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RESEARCH ARTICLE

Synthesis and Characterization of Novel Cationic Hydrophobic Benzyl Piperazinium Polyelectrolytes: Effect of Counter Ions on the Flocculation Efficiency

M. Dharani, S. Balasubramanian[*]
Department of Inorganic Chemistry, University of Madras
(Guindy Campus), Chennai-600025, India.

Manuscript Info   Abstract

S. Balasubramanian
bala2010@yahoo.com

Water soluble poly (4-acryloyl 1-benzyl) piperazinium polyelectrolytes with same hydrophobic moiety and variations in their counter ion were synthesized and characterized by Nuclear magnetic resonance (NMR) and Fourier transform - infrared spectroscopy (FT-IR). Thermal stability of the polyelectrolytes determined by TG and DSC analysis indicate that the polyelectrolytes are highly stable (Char yield > 90%). The effect of counter ions on flocculation efficiency is proved by zeta potential measurement and intrinsic viscosity. The polyelectrolytes show its flocculation efficiency in the order of PABPC > PABPP > PABPS> PABPN > PABPB > PABPPC. The optimum amount of flocculant PABPC (poly (4-acryloyl 1-benzyl) piperazinium chloride) for efficient phase separation in dispersions is 60 ppm, at pH 7 with 10 min settling time, which proved by nephelometric turbidity measurements on bentonite clay and chemical oxygen demand (COD), biological oxygen demand (BOD) on industrial waste water

1. INTRODUCTION

Flocculation is one of the simple, cheap and effective techniques, which plays a predominant role in water and wastewater treatment, to remove suspended particles and dyes (1, 2). There are many problems associated with natural organic impurities in water, such as the formation of harmful byproducts (especially trihalomethanes) on chlorination, and the presence of undesirable color, taste, and odor in drinking water. Polyelectrolyte flocculants are widely used in solid–liquid separation processes where colloidal particles fail to settle by themselves to improve the efficiency of sedimentation, clarification, filtration and centrifugation of small particles (3). In polar solvents such as water, these polyelectrolyte groups can dissociate, leaving charges on polymer chains and releasing counter ions in solution. Cationic polyelectrolytes having quaternary ammonium salts are widely used in various fields like treatment of wastewater from city sewer system and industries (4), the concentration or thickening of the sludge in plastic industries (5), paper retention aids (6), mineral processing (7), and controlled release of drugs (8). Even small amount of proper flocculant can show high removal efficiency, which generate a small volume of sludge output (9). Polyelectrolytes often tend to adopt a rather flat adsorbed configuration and in this state their action is mainly through charge effects, including electrostatic patch attraction (10). Random copolymers of acrylamide and the cationic ester formed by quaternization of DMAEA (acryloyloxyethyl) trimethyl-ammonium chloride) with methyl chloride are extensively used in the water treatment plants (11, 12). Polyacrylamide is the basis of many commercial flocculants (13). Piperazine derivatives are a class of materials that are easily available commercially and act as potential drug intermediates. Since there is a gradual increase in demand for new synthetic polymer flocculants that are highly efficient, a new class of piperazine-based polyelectrolytes for wastewater treatment has been synthesized. The mechanism of flocculation of colloidal particles was mostly based on the final results of flocculation, e.g., the residual turbidity, the settling rates and the viscosity (14–16). The application of polyelectrolytes as flocculating agents is determined by the chain flexibility, solubility, molecular weight, and charge density.

In the present study, we are reporting the synthesis and characterization of six different cationic piperazinium polymers with chloride, phosphate, sulfate, bromide, perchlorate and nitrate as counter ions. The polyelectrolytes were characterized by IR and NMR spectral techniques and the thermal stability of these polyelectrolytes was

investigated by TGA, DSC analysis. The effect of counter ion on zeta potential, viscosity, COD, BOD and turbidity were also investigated.

2. EXPERIMENTAL

2.1 Materials and methods

Piperazine derivatives were purchased from Catapharma chemicals private limited, Maharashtra, India. Acryloyl chloride was synthesized from acrylic acid and benzoyl chloride by the reported procedure and was used after re-distillation (17). Triethylamine and common solvents such as tetrahydrofuran and acetone were distilled before use and mineral acids like hydrochloric acid, hydro bromic acid, nitric acid, sulphuric acid, perchloric acid and phosphoric acid were purchased from Merck (India) limited and were used without any further purification.

2.2 Synthesis of Monomers and polymers

2.2.1 Synthesis of 4-acryloyl 1-benzyl piperazine

Benzyl piperazine (10.00 g, 0.0567 mol) and triethylamine (8.59 g, 0.0850 mol) were dissolved in DCM (250 mL) in a round-bottom flask and maintained at 0^oC in an ice bath. Acryloyl chloride (7.65 g, 0.085 mol) dissolved in DCM (50 mL) was added drop wise over a period of 1 h. The reaction mixture was allowed to stir for 12 h at room temperature. The resulting clear solution was washed with water (100 mL), the organic layer was separated and washed with 1M $KHSO_4$ (100mL, 2 times) and $NaHCO_3$ (5% solution, 100 mL) respectively. The organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure to get a pale yellow liquid (Yield: 9.17g, 70%)

2.2.2 Synthesis of 4-acryloyl 1-benzyl piperazinium salts

To the solution of 4-acryloyl 1-benzyl piperazine (3.0 g, 0.0129mol) dissolved in dry THF (10 mL) at $0 \ ^oC$ in an ice bath, the desired mineral acid (HCl = 1.57 g, HBr = 2.15 g, H_2SO_4 = 1.29g, HNO_3 = 1.25g, $HClO_4$ =1.85 g, H_3PO_4 =1.29 g) dissolved in THF (20 mL) was added slowly. The resulting mixture was allowed to stirr at room temperature for 1 h. The precipitated salts were filtered and dried in a vacuum desiccator and stored under vacuum. Yield: 75–85%. [(PABPC) 2.7 g, (PABPB) 3.0 g, (PABPS) 3.6 g, (PABPN) 2.8 g, (PABPPC) 3.2g and (PABPP) 3.6g]

2.2.3 Synthesis of 4-acryloyl 1-benzyl piperazinium polymers

The polymers were synthesized by free radical initiator pathway. The general procedure for the synthesis of polymers is described below. 4-acryloyl-4-benzyl piperazinium salt (2.5-3.5 g, 0.01 mol) and the free radical initiator potassium peroxydisulfate (1 wt. %) were dissolved in distilled DMSO, (50mL) kept in a polymerization tube and flushed with nitrogen for 15-20 min. The solution was heated at 60°C for 8 h and then allowed to cool to room temperature. The polymer was precipitated by the addition of methanol, filtered and dried in a vacuum oven at 50° C. Yield: 60–85% (PABPC 2.3g, PABPB 2.1 g, PABPS 2.4 g, PABPN 1.9 g, PABPPC 2.45g, PABPP 2.3g)

2.2.4 Spectral studies

All the synthesized monomers and polymers were characterized by IR, Mass and NMR spectral studies. The infrared spectra were recorded on a Shimadzu FTIR 8300 spectrophotometer in the range of 4000–400 cm^{-1} by KBr disk method. The ^{1}H NMR spectra were recorded on a Bruker 400MHz NMR spectrometer. The spectra were recorded in $CDCl_3$ using tetramethylsilane as a reference. D_2O was also used in some cases. The Mass spectra were recorded using Thermo Finnigan - ESI Mass Spectrometer.

2.2.5 Thermal Studies

Thermo Gravimetric Analysis (TGA) was carried out using a Seiko model SSC 5200H thermal analysis system attached to a TG 220 module. All the experiments were carried out under nitrogen atmosphere, with a gas flow rate of 100 mL/min. The thermal analyzer was calibrated using calcium sulfate as standard. Differential Scanning Calorimetry was performed on a Seiko SSC 5200 H thermal analysis unit attached to the DSC 220 module. The experiments were carried out under nitrogen atmosphere, with a nitrogen flow rate of 50 mL/min. The temperature of the sample was varied in the range of 30–400°C, at a heating rate of 10°C/min.

2.2.6 The Zeta potential (ξ) measurements

The zeta potential **(ξ)** measurements of the polyelectrolytes in distilled water (polyelectrolyte=1mg/mL) were performed on a Malvern Zetasizer Nano-ZS ZEN3600.

2.2.7 Viscosity Studies
The intrinsic viscosity of the samples was determined by Ubbelohde viscometer, at constant temperature (30 ± 0.2) °C with the flow time was 60 sec (the time of DD water being 242.3± 0.1 Sec). Polymer stock solutions were prepared by dissolving 50 mg of the polymer in 100 mL of distilled water.

2.2.8 Flocculation studies
Flocculation efficiency of polyelectrolytes was ascertained with bentonite suspensions. The tests were carried out in a 100 mL graduated cylinder. Different doses of polymer were added to a bentonite suspension (1000 ppm), stirred for 2 min and kept aside for 10 min without any disturbance. The supernatant liquid was taken out by a long needle syringe for the measurement of turbidity.

2.2.9 COD and BOD Studies
The flocculation efficiency of the polyelectrolytes was also investigated by COD and BOD measurements (18). The amount of oxygen needed to consume the organic and inorganic materials is called the Chemical Oxygen Demand (COD). The oxygen required for the degradation of the organic matter biologically is called the Biochemical Oxygen Demand (BOD). There exists a definite correlation between the COD and BOD under certain conditions and by determining the COD, the information about the BOD of the water/waste water can be derived. Potassium dichromate is considered the best oxidant due to its strong oxidizing ability, its applicability to a wide variety of samples and ease of manipulation. COD [1] and BOD [2] can be calculated by the following equation:

$$COD = 8000 * (V_{bl} – V_s)* M/ \text{ original volume of sample taken mg/l} \ldots\ldots\ldots\ldots \quad [1]$$
Where,
V_{bl} = Titer volume for the blank
V_s = Titer volume for the sample
   M = Molarity of FAS titrant

$$BOD \text{ mg/l} = (\text{Initial DO} - DO_5) \text{ x Dilution Factor} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad [2]$$
 Where,
   Dilution Factor = Bottle Volume (300 ml)/Sample Volume

3. RESULTS AND DISCUSSION
3.1 Polyelectrolyte characteristics
## 3.1.1 Synthesis and spectral studies

All the synthesized polyelectrolytes **(Scheme. 1)** were pale white in color, highly soluble in water and insoluble in organic solvents like benzene and toluene. The formation of the polyelectrolytes was confirmed by FT-IR and NMR spectroscopic techniques. The FT-IR spectral studies of 4-acryloyl 1-benzyl piperazine and 4-acryloyl 1-benzyl piperazinium salts confirm the presence of expected functional groups.
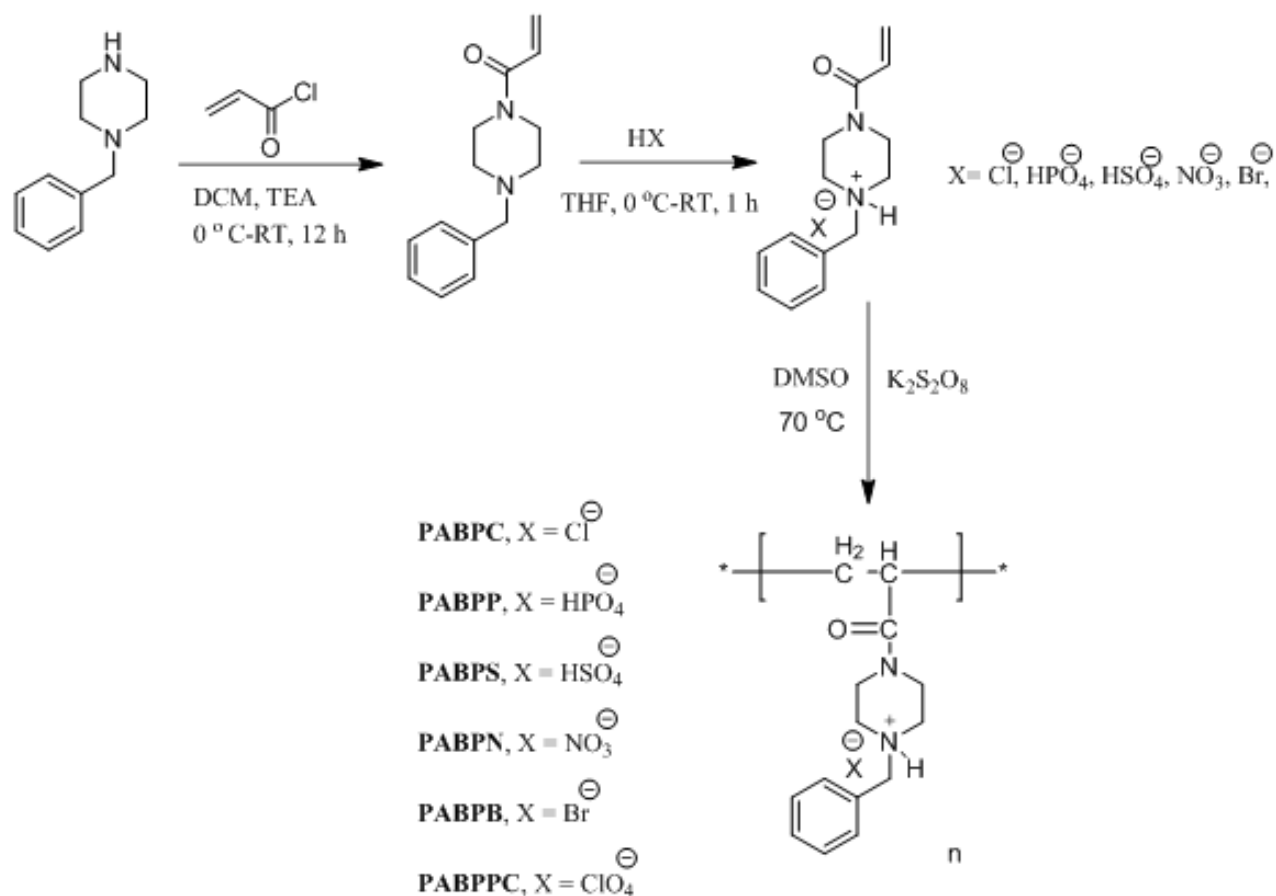
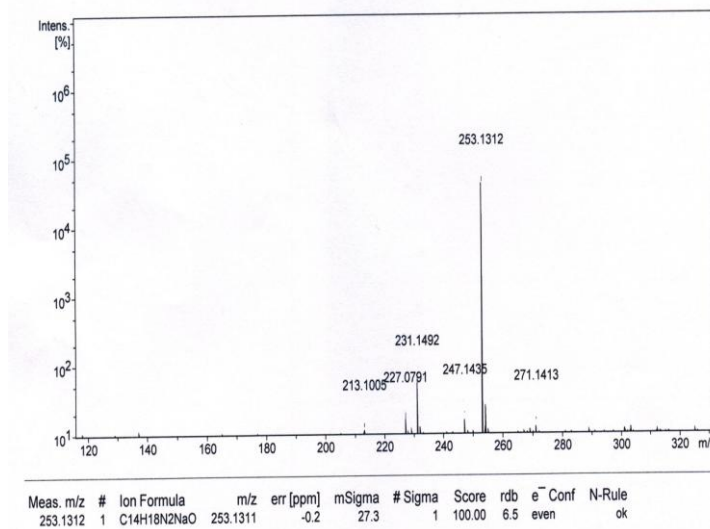**Scheme. 1 Synthesis of Polyelectrolytes PABPC, PABPP, PABPS, PABPN, PABPB, PABPPC**

FT-IR:

The absorption bands around $1640cm^{-1}$ corresponding to the stretching frequency of the carbonyl group (-C=O), N-H stretching frequency around $3400cm^{-1}$ and the stretching frequency of acryloyl (-C=C-H) observed at 800-900cm^{-1}(reference to be included) confirm the formation of 4-acryloyl 1-benzyl piperazine (**Figure 1a**). The disappearance of acryloyl peak (-C=C-H) at 800-990 cm^{-1} in the FT-IR spectrum of polymer (**Figure 1c)** indicates that unsaturated (-C=C-H) system became saturated (-C-C-H), which shows the conversion of monomer in to polymer.
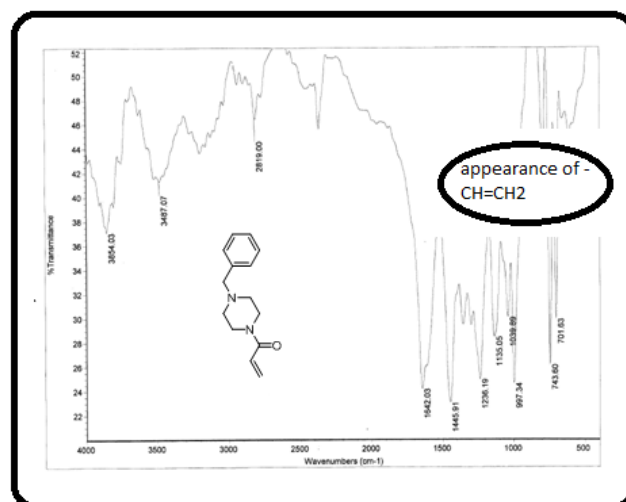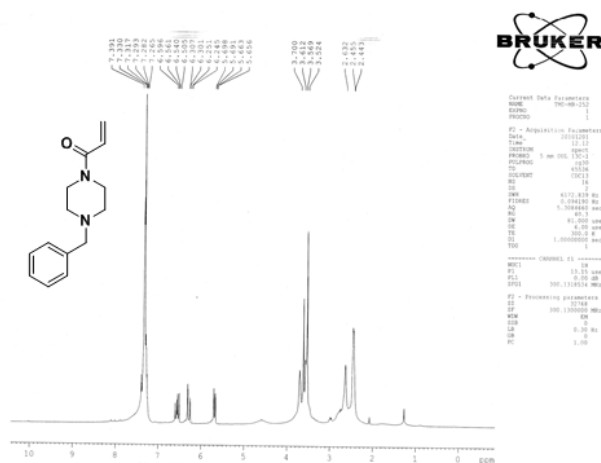
Figure 1a.IR spectrum of N-acryloyl N-benzyl piperazine
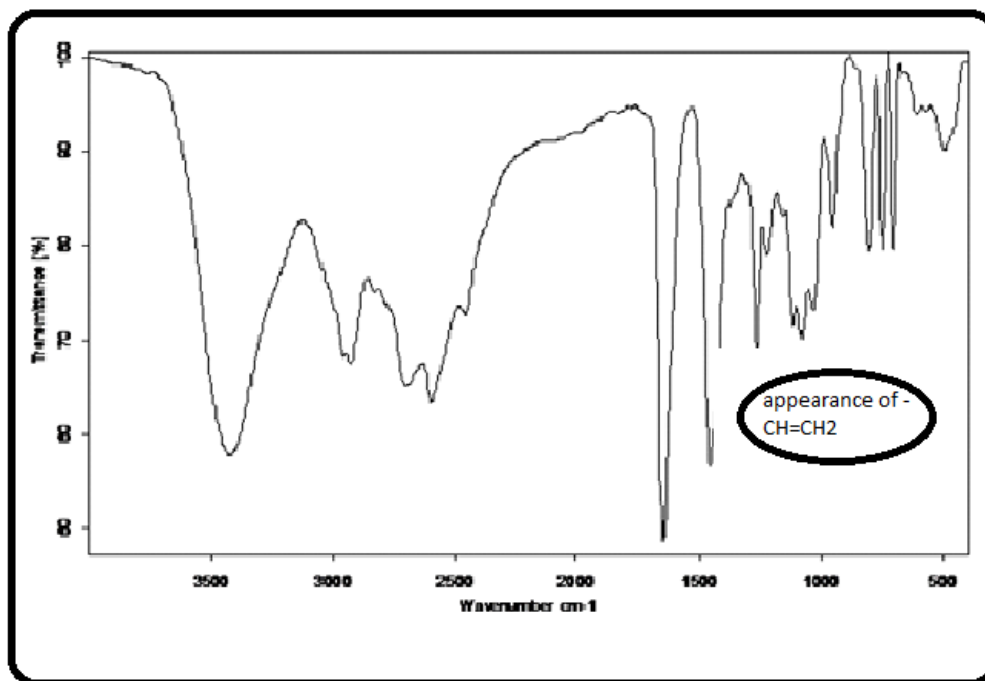
Figure 1b IR spectrum of N-acryloyl N-benzyl piperazinium chloride
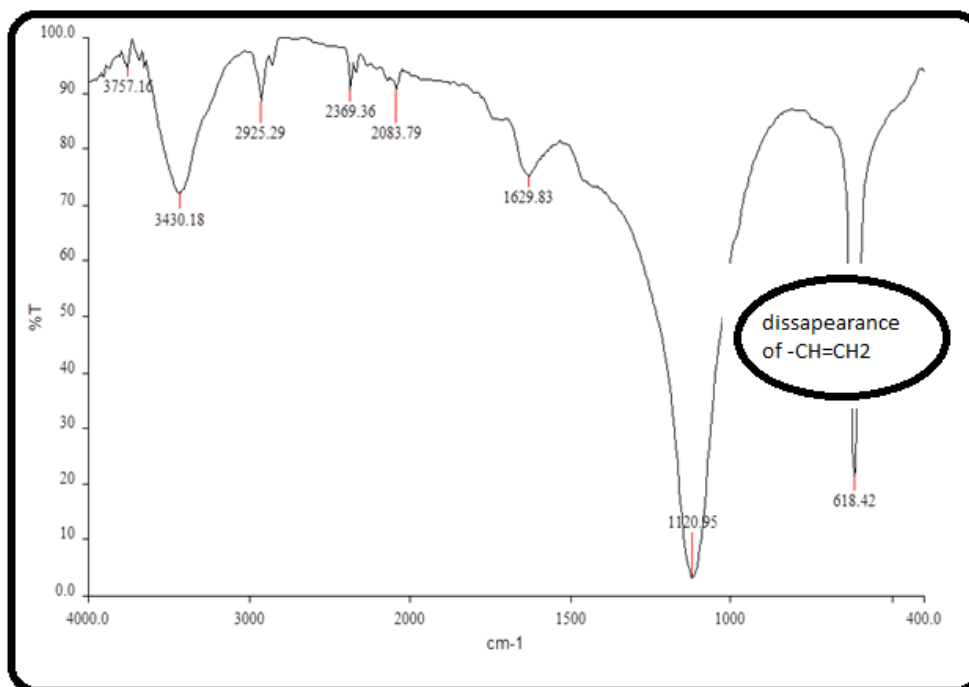
Figure 1c. IR spectrum of polyelectrolyte PABPC

NMR:

The observation of acryloyl proton CH_2=CH–C=O resonances at δ 5.68 ppm (dd, 1H, J = 2.1 Hz), CH_2=CH–C=O resonances at δ 6.28 ppm (dd, 1H, J = 1.8 Hz) and CH_2=CH–C=O resonances at δ 6.53 ppm (dd, 1H, J= 10.5 Hz) in the ^{1}H NMR spectrum of 4-acryloyl 1-benzyl piperazine (**Figure 3)** confirms the formation of the desired product. The aromatic C-H protons appeared in the range of δ 7.2-7.4 ppm (m, 5H) and benzyl CH_2 protons Ph-**CH₂**-N and piperazine –(**CH₂**)₂-N-C=O protons resonances together at δ 3.4-3.7 ppm (m, 6H) and Ph-CH₂-N-(**CH₂**)₂ protons is observed at δ 2.4 to 2.7 ppm (m, 4H). The formation of the 4-acryloyl 1-benzyl piperazine is further confirmed by ESI-MS analysis. This compound shows M+H peak at m/e 232 as a molecular ion peak as well as base peak. (**Figure 2**).The similar ^{1}H-NMR pattern is observed even in the case of 4-acryloyl 1-benzyl piperazinium chloride The polymerization of 4-acryloyl 1-benzyl piperazinium chloride is confirmed by the disappearance of acryloyl proton peaks resonated at δ 5.5-6.8 ppm (**Figure 4**). The acrylic protons which were observed in the range of δ 5.5-6.8 shifted to δ 2.5-2.8 range and are merged with piperazine protons. (twosinglets, 14H). The aromatic protons of the synthesized polymer appeared as a singlet at δ 7.5 ppm (S, 5H)**.**

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
253.1312	1	C14H18N2NaO	253.1311	-0.2	27.3	1	100.00	6.5	even	ok

Figure 2. The mass spectrum of 4-acryloyl 1-benzyl piperazine (Methanol)

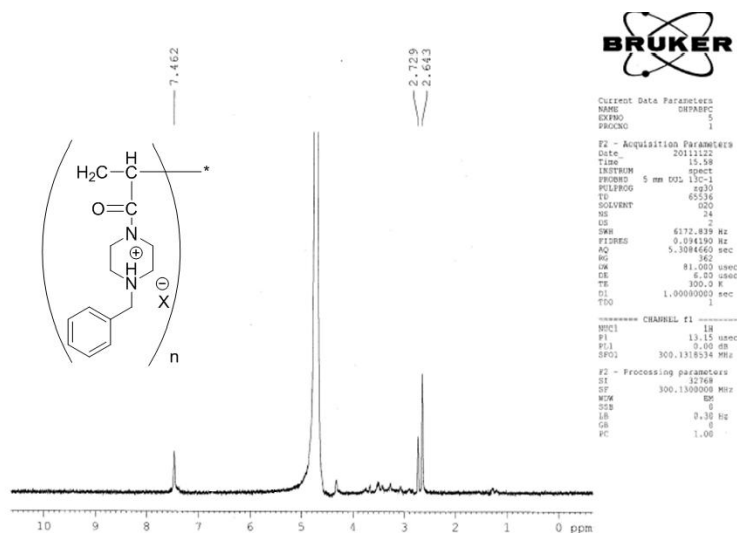**Figure 3.^{1}H NMR spectrum of 4-acryloyl 1-benzyl piperazine (CHCl₃)**

Figure 4. ¹H NMR of poly acryloyl benzyl piperazinium chloride (D₂O)

3.2 Thermal Studies
3.2.1 TGA and DSC Studies

Thermal behaviour of the polyelectrolytes was analysed by TGA, DSC analysis to investigate the thermal stability of these polyelectrolytes (**Figure 5, 6).** The TGA curve of the polyelectrolytes clearly indicates that all the polyelectrolytes are thermally stable and that the polymers undergone only a mild degradation in different stages. The experiments were conducted in the nitrogen atmosphere and all the samples leave a definite amount of residue after the complete degradation process.
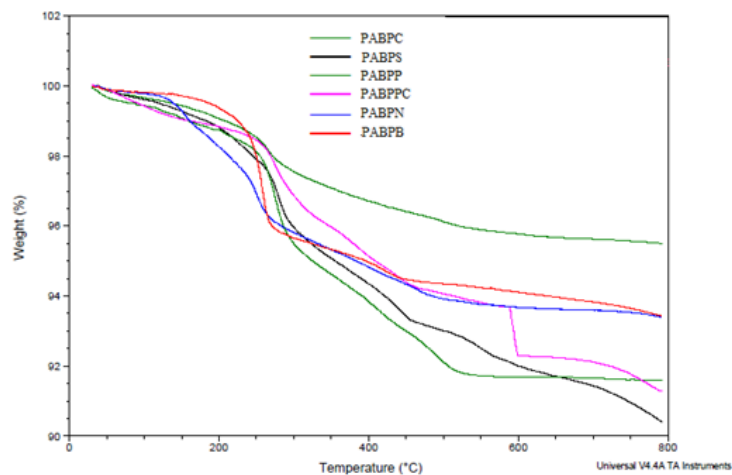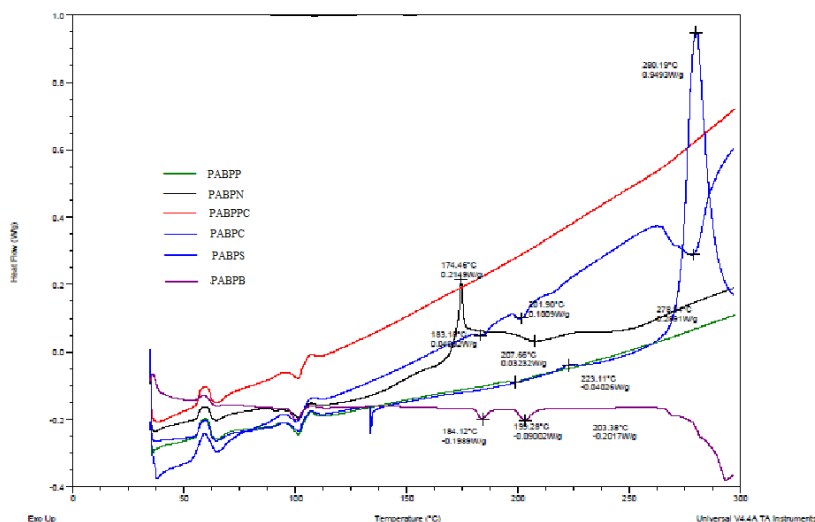

Figure 5. The overlaid thermogram of polyelectrolytes

Figure 6The overlaid DSC of polyelectrolytes

All the polyelectrolytes shows maximum weight loss in the range of 100-300°C, this clearly indicates the weight loss of the polyelectrolytes was mainly due to dehydration process or some residual organic solvents. Above 300°C the polyelectrolytes were not showing considerable degradation confirms the effective stability of the polyelectrolytes. Degradation of the polyelectrolytes is very less (<1%) in the range of 400-600° C illustrates that these polyelectrolytes are free from unreacted monomers. The observed Initial decomposition temperature (IDT) of the polyelectrolytes ranging from 100–265°C. In the case of PABPC which undergone decomposition in two stages, and the weight loss of the compound is around 1.5% in IDT. PABPP, PABPB, and PABPPC undergone decomposition in three different stages and its IDT are 247,245 and 248°C respectively. PABPS and PABPN underwent decomposition in three different stages. The char yields of the polyelectrolytes are more than 90%. **(Table 1)**

Table 1. TGA data of the synthesized polyelectrolytes

S. No	Polyelectrolytes	Initial decomposition temperature (C)	Temperature range for each stage (^{o} C)			
			I stage	II stage	III stage	Char Yield % at800^o C
1	PABPC	250	50-170	250-300	300-350	95.5-
2	PABPS	262	100-210	300-450	460-600	90.4
3	PABPP	247	70-200	300-430	410-650	93
4	PABPN	126	50-100	150-300	310-500	95.4
5	PABPB	245	100-190	250-290	320-490	91.6
6	PABPPC	248	100-200	310-450	470-600	91.3

From DSC, the polyelectrolyte PABPN exhibit a sharp exothermic peak corresponds to the phase transition to crystalline nature with the crystallization temperature (T$_C$) at 280.1^o C, similarly PABPC shows the crystallization

temperature at 174.5^o C. The polyelectrolytes PABPS, PABPB exhibit endothermic peaks at 278.9 and 295.2^o C respectively corresponds to their sharp melting points **(Table.2).**

Table 2. DSC data of the polyelectrolytes

S.No	Polyelectrolytes	T_m (^{o}C)	T_c(^{o}C)
1	PABPC		280.1
2.	PABPS	278.9	
3.	PABPP	-	-
4.	PABPN		174.5
5.	PABPB	295.2	
6.	PABPPC	-	-

3.3 Zeta potential (ξ) measurements

TheZeta potential (ξ) values of the polyelectrolytes decrease in the following order: PABPC > PABPP > PABPS> PABPN > PABPB > PABPPC, indicating that counter ion shows considerable effect on polymerization. The measuredZeta potential (ξ) values of the polyelectrolytes (**Table. 3**) clearly indicate that charge density of the polyelectrolytes was more in case of PABPC (9.4±2.2) and PABPP (8.7±1.2) > PABPS (8.1±1.0) > PABPN (6.5±1.4) > PABPB(6.1±1.1) > PABPPC (5.9±1.2).

Table 3. Comparison of Viscosity data, ξPotential of the synthesized polyelectrolytes

| S.No	Polyelectrolytes	Huggins method(dL/gm)	Fuoss method(dL/gm)	Fedors method(dL/gm)	ξ Potential(mV)
1	PABPC	14.095	20.45	14.1243	9.4±2.2
2	PABPP	10.13	18.6	12.1654	8.7±1.2
3	PABPS	4.7173	4.688	4.1254	8.1±1.0
4	PABPN	3.8977	3.635	3.4130	6.5±1.4
5	PABPB	3.2595	3.3145	3.0030	6.1±1.1
6	PABPPC	2.6252	3.045	2.6021	5.9±1.2

3.4 Viscosity Studies

The polyelectrolytic behavior of the above mentioned cationic polymers was obtained by studying their viscosity (19) in dilute aqueous solutions. The intrinsic viscosity of the polyelectrolytes was calculated using three different methods viz. Huggins [3], Fuoss [4] and Fedors [5] equations. (**Figure 7a-c**)
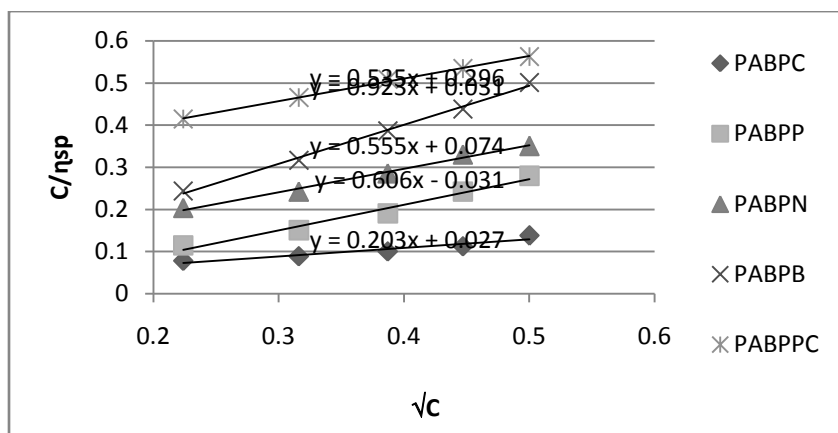
$(\eta_{sp}/C) = [\eta]+K'[\eta]^2C$…………………………………………..[3]
$(C/ \eta_{sp}) = 1/A + B/AC^{1/2}$………………………………………...[4]
$1/[2(\eta_r^{1/2}-1)] = 1/[\eta]C – 1/[\eta]Cm$……………………………[5]
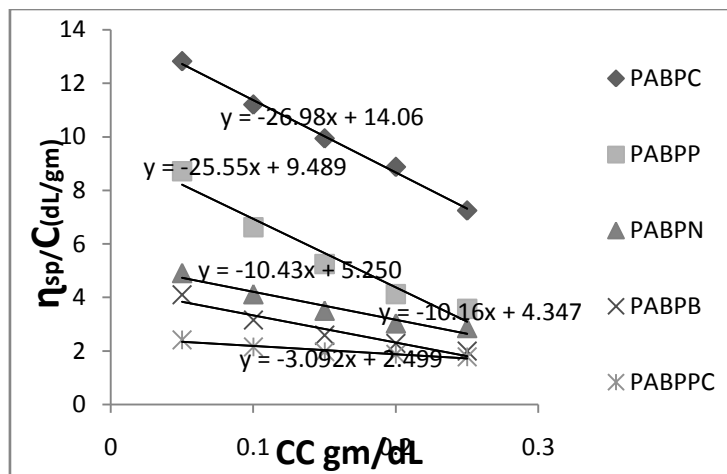
(a)

(b)
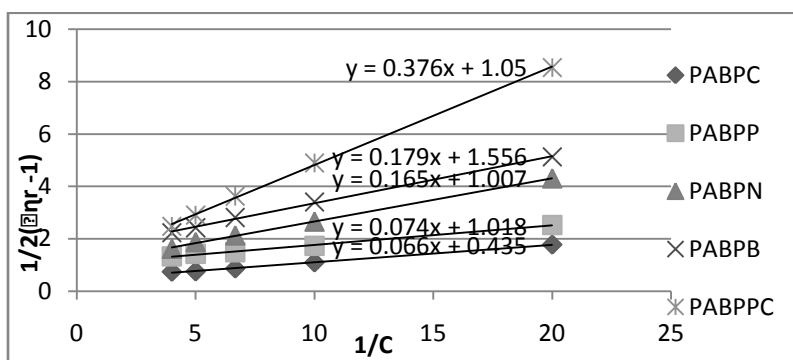
(c)

Figure 7 (a-c) Viscosity plots of Huggins, Fuoss and Fedors.

3.5 Polyelectrolytes behaviour in pure water
The polyelectrolytes showed typical polyelectrolytic behavior. The reduced viscosity of the polyelectrolytes decrease with increase in their concentration. The reduced viscosity as well as the intrinsic viscosity was

investigated in pure water. The observed reduced viscosity values are higher in the case of PABPC in all dilutions indicating that PABPC has high molecular weight compared to that of other polyelectrolytes. The reduced viscosity varies in the following order: PABPC > PABPS > PABPP > PABPN >PABPB > PABPPC.

The intrinsic viscosity of polyelectrolytes was calculated at different concentrations ranging from 0.05 to 0.25 dL/g by Huggins, Fuoss, Fedors methods and the values are tabulated (**Table 3**). In all these methods the intrinsic viscosity of the polymers was high at lower concentrations (0.05-0.1 g/dL) when compared at higher concentrations (0.15-0.25 g/dL). This may be due to the higher degree of dissociation of the polyelectrolytes at lower concentrations resulting in higher charge repulsion of the polymer chains. Even at lower concentrations, the intrinsic viscosity of the polyelectrolytes was highly dependent on the nature of the counter ion

The intrinsic viscosity is found to vary in the following order: PABPC > PABPS > PABPP > PABPN> PABPB > PABPPC, indicating that the charge repulsion among the polymer chains was more in case of PAPBC compared to other members of the series. This may be attributed to the high charge on the PABPC polyelectrolytes. Based on the above observations, it can be suggested that chloride ion facilitates the higher degree of polymerization resulting in high molecular weight and high charge density for PABPC when compared to other polyelectrolytes in the present series. (21)

3.5 Molecular weight calculation
The molecular weight of the polyelectrolytes was determined using Mark-Houwink equation [6]
$$[\eta] = K\,M^{\alpha} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..[6]$$
K and α are constants for a particular solvent. α for water is 0.64.
The calculated values were

$M_{(PABPC)} = 1.7\,M_{(PABPP)} = 5.5M_{(PABPS)} = 7.4_{(PABPN)} = 9.8_{(PABPB)} = 13.7_{(PABPPC)}$
From the calculated values it was clear that molecular weight of the PABPC is high than that of the other polyelectrolytes indicating that degree of polymerization is more in the case of monomer with chloride ion when compared to that of the other counter ions.

3.6. Effect of polyelectrolyte on flocculation efficiency
The flocculation efficiency of the polyelectrolytes was tested towards bentonite suspension. Different dosages of polyelectrolytes were added (10–100ppm) to bentonite suspension (1000 ppm) and the turbidity was measured for supernatant solution to determine the extent of flocculation. The flocculating ability of these polyelectrolytes (**Table 4** and **Figure 8)**, increases initially by increasing the amount of the polyelectrolyte added and reached maximum around 60 to 70 ppm dosage. Interestingly among all the polyelectrolytes PABPC exhibits maximum flocculation behaviour around 60 ppm concentrations when compared with that of other PABP derivatives. PABPC shows better flocculating ability followed by PABPS> PABPP > PABPN > PABPB > PABPPC. This indicates that the nature of counter ion used for the quaternization greatly affects the flocculation efficiency of polyelectrolytes.

Table 4. Turbidity values of polyelectrolytes with Bentonite suspension

Polyelectrolytes	Polyelectrolyte Concentration (ppm)									
	10	20	30	40	50	60	70	80	90	100
PABPC	261	247	159	157	121	54	88	92	97	112
PABPS	378	354	287	257	228	64	78	89	92	96
PABPP	313	307	285	270	163	92	156	155	164	198
PABPN	401	387	364	310	252	176	87	118	176	192
PABPB	484	438	381	287	216	181	67	112	128	136
PABPPC	498	497	472	396	364	217	98	156	162	167
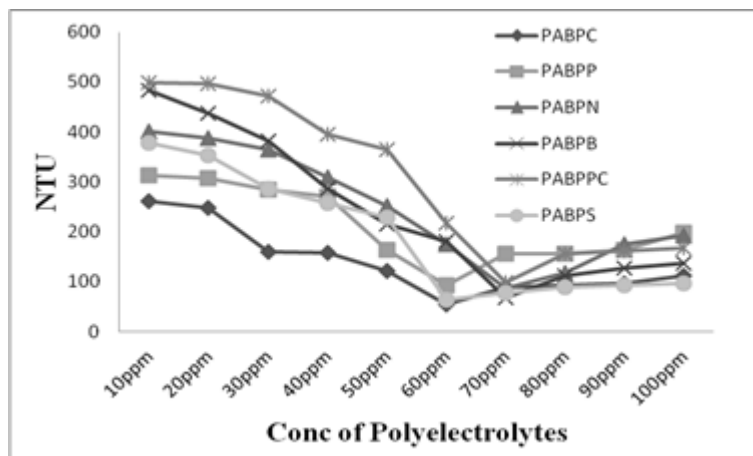
Figure. 8Turbidity Values of Polymers with Bentonite Suspension

The observed flocculation properties of the polyelectrolytes are in agreement with the viscosity and zeta potential (ξ) values. In the case of the PABPC, the chloride counter ion facilitates the polymerization process which results in the formation of larger polyelectrolyte chains there by increase of the molecular weight of the polyelectrolytes and shows more intrinsic viscosity (22) of the polyelectrolyte. The more intrinsic viscosity of the polyelectrolyte results more zeta potential (ξ) values which is attributed to the electrostatic repulsion in the dispersed medium of the polyelectrolyte which directly influence the flocculation efficiency of polyelectrolyte and also an increase of the molecular weight of the polyelectrolytes first results in the formation of larger polyelectrolyte patches, which provide more efficient attractive interactions at partial surface coverage (23), which leads to the efficient flocculation of chloride counter ion. However, further increase in the concentration of polyelectrolyte was not effective to a greater extent.

On the contrary, the turbidity values (**Figure 9**) showed a marginal increase when the concentration of the polyelectrolyte exceeded 80 ppm. This behaviour can be attributed to the deflocculation of the settled particles due to increase in the cationic charge density. The same trend was observed in the case of COD and BOD of industrial effluent (**Tables 5 Figure 10a-b**). It can be concluded that PABPC is the most efficient flocculant for ternary effluents compared to the other polyelectrolytes synthesized as well as some of the commercially available polyelectrolytes.

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**Table5. COD values of polyelectrolytes at different concentrations**

Polyelectrolytes	Polyelectrolyte concentration (ppm)										
	0	10	20	30	40	50	60	70	80	90	100
PABPC	5784	3960	3668	2587	2298	1687	984	997	1018	1032	1094
PABPS	5784	4924	4218	3948	2890	1784	1187	1270	1311	1348	1384
PABPP	5784	4818	4012	3784	2987	2667	1381	1302	1297	1287	1274
PABPN	5784	5241	4647	3941	3218	2542	1384	1321	1317	1301	1287
PABPB	5784	5687	4894	4217	3694	2791	1847	1218	1202	1264	1294
PABPPC	5784	5704	4941	4467	3781	2647	1980	1431	1384	1376	1368

Table 6. BOD values of polyelectrolytes at different concentrations

Polyelectrolytes	Polyelectrolyte concentration (ppm)										
	0	10	20	30	40	50	60	70	80	90	100
PABPC	2214	1380	1241	947	814	621	324	340	347	344	367
PABPS	2214	1647	1406	1316	968	594	395	423	437	449	461
PABPP	2214	1694	1347	1261	892	657	460	428	432	429	428
PABPN	2214	1747	1556	1341	1084	841	467	448	439	433	429
PABPB	2214	1904	1631	1427	1247	941	621	406	402	418	424

PABPPC	2214	1921	1654	1481	1264	894	660	478	461	458	456

Figure. 9 Percentage removal of COD (a), BOD (b) at different concentrations of polyelectrolytes.
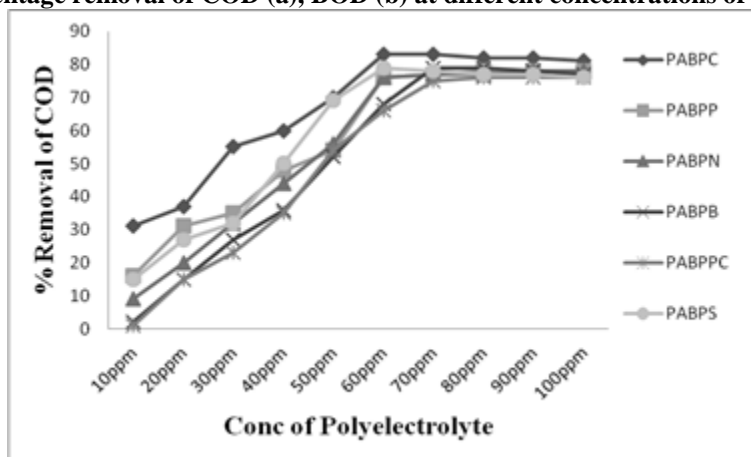
(a)
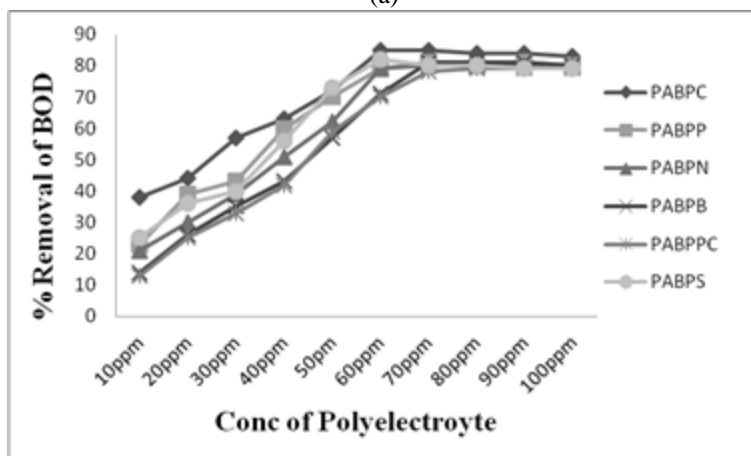
(b)

4. Conclusions

In conclusion, a series of acryloyl benzyl piperazinium polyelectrolytes and their monomers have been synthesized with different counter ions. NMR, Mass and IR spectral techniques were employed to characterize these systems. The intrinsic viscosity of the polyelectrolytes measured by Huggins, Fuoss and Fedors methods indicate that the polyelectrolytes with chloride counter ion exhibit the maximum value and the zeta potential (ξ) measurements also indicate the same trend. Thermal behavior of the polyelectrolytes was investigated by TGA and DSC analysis. The effect of counter ion on their flocculation behavior has been investigated with respect to the COD, BOD and Nephelometric turbidity. The effect of the counter ion chloride (PABPC) on the flocculation is found to be more pronounced when compared to the other counter ions investigated in the present series of polyelectrolytes

Acknowledgements

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