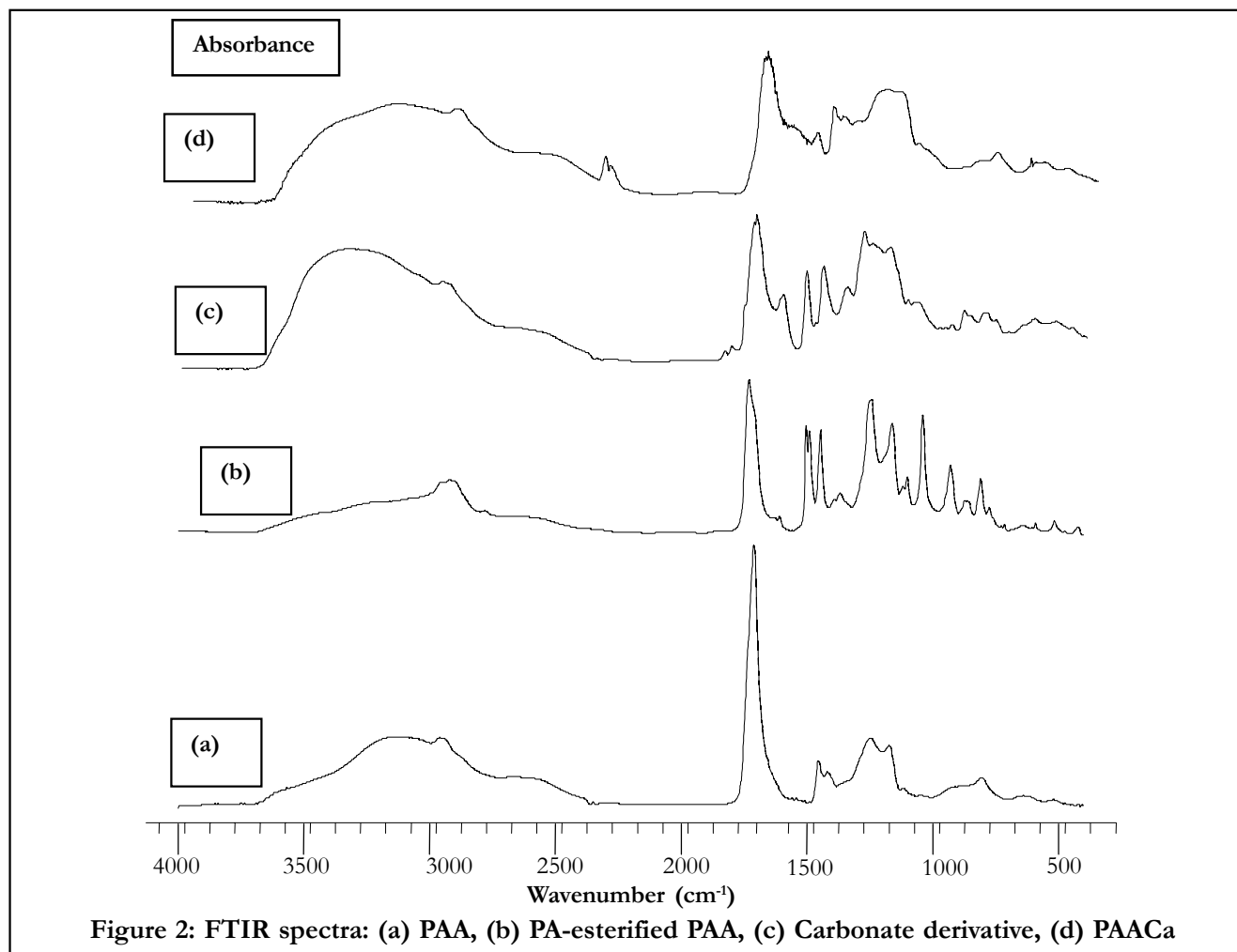**Figure 2: FTIR spectra: (a) PAA, (b) PA-esterified PAA, (c) Carbonate derivative, (d) PAACa**

Figure 3: Degree of esterification, DE, as a function of [PA][PAA] molar ratio. Esterification of PAA by PA in water, closed system; time=3 h; T=110°C
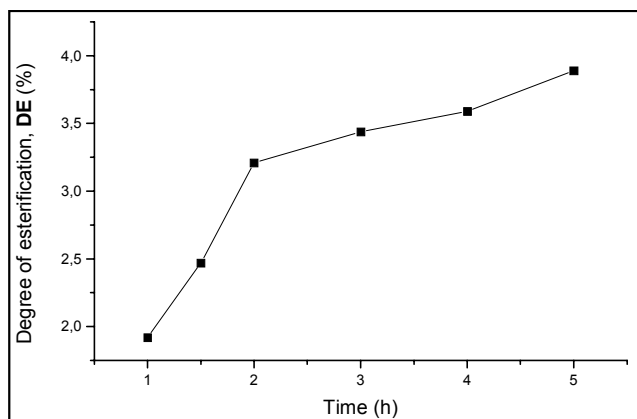

Figure 4: Intrinsic viscosity, [η], as a function of time. Esterification of PAA by PA in water; closed system; time=3 h; T=110°C

assuming 100% of esterification and no alteration of the polymer chain length. Thus, a different phenomenon would account for the high values of [η]. Probably, upon introducing piperonyl units into the PAA chains, some polymer chain interactions (inter-chains) may ensue as a result of an extensive hydrogen bonding between the remaining unreacted carboxylic groups. The occurrence of these interactions may have led to an assembling of the polymeric chains in bundles, hence, a higher viscosity of
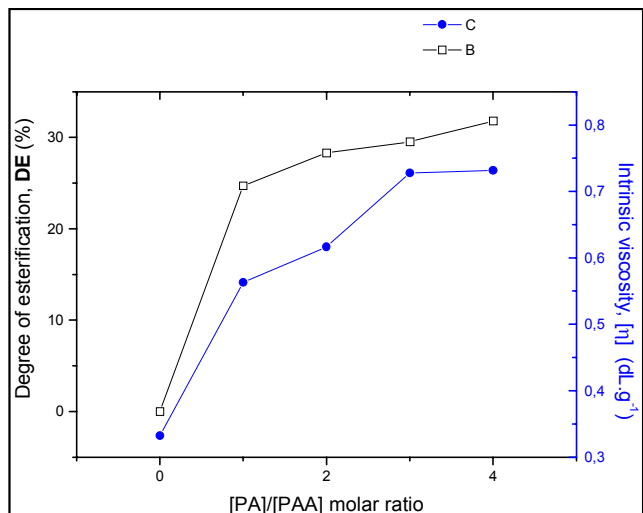
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Figure 5: Degree of esterification, DE, and intrinsic viscosity, [η], as a function of time. Esterification of PAA by PA in dioxane, open system. [PA][PAA] molar ratio = 4; T = 110°C
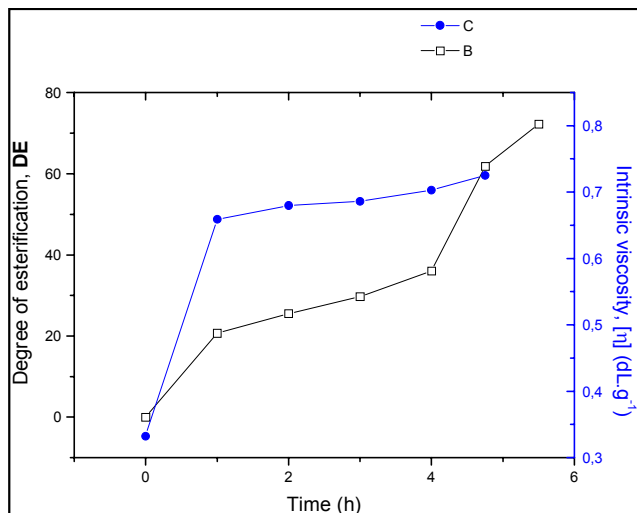

Figure 6: Degree of esterification, DE, and intrinsic viscosity, [η], as a function of time. Esterification of PAA by BA in dioxane, open system. [BA][PAA] molar ratio = 4; T = 110°C
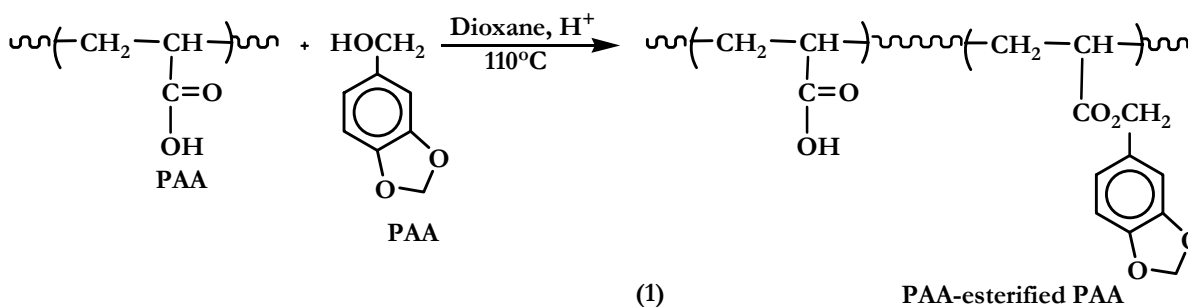
the polymer solution. Yet, its ready solubility would suggest that the bundles consist of only a very few polymeric chains.

The solubility of esterified PAA differed from that of the parent PAA; it defied water-solubility but was rather soluble in dioxane and THF.

To ascertain the link between the high viscosity observed with the anchoring of piperonyl groups, the esterification of PAA($[η]=0.228$ dL·g^{-1}) was attempted with benzyl alcohol (BA) under the same reaction conditions. First, it can be noted that the esterification took place in two different rates as observed with PA; both rates are about thee times lower than that with PA, figure 6. This can be explained by the donating capacity of the methylenedioxyl group in PA. Within, the first 10 hours, DE was no substantial but increased at longer times. Second, the intrinsic of BA-esterified PAA was also unexpectedly of high viscosity, even for products of

low DEs (Figure 6). Following the same reasoning as above, a 100% esterified PAA would be of a molecular weight no greater than 202500. Thus, the same phenomenon discussed above may apply to explain the high values of [η].

The esterification of PAA($[η]=0.3325$ dL·g^{-1}) with PA was also studied in a closed system, that is, the water produced during the reaction was not removed. The variations of DE and[η] as a function of[PA/PAA] molar ratio, maintaining the reaction time constant at 3 h, are shown in figure 7. Both parameters increased with[PA/PAA] molar ratio. However, DE did not rise significantly, as expected, when compared to the results obtained for an open system. Again, it can be remarked that the viscosity of the esterified PAA was excessively high, and remained constant beyond a DE of 29% and a [PA/PAA] molar ratio of 3. Insoluble resins were formed beyond a reaction time of 3 h and for [PA/PAA]

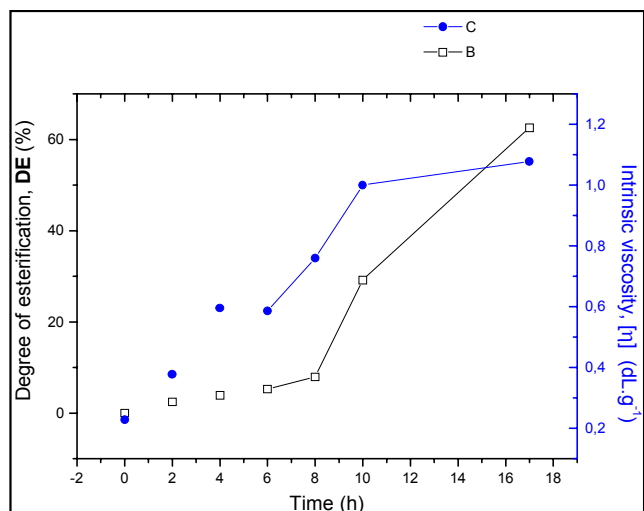**(1)**   **PAA-esterified PAA**

Figure 7: Degree of esterification, DE, and intrinsic viscosity, [η], as a function of [PA][PAA] molar ratio. Esterification of PAA by PA in dioxane, closed system, time = 3 h; T = 110°C

molar ratio of 4.

Bogoczek and Pinkowska reported the results of the esterification of crosslinked poly(acrylic acid-co-divinylbenzene) resin in its macroporous and gel states, with n-alcohols (C_1-C_4), in the presence of sulfuric acid as a catalyst[13]. They found that the degrees of conversion were not quantitative, 10-26%, for the two forms of resins, after a time of 50 h and at the boiling temperature of the alcohol. Moreover, the alternative of an open system (azeotropic removal of water) did not enhance appreciably the degrees of conversion, up to only 31%.

That, in contrast to the Bogoczek and Pinkowska's work, the degrees of substitution were found relatively more quantitative owes to the fact that our PAA resin is used in its dissolved state; that is, the carboxylic groups were more accessible to the reactants.

Poly(acrylic acid-co-3,4-dihydroxybenzyl acrylate)

Bronsted acids are commonplace reagents in effecting the dealkylation of ethers. For example, hydrobromic acid was efficient in the demethylation of dimethoxylated phenyl-containing polymers[14,15]. Herein, the use of HBr in the removal of the methylenedioxyl group was avoided to prevent the plausible de-esterification which may afford back poly (acrylic acid). Also the cleavage of methylenedi
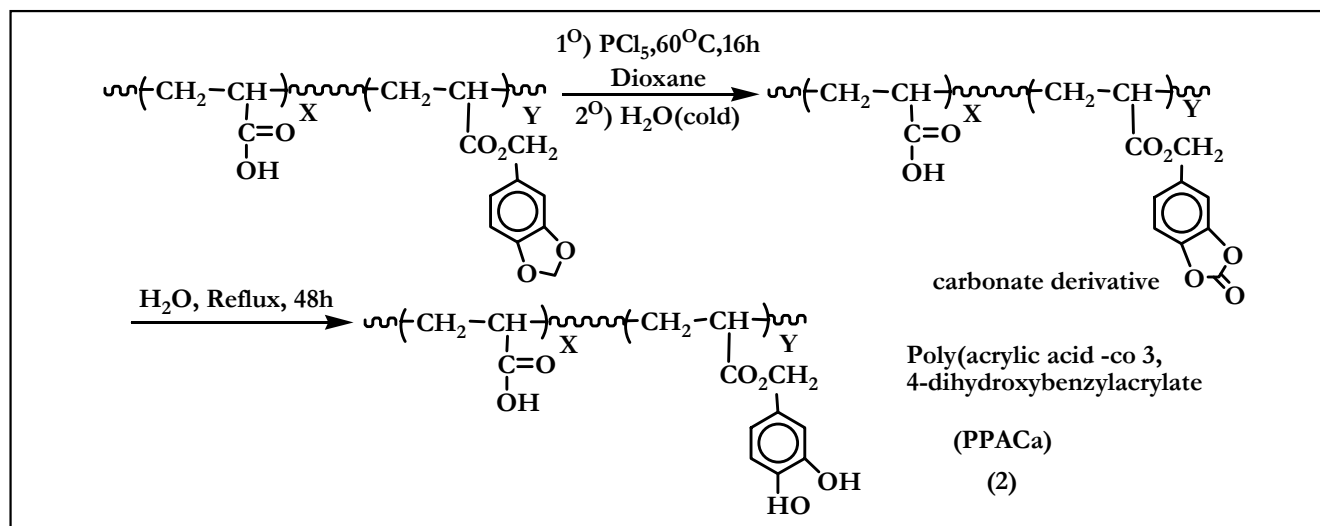
oxyl group in benzodioxole-containing polymers was promoted by BCl_3/dodecyl mercaptan system[16,17] and BCl_3/Me_2S[18] to liberate the catechol functionality. Tetrabutylammonium fluoride (TBAF) was found to be effective mostly in the desilylation of silyl-protected alcohol. In an early work, this reagent was reported to promote efficiently the removal of phosphate protecting groups in nucleotide triesters[19].

In the present work, the removal of formal linkage in the PA-esterified PAA (DE = 72%) was effected by reaction with PCl_5 followed by hydrolysis[20] as depicted in eq. (2). This treatment entailed the formation of a black resin in form of copolymer of AA and 3,4-dihydroxybenzylacrylate, PAACa.

The water solubility of the resulted poly(acrylic acid-co-3,4-dihydroxybenzyl acrylate) (PAACa) would account for the success of a quantitative removal of the formal group. IR spectrum(Figure 2d) revealed the disappearance of the absorption band at 1037 cm^{-1} of the methylenedioxyl group and the appearance of two adjacent sharp bands at 2340 and 2360 cm^{-1} assigned for the chelating property of the catechol unit. In addition, the absorption band at 3 500 cm^{-1}, present in the IR spectrum of PAA and attributable to OH of the carboxylic group, was enhanced (broader and more intense) owing to the dihydroxy group of the catechol entity formed by the deblocking operation. The UV spectrum(Figure 1c) showed an absorption band at λ_{max} =280 nm, a band closer to that of catechol (λ_{max}=275 nm); a slight bathochromic shift (≈ 5 nm) may be due the ester functionality, a chromophoric group. The UV spectrum of the carbonate derivative polymer (before hydrolysis) revealed a band at λ_{max} = 286 nm, a characteristic band for the PA-esterified PAA. Another feature of this polymer is that the profile of the plot of η_{red} = f (C) in water is similar, as with PAA, to that of a polyelectrolyte.

The removal of the methylenedioxyl group in the PA-modified PAA(72% substitution) using tetrabutylammonium fluoride(tBu_4NF), after a 24 hour-reaction under reflux, was partially successful and minute. While most of the polymer remained soluble in dioxane, the reaction solvent, a concomitant precipitation of a small fraction occurred(10 %). Surprisingly, the isolated soluble part and the latter pre-

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cipitate, after drying process, became insoluble in all solvents. Their IR spectra showed, besides the bands pattern of the non-deblocked polymer, the two catechol-related bands at 2340 and 2372 cm^{-1}; furthermore, the lower absorbance intensities of these bands and the water-insolubility of this material would suggest a low extent of the cleavage. However, with a 4% modified polymer (the product from the esterification run in water), an instantaneous precipitation occurred giving a water-soluble material; an acid-base reaction rather took place between the carboxylic groups of the PA-modified PAA and the tBu$_4$NF affording tetrabutylammonium polyacetate($\sim$COO$^-$ $^+$N(tBu)$_4$).

Metallic adsorption and pH-metric studies

The aim was to anchor the catechol frame onto the PAA matrix because we anticipated a better adsorption capacity, the catechol group being a bidentate ligand (one catechol unit is equivalent to two carboxylic groups or two acrylic acid units). The adsorption capacities of PAA and PAACa were estimated with two metallic ions, Cu^{2+} and Cd^{2+} at pH 2-3 at a temperature of 17°C. The results are compiled in TABLE 1. The mixture of 10 mL of 2.78 ×

10^{-4} M aqueous solution of each of the two polymers with 0.1 M of CuSO$_4$.5H$_2$O yielded precipitates after 1 and 5 min for the former and the latter polymers, respectively. The results of adsorption were about 58 and 48 % for the two polymers, respectively. These results would indicate that the catechol-containing PAA (PAACa) displayed lower adsorption capacity in the case of Cu^{2+} than PAA.

However, the Cd^{2+} adsorption study was featured with two distinct differences. First, while in the case of PAACa the precipitate was formed for 0.1 M of CdCl$_2$·2H$_2$O and the adsorption extent was 71%, in the case of PAA the precipitate was promoted only when a concentration of 1 M was used, for the same concentration of the polymer; the time of precipitation for 1 M of CdCl$_2$.2H$_2$O was 48 h at pH 5-6. Second, under these conditions, a quantitative adsorption of Cd^{2+}, about 100%, was found for PAA. The greater values of the adsorption extent would suggest a higher adsorption activity of the polymers towards cadmium.
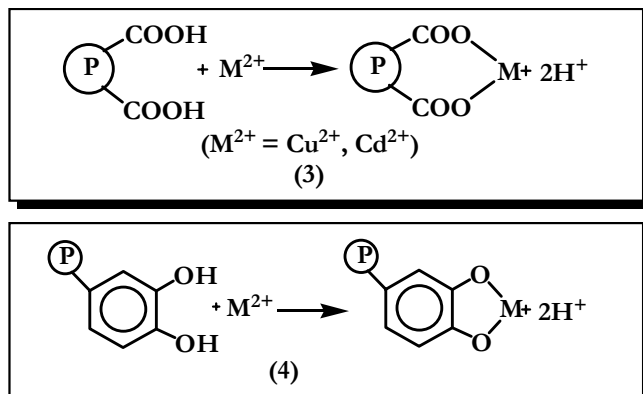
A pH-metric study(pH=f(V$_{NaOH}$)) was undertaken for PAA and PAACa, in the absence and in the presence of metallic ions, by performing titrations of their aqueous solutions (10 mL of 2.78×10^{-4} M)

TABLE 1: Conditions and results of the metallic adsorption study. Polymer concentration in water, 2.78 × 10^{-4} M; temperature, 17°C; volume of the salt solution, 10 mL.*

	CuSO$_4$·5H$_2$O (0.1 M)			CdCl$_2$·2H$_2$O (0.1 M)			CdCl$_2$·2H$_2$O (1 M)		
	pH**	t$_p$ (min)	Ads.(%)	pH	t$_p$ (h)	Ads.(%)	pH	t$_p$ (h)	Ads.(%)
PAA	2.88	1	58.56	2.25	No ppt.	-	5.69	48	99.80
PAACa	2.72	5	48.52	2.24	24	71.43	-	-	-

* t$_p$, the time for precipitation ; Ads., the extent of metallic adsorption ; ppt., precipitate
** pH, the measured values.

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(3)

(4)

by 0.1 N aqueous NaOH. The results are illustrated in figures 8 and 9. The titration curves show that the pHs of the PAACa are slightly lower than those of PAA. A general and interesting observation is the pHs were more acidic in the presence of a metallic ion. For example, the pHs for PAA and PAACa, matched at 12-12.5 for volumes of titrant ranging from 5 to 12 mL, and for the same titrant volumes these pHs decreased to 7.5 and 5-5.5 in the presence of Cd^{2+} and Cu^{2+}, respectively. This would suggest that the metallic adsorption enables the dissociation of the hydroxyl groups of both the catechol and carboxylic acid units, making the materials more acidic. The pH decrease could stem from the deprotonation according to eqs.(3) and (4). The chelation of copper by these materials may afford complexes more stable than those with cadmium; that is, the copper-complexed materials became more acidic than those with cadmium. The difference in the formation constants, K_2, of Cu- and Cd-complexes may explain this finding. In fact, the formation constants, K_2, of Cu-complexes (~10^{23} for Cu-succinic acid and Cu-catechol) are greater than those of cadmium (~10^{13} for Cd-succinic acid and Cd-catechol)[21]; the greater the K_2 the more stable is the complex and, consequently, the higher the rate of the deprotonation. Roma-Lucio et al. observed the same pH decrease in the titration curves of PAA in the presence of metallic ions[2]. Also, Annenkov et al. reported a pH-metry study of PAA, PVI(polyvinylimidazole), and poly(acrylc acid-co-vinylimidazole) using 0.1 N HCl and observed a pH decrease when Cu^{2+} was added[22].

CONCLUSION
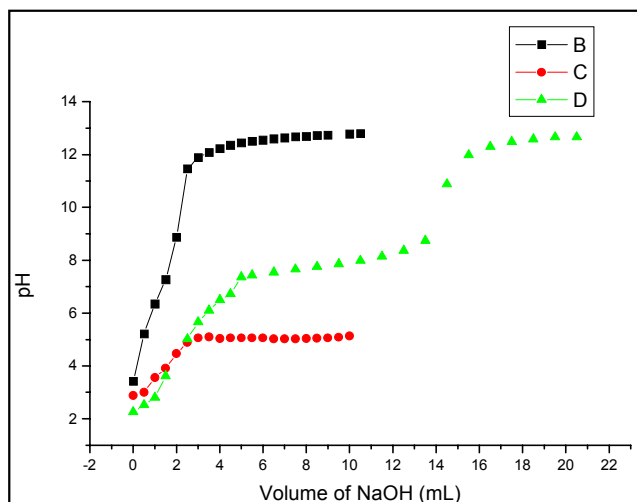
The esterification of poly (acrylic acid) with pip-

Figure 8: Plots of the potentiometric titrations, pH = f(V_{NaOH}), with 0.1 N NaOH: B, PAA; C, PAA in the presence of CuSO$_4$·5H$_2$O; D, PAA in the presence of CdCl$_2$·2H$_2$O
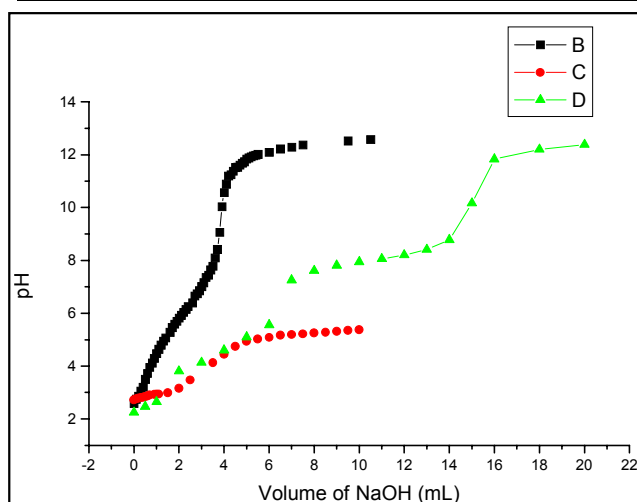

Figure 9: Plots of the potentiometric titrations, pH = f(V_{NaOH}), with 0.1 N NaOH: B, PAACa; C, PAACa in the presence of CuSO$_4$·5H$_2$O; D, PAACa in the presence of CdCl$_2$·2H$_2$O

eronyl alcohol was more quantitative in an open system than in a closed one. Phosphorus pentachloride/hydrolysis system is more effective in deblocking the methylenedioxyl group of the esterification product. The catechol-containing poly (acrylic acid) is unexpectedly not superior to poly (acrylic acid) with respect to the metallic adsorption, but they both showed a greater adsorption activity towards cadmium than cupric ion. However, the catechol-containing poly (acrylic acid) is characterized by a lower acidity than poly (acrylic acid).

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