



Synthesis and Characterization of Poly Acrylic Acid Modified with Dihydroxy Benzene-Redox Polymer

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Abstract

Poly acrylic acid was functionalized with catechol, hydroquinone, catechol-hydroquinone, a homolytic modification by an oxidative decarboxylation using ammonium persulphate as an oxidant. The chemically modified PAA/Catechol, PAA/Hydroquinone and PAA/Catechol-Hydroquinone were characterized using UV and FT-IR. Thermal analysis shows PAA/Catechol, and PAA-Hydroquinone are stable above 700^oC and their Ea are lesser for PAA/Hydroquinone with the highest percentage of substitution than the other two polymers. The kinetic parameters were calculated from the TGA curves and the average molecular weight measured by viscometer was found to be around 1.1X10⁶g/mol. From XRD studies the prepared polymers were found to be semi crystalline nature which is confirmed from the SEM analysis. The morphology of the redox polymer was found to be rod and cage like microstructure. From the CV studies, the potential difference was calculated.

Keywords: Polyacrylic acid, Catechol, Hydroquinone, Redox polymer, Mid potential.

Introduction

Polymers can be prepared through various techniques such as radical, cationic and anionic polymerization¹⁻⁶. The mechanical, thermal and structural properties can be studied through different kinds of characterization methods to determination of structure–property relationships^{7,8}. Recently, polymers have been applied in various fields such as automotive, construction, electronic, cosmetic and pharmaceutical industries due to its advantageous material properties. Functional polymers of controlled refractivity⁹, photochromic¹⁰, electrochromic¹¹ and optoelectronic¹² functions were developed recently. The use of polymers with tunable refractive properties as optical modulators, optical filters, or electro optic waveguide devices has been reported¹³. The functionalization of bioactive molecules can be carried out due to presence of carboxylic groups in Poly Acrylic Acid. The interactions due to the electrostatic forces, hydrophobic nature, hydrogen bonding, vanderwaals forces or the combination of these interactions leads to the formation of polymer complexes. The formation of complexes may strongly affect the polymer solubility, rheology, conductivity, and turbidity of polymer solutions, mechanical properties permeability, electrical conductivity of the polymers. Particularly, polyelectrolyte complexes are formed by the reaction of a polyelectrolyte with an oppositely charged polyelectrolyte in an aqueous solution. Electrostatic interactions are considerably stronger than most secondary binding interactions. Thus, electrostatic polyelectrolyte complexes exhibit unique physical and chemical properties with reasonable biocompatibility¹⁴. Stability of the complex is influenced by the polymer composition and structure, as well as by hydrophobic interactions. In addition, stability of the complex is dependent

on many environmental factors, such as temperature, the nature of the solvent, pH, or ionic strength. The polymers with redox entities can act as redox agents, corrosion inhibitors, super adsorbent and metallic adsorbents^{15,16}. The metallic adsorption is through their chelating ability¹⁷. The other feature of these molecules is their phenolic nature, implying a unique chemistry¹⁸. In the present work a homolytic modification by decarboxylation of PAA modified with catechol, hydroquinone and catechol-hydroquinone was synthesized.

Material and Methods

The chemicals were purchased from Merck. The viscometric measurements were performed in dioxane at 30^oC using Cannon Ubbelohde capillary viscometer. The average molecular weights (Mw) were estimated by the standard relation of Mark–Houwink–Sakurada^{19,20}. UV–Vis spectra were recorded using a UV–Vis spectrophotometer Systronics 34215. Infrared spectra were taken with a Bruker FT-IR. X-ray diffraction measurement was carried out using Diffractometer system XPERT-PRO with Cu K α radiation ($\lambda = 0.154$ nm) at the scanning rate of 2^o/min. The average crystallite size was calculated from the Scherrer's formula²¹. The SEM of polymer samples has been scanned at 12000X magnification by FEI Quanta FEG 200 High Resolution SEM. The thermal studies were carried out on SDT Q600 V8.3 build 101 with the heating rate of 10^oC min⁻¹ under nitrogen atmosphere and Ea were calculated from the thermograms using Sharp-Wentworth, Freeman-Carroll methods²².

Synthesis and Chemical modification of poly acrylic acid: Poly acrylic acid (PAA) was synthesized through a radical polymerization using hydrogen peroxide²³ as radical initiator

and chemically modified using ammonium persulphate as an oxidant. An aliquot from the reaction mixture was taken at the end of each hour and the absorbance value was observed to calculate the percentage of substitution^{24,25}.

Results and Discussion

Degree of substitution: The degree of substitution of dihydroxybenzene in PAA increases with time. It is because the dihydroxybenzene moieties gradually increase with the removal of the carboxylic group present in the PAA figure-1. At the end of 7th hour, the degree of substitution was found to be 84%, 91% and 87% for modified PAA/CAT, PAA/HQ and for PAA/CAT-HQ. The higher substitution in PAA/HQ is also proved by the lower Ea values.

UV FT-IR spectra: The absorption bands of poly acrylic acid at 264 nm is due to $n \rightarrow \pi^*$ transition of and the band at 365, 296 and 288 nm in chemically modified poly acrylic acid with catechol, hydroquinone and catechol-hydroquinone is due to $\pi \rightarrow \pi^*$ transition²⁶ and the corresponding spectra are given in figure-2.

FT-IR spectra: The FT-IR spectra of the PAA and PAA modified with catechol/Hydroquinone and catechol-hydroquinone are presented in figure-3. Due to the incorporation of the dihydroxybenzene moieties into the poly acrylic chain the intensity of the acid O-H stretching band was enhanced around 3500cm^{-1} . A shoulder-looking band around $1300\text{-}1400\text{cm}^{-1}$ is assigned to O-H deformation vibration mode of the dihydroxybenzene. When compared with PAA there exists a broadening at 1625 and 1800cm^{-1} due to substitution of the aromatic group. The presence of band at 755, 876, and two

bands at 755 and 857 confirms the presence of catechol, hydroquinone and both catechol and hydroquinone moieties attached to the PAA chain²⁷.

Molecular weight: The average molecular weight of PAA, PAA/CAT, PAA/HQ and PAA/CAT-HQ are represented in the table-1. The intrinsic viscosity (η) Voluminosity (Ve) and the simha shape factor (v)^{24,28} were calculated. The simha shape factor value was approximately 12.5 shows asymmetric prolate ellipsoid shape²⁹ for the macromolecules. The table clearly illustrates that as the intrinsic viscosity increases the molecular weight increases in the case of PAA/HQ and the polymer exists in an elliptical shape with rod like arrangement in solutions. It is observed that as the percentage of substitution increases, the average molecular weight also increases linearly from pure PAA to chemically modified PAA. The higher branches and longer chain lengths of PAA on the backbone of PAA leads to the higher molecular weight of the chemically polymer³⁰.

X-Ray Diffraction studies: The XRD spectra of PAA and chemically modified PAA are given in figure-4 and different parameters calculated from the spectra are presented in table-2. The poly acrylic acid is amorphous in nature, whereas in the chemically modified PAA/CAT found to have a small peak at 16.3° , d-spacing 5.40628\AA , with the crystalline size of 0.70 nm. The 100% relative intensity exists at 23.5° and 65.3° with the d spacing of 3.77695\AA , 1.42871\AA with the crystalline size of 0.33nm and 0.54nm for PAA/HQ and PAA/CAT-HQ. From the XRD studies it was confirmed that the synthesized chemically modified polymer exhibits polycrystalline nature which is evident from the sharp peaks³¹.

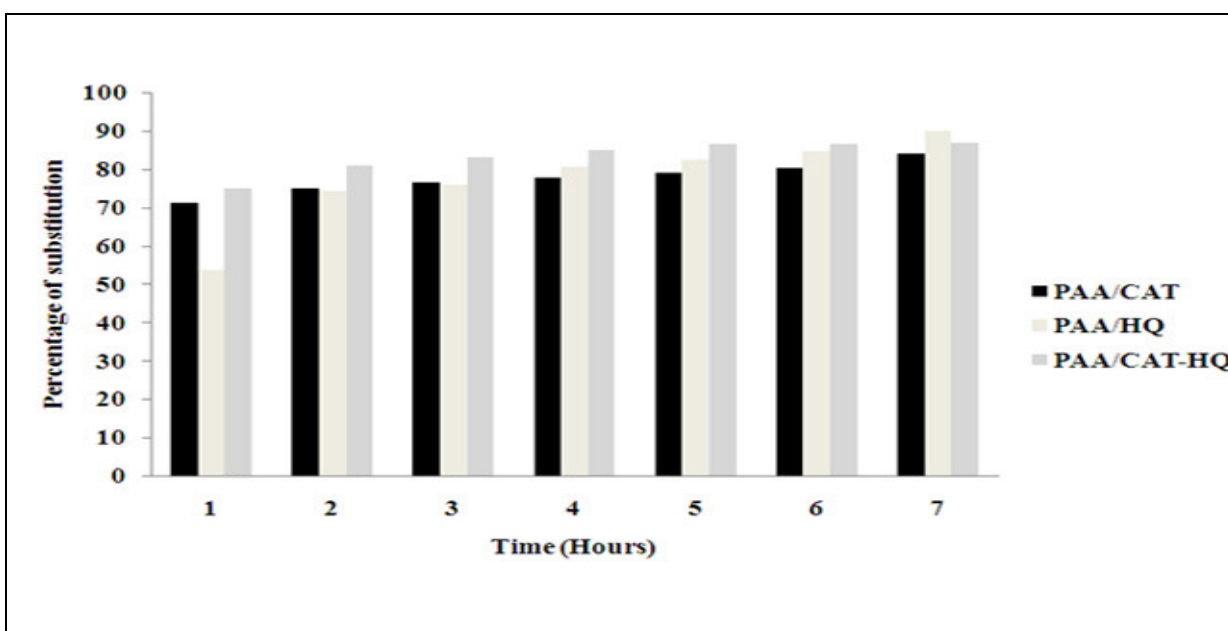


Figure-1
Effect of time on the percentage of substitution in chemically modified PAAs

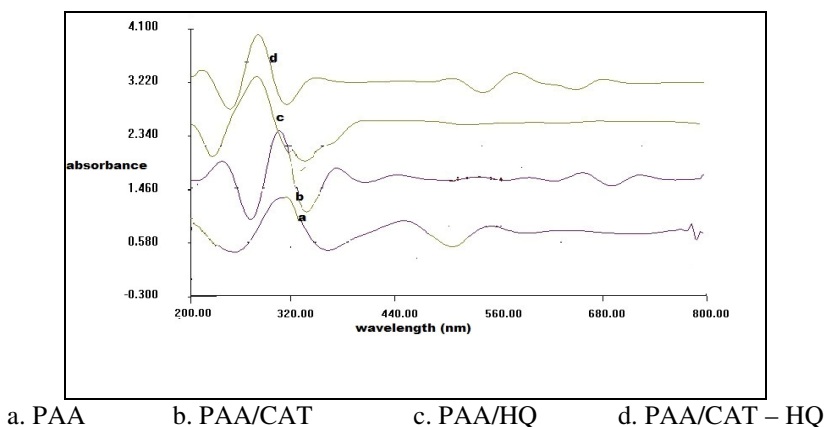


Figure-2
UVspectra of PAA and Chemically modified PAA

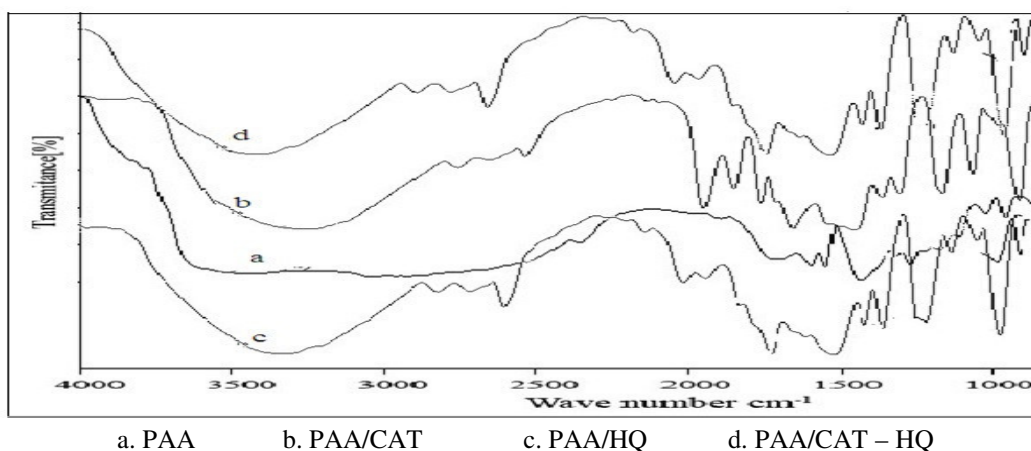


Figure-3
IR spectra of Poly Acrylic Acid and Chemically modified Poly Acrylic Acids

Table-1
Comparison of Molecular weight, intrinsic viscosity, Voluminosity, Shape factor of PAA and chemically modified PAA at 30^oC

Polymer	η dl g ⁻¹	Mw(g/mol)	(Ve)	(v)
PAA	0.58	5.8x10 ⁵	0.06	9.6
PAA/CAT	0.74	9.3 x10 ⁵	0.05	12.3
PAA/HQ	0.77	1.01x10 ⁶	0.06	15.4
PAA/CAT-HQ	0.75	9.6x10 ⁵	0.05	12.5.

Table-2
XRD data for the calculation of crystalline size

Polymer	2 θ (°)	Height [cts]	FWHM Left 2 θ (°)	d-spacing [Å]	Rel. Int. [%]	Crystallite size (nm)
PAA/CAT	16.3830	30.21	0.6000	5.40628	100.00	0.69803
	23.5555	44.36	0.5904	3.77695	100.00	0.333287
	25.1190	7.64	0.5904	3.54530	17.23	0.234914
PAA/HQ	35.7939	4.09	0.4920	2.50869	9.22	0.486385
	51.9364	10.85	0.5904	1.76065	24.46	0.350172
	60.2254	7.73	0.5904	1.53664	17.42	0.888498
PAA/CAT-HQ	77.3485	2.13	0.5904	1.23371	4.81	0.418692
	60.0376	1.71	0.5904	1.54100	20.62	1.359439
	65.3134	1.21	0.7872	1.42871	14.60	0.543661

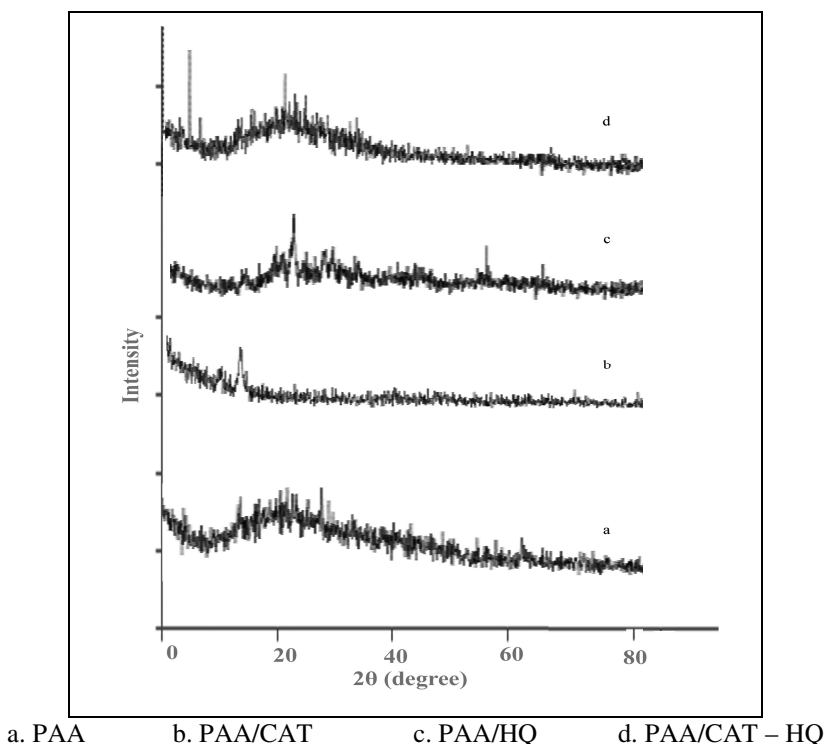


Figure-4
XRD of PAA and chemically modified Poly Acrylic Acid

SEM Analysis: The SEM images from the figure-5 shows PAA has lamellar arrangement with amorphous surface nonporous solid microstructure and for PAA modified with catechol shows bird nest like polymeric arrangement. The SEM micrograph for the polymeric intermediate prepared with chemically modified PAA/HQ showed polymeric solid structure with big voids and this may be due to the functionalization of hydroquinone moiety into the poly acrylic acid matrix. The better polymerization in PAA/HQ is consistence with FT-IR, XRD and the highest percentage substitution UV absorbance studies. The polymeric flakes with large number of micro voids exists a porous nature in PAA/CAT-HQ³².

Thermo Gravimetric Analysis studies: The Thermo Gravimetric Analysis of the prepared polymers is presented in figure-6 and in the three chemically modified PAA namely PAA/CAT, PAA/HQ and PAA/CAT-HQ, the first degradation peak is due to the radical transfer occurred at 150°C. After the H-H scission, some termination occur leading to unsaturated ends which degrades around 270°C. The third step was due to the degradation initiated by the radical transfer to the unsaturated ends formed in the second stage. Since there is no simultaneous decrease of the second and third transition no coupling took place and the fourth transition occurred at 600°C would correspond to the random scission of the polymeric chains. The side-chain elimination could not be an initiation route for depropagation because of the amount of chars produced³³. It is noticed that for the chemically modified PAA studied in the present work, the amount of char did not exceed

to 1% in the case PAA/HQ, PAA/CAT-HQ but in the case of PAA/CAT the char was found to be 1.79%. The char obtained substantiates that the initial route for depropagation took place without the side chain elimination.

The activation energy calculated from the TGA curve for PAA and chemically modified PAA are found to be 13.42, 11.26 and 13.09 KJ/mol by Sharpwent Worth method and 17.06, 15.5 and 16.5 KJ/mol by Freeman Carroll method for PAA/CAT, PAA/HQ and PAA/CAT-HQ. The various kinetic parameters represented in the table 3, calculated by Freeman-Carroll method are about same, indicating common mode of decomposition reaction. The plots of Sharp Wentworth method and Freeman-Carroll method are represented in the (figure-7, 8, 9). Abnormally, the low values of frequency factor may be indicated that the decomposition reaction can be classed as slow reaction. The slow reaction is also predicted by negative values of entropy change. The negative values indicate that the disorder is less and the reaction is carried by more orderly manner, making it slower. The graphs obtained by Sharp-Wentworth and Freeman-Carroll methods are liners by ignoring some abnormal points, indicating that the decomposition does not obey first order kinetics. The comparative parameters of Ea, free energy change and frequency factor show that PAA/CAT is found to be thermally more stable than the PAA/HQ and PAA/CAT-HQ³⁴.

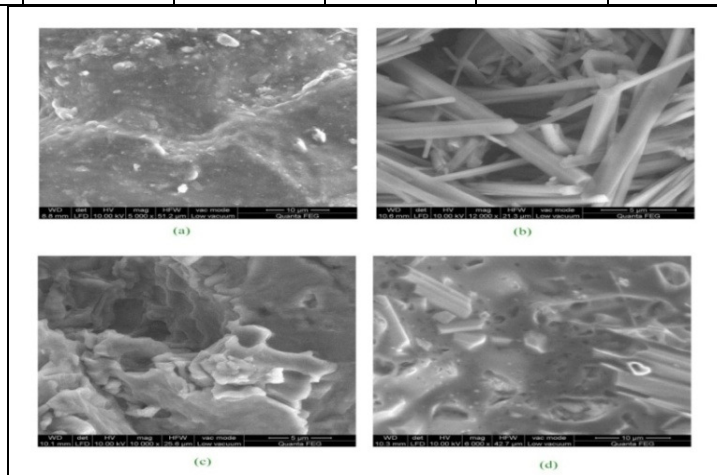
Differential Scanning Calorimetry Studies: The different phase temperature was observed from DSC curve figure-10 The DSC curve of unmodified PAA, the Tg was observed at

127°C³⁵. Upon modification with PAA/CAT, PAA/HQ and PAA/CAT-HQ, the Tg of PAA/HQ increases gradually with increasing HQ content. It also indicates that original carboxylic acid association could be a main factor to keep a relatively higher Tg in unmodified PAA. The Tg of PAA/CAT was 88°C, and an endothermic peak at 419°C was observed related to crystalline temperature (Tc) with the ΔH of 904.4 J/g. The exothermic peak at 686 °C correlates with the melting temperature (Tm) of the polymer and has the ΔH value of 161 J/g. The Tg of chemically modified PAA/HQ was 159°C with

the ΔH of 105.9 J/g, the Tc 323°C with the ΔH of 291.1 J/g, and Tm was 448°C with ΔH of 146 J/g. In the case of PAA/CAT-HQ, the second endothermic peak appeared at 281°C with the ΔH= 136.6 J/g which corresponds to the Tc. The absence of endothermic peak in PAA/CAT-HQ after 323°C relates to the lack of melting process of the crystalline fraction which further confirms the presence of strong interactions between the polymeric back bone and the aromatic moiety³⁶.

Table-3
Kinetic parameters calculated from the Thermogravimetric analysis

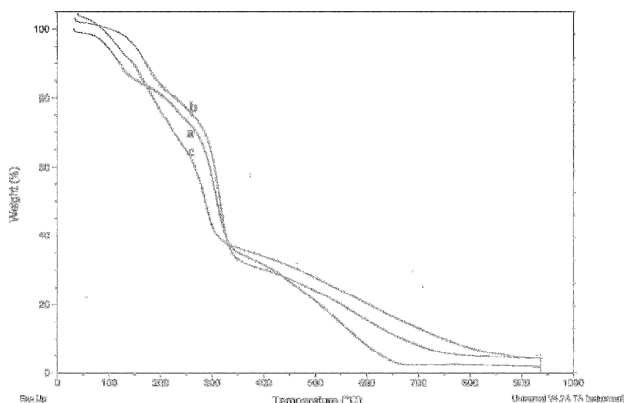
Polymer	Half decomposition temperature (K)	Ea (KJ/mol)		Entropy Change ΔS(J)	Free Energy change ΔF(KJ)	Frequency Factor (sec)	Apparent Entropy Change ΔS*	Order of reaction found (n)
		Freeman-Carroll method	Sharp-Wentworth h method					
PAA/CAT	573	17.06	13.42	-277.6	230	181	-55.78	1.2
PAA/HQ	583	15.59	11.26	-266.5	190	166	-55.89	1.4
PAA/CAT-HQ	553	16.51	13.09	-229.6	194	96	-56.11	1



a. PAA b. PAA/CAT c. PAA/HQ d. PAA/CAT – HQ

Figure-5

SEM images of of PAA and chemically modified Poly Acrylic Acids



a. PAA/CAT b. PAA/HQ c. PAA/CAT – HQ

Figure-6

TGA of Chemically modified Poly Acrylic Acids

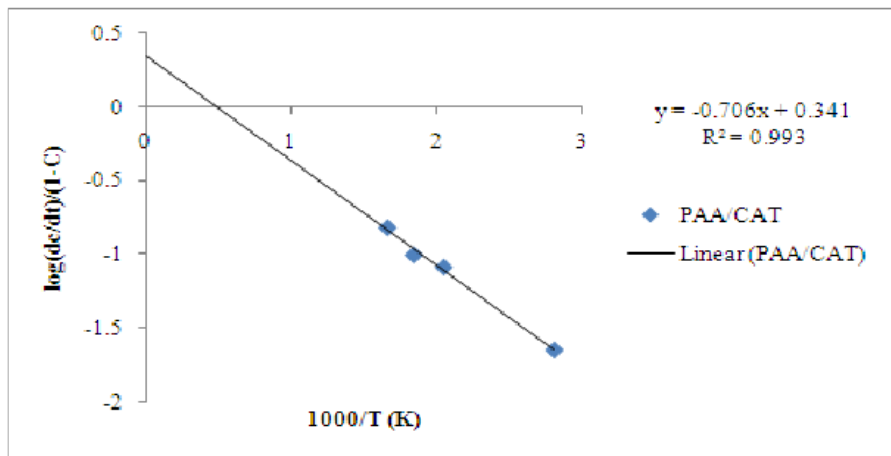


Figure-7
Sharp-Wentworth plot of PAA/CAT

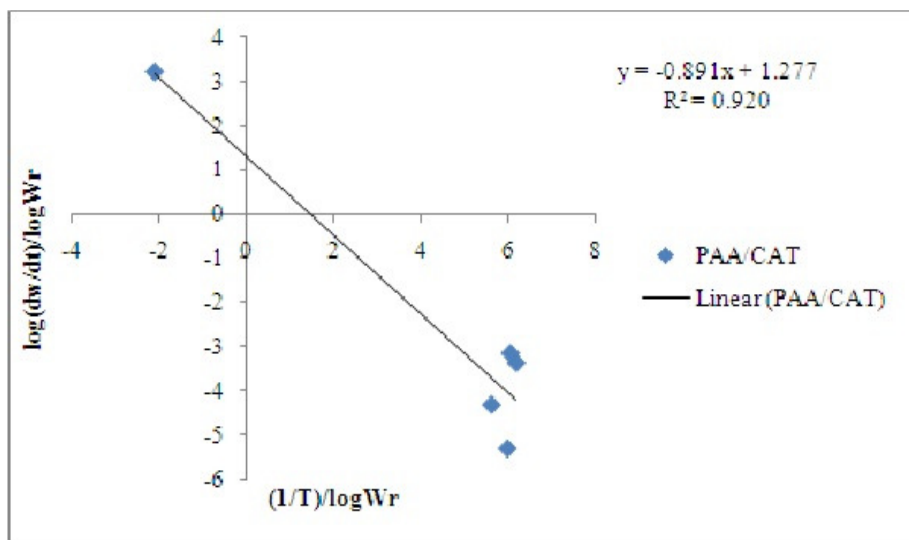


Figure-8
Thermal activation energy (Freeman- Carroll) plot of PAA/CAT

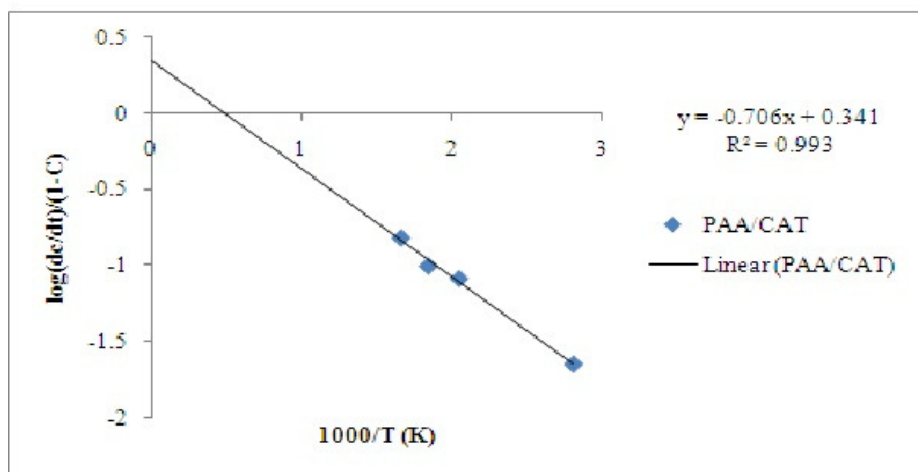
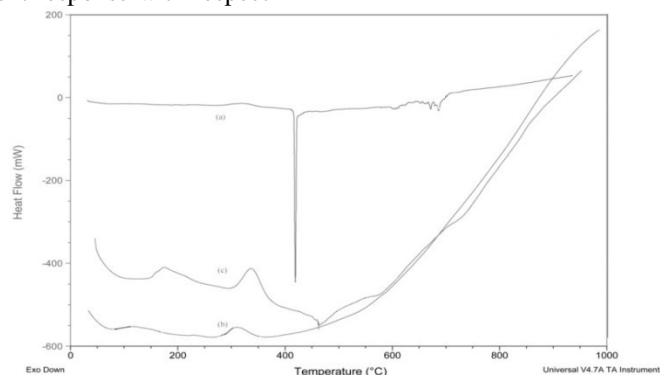


Figure-9
Freeman-Carroll plot of PAA/CAT

Cyclic voltammetry studies: The cyclic voltammograms of the chemically modified PAA is given in figure-11 and their corresponding potential differences are presented in table-4. The well defined votammograms were obtained in the case of PAA/CAT. In acidic medium, the current response with respect

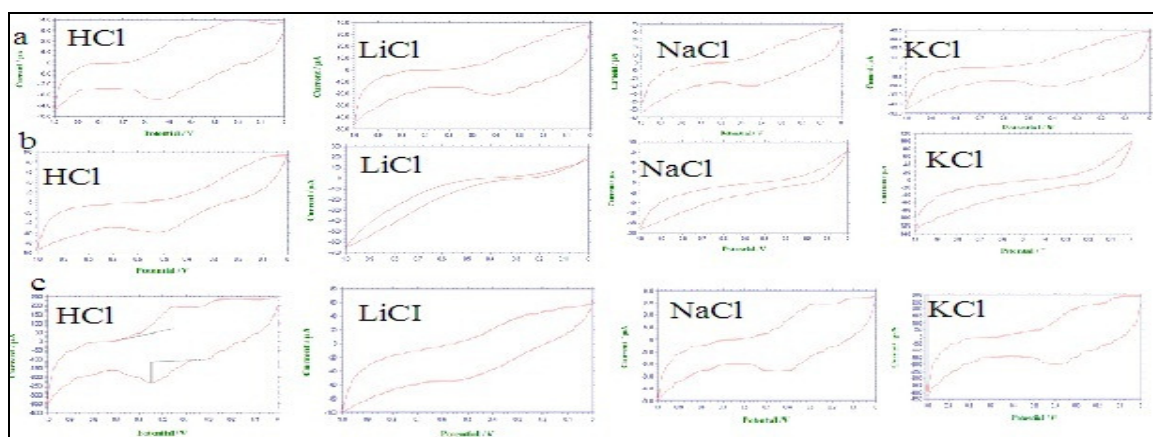
to the potential difference was quiet good when compared to the other electrolytes. This is due to the doping and de-doping of the H⁺ ion in to the polymeric matrix coated over the electrode surface³⁷.



a. PAA/CAT b. PAA/HQ c.. PAA/CAT – HQ

Figure-10

DSC of Chemically modified Poly Acrylic Acids



a. PAA/CAT b. PAA/HQ c. PAA/CAT – HQ

Figure-11

CV studies for chemically modified PAA with Catechol, Hydroquinone, Catechol-Hydroquinone with different electrolytes

Table-4
Comparison of potential difference of chemically modified PAA

Polymer	Electrolyte (0.1M)	E _{pa} (V)	E _{pc} (V)	ΔE _p	I _a (µA) x10 ⁻⁵	I _c (µA) x10 ⁻⁵
PAA/CAT	HCl	0.5516	0.4623	0.0893	-2.051	1.429
	LiCl	0.8197	0.2945	0.5252	-2.395	1.946
	NaCl	0.7720	0.2615	0.5105	-3.350	2.818
	KCl	0.8161	0.2720	0.5441	-2.358	2.003
PAA/HQ	HCl	0.0779	0.4549	0.377	-2.324	1.934
	LiCl	No well defined peaks				
	NaCl	No well defined peaks				
	KCl	0.45	0.488	-0.04	-3.298	1.229
PAA/CAT-HQ	HCl	0.5492	0.4476	0.1016	-2.324	1.934
	LiCl	No well defined peaks				
	NaCl	0.4304	0.2933	0.1371	-2.528	2.874
	KCl	0.2369	0.1084	0.1285	-1.002	2.868

Conclusion

The PAA and the modified PAA were synthesized by oxidative decarboxylation process and they were characterized using different spectroscopic techniques like UV, FT-IR and show the substitution of dihydroxy benzene moieties in the PAA backbone. The thermal study shows that the synthesized polymers were thermally stable and the activation energy confirms the decomposition of the polymers with the same mechanism. The SEM study reveals the micro structured nature of the chemically modified PAA. The CV studies confirm that the chemically modified PAA has well defined voltammogram in acidic medium when compared to the other electrolytes.

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