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Synthesis, Characterization and Ion-exchange Study of Organo-soluble Copolymer from 8-Quinolinyl Methacrylate and Styrene

SAMIR A. PATEL, RAJNI M. PATEL* and PRAVIN M. PATEL†
Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, India

The monomer, 8-quinolinyl methacrylate (8-QMA) was synthesized and characterized by IR and H^1-NMR spectroscopy, high performance liquid chromatography (HPLC) and elemental analysis. The homopolymer poly(8-QMA) and copolymers with styrene in different feed ratio were prepared by free radical polymerization using dimethyl formamide (DMF) as a solvent and 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The resulting polymers were characterized by IR-spectroscopy, UV-visible spectrophotometry, gel permeation chromatography (GPC) and the thermal properties were measured by TG and DSC. The metal ion uptake capacity of synthesized copolymers was estimated by batch equilibrium method using different metal ion solutions under three different experimental conditions. It was observed that due to the presence of a pendent ester bound quinolinyl group, the copolymers are capable of adsorbing the tested cation from their aqueous solutions.

Key Words: Synthesis, Characterization, Ion-exchange study, Organo-soluble copolymer, 8-Quinolinyl methacrylate, Styrene.

INTRODUCTION

Ester polymers of methacrylic and acrylic acids are important in a wide range of applications. They are used in dental materials, glazing, adhesives, plastic bottles, elastomers, floor polishes as they have very good sparkling crystal clarity and outstanding surface hardness together with superior weatherability and good chemical resistance. The chemistry of the functional monomers and polymers containing 8-hydroxyl quinoline (8-HQ) or its derivatives has received considerable attention in recent years. These materials find numerous applications in many fields of modern science and technology due to their antimicrobial and ion exchange properties[1–3]. There are some reports on the synthesis of monomeric and polymeric derivatives of 8-hydroxy quinoline. Patel *et al.*[4, 5] reported the synthesis and ion-exchange properties of 8-HQ-furfural condensation polymers. Kirienko and co-workers[6–8] synthesized several acrylic esters by esterification of alkali metal salts of halogen and alkyl substituted 8-HQs with methacryloyl and

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†Industrial Chemistry Department, V.P. & R.P.T.P Science College, Vallabh Vidyanagar-388 120, India.

acryloyl choride using benzene or ethyl alcohol as a medium. The resulting esters were mostly studied for their biological activity. Liu and co-workers[9] studied the chelating ion exchange resin containing 8-HQ which could be used to enrich heavy metal ions including Cu(II), Hg(II), Pb(II) and Mg(II) in water and their analysis. Bankova *et al.*[10] synthesized homopolymers of 5-chloro-8-quinolinyl acrylate and methacrylate with hydrophilic monomers and studied the interpolymer complex formation between polyacids and polybases segments. They have also evaluated the antibacterial activity of the homo and copolymers against some selected microorganisms.

The present work describes the synthesis and characterization of 8-quinolinyl methacrylate monomer, its homopolymer and copolymers with styrene. The effect of 8-QMA content in the copolymers on molecular weight, molecular weight distribution and thermal properties of the resulting copolymers has been discussed. We also studied the metal ion binding capacity of 8-QMA-styrene copolymers by batch equilibrium method. The effect of various experimental parameters, such as pH of the medium, shaking time and electrolytes and its ionic strength; on the metal ion uptake capacity of the polymers has also been discussed.

EXPERIMENTAL

Methacrylic acid, benzoyl chloride, 8-hydroxy quinoline, absolute alcohol, DMF, styrene and AIBN used were of analytical grade reagents.

8-Quinolinyl methacrylate and methacryloyl chloride were prepared as per the reported process[11] and used for the further reaction. The monomeric ester 8-quinolinyl chloride was added to the sodium salt of 8-hydroxy quinoline in absolute alcohol at 0–5°C with constant stirring. The precipitated ester was filtered, washed with cold water, dried and recrystallized from petroleum ether. The recrystallized product yield was 62% and melting point was 49°C. % Analysis. Found (Calcd.): C = 73.23 (73.24), H = 5.18 (5.16), N = 6.55 (6.57).

Homo and copolymerization of 8-QMA and styrene: The homopolymer was prepared by free radical polymerization of 8-quinolinyl methacrylate using DMF as a solvent and AIBN (1 % w/w of the monomer) at 70°C for 5 h with constant stirring. The resulting polymer solution was slowly poured in a large volume of methanol with stirring, where the polymer was precipitated out, filtered, washed with methanol and vacuum dried at 50°C. The copolymers of 8-quinolinyl methacrylate and styrene were prepared by the same procedure using different monmer-feed ratio (Table-1).

Determination of the metal ion uptake capacity

Batch equilibrium method[12, 13] was adopted for the determination of the metal ion uptake capacity of the polymers using different experimental variables such as electrolyte, its concentration and pH of the medium. Three metal ions, *viz.*, Cu^{2+}, Ni^{2+} and Co^{2+} were tested in the form of aqueous metal nitrate solutions. In experimental procedure the finely powdered dried polymer sample (50 mg) was suspended in 40 mL of electrolyte solution of specific ionic strength. The pH of the suspensions was adjusted to specific value. This content was stoppered and shaken for 24 h, to allow the swelling of the polymer at room temperature. To this, 0.1 M metal nitrate solution (2 mL) was added and the pH was again adjusted. The content was again mechanically stirred for 24 h, then filtered and washed with distilled water. From the filtrate the unadsorbed metal ion was estimated by back titration with standard EDTA solution using appropriate indicator. A separate blank experiment was also carried out in the same manner. The amount of metal adsorbed by the polymer was calculated and expressed in terms of milliequivalent per gram of the polymer (meq g^{-1}).

TABLE-1
REACTION PARAMETERS FOR THE SOLUTION (CO) POLYMERIZATION OF 8-QUINOLINYL METHACRYLATE (8-QMA) AND STYRENE

Sample No	Designation of polymer/ copolymer	Monomer feed composition						Compo-sition of P(8-QMA)	Yield (%)	Softening range (°C)
		(8-QMA)			Styrene					
		Mol	g	% wt.	Mol	g	% wt.			
P-1	P(8-QMA-co-S) 50 : 50	0.0235	5	50	0.0451	5	50	68.00	73	185–210
P-2	P(8-QMA-co-S) 40 : 60	0.0188	4	40	0.0577	6	60	64.00	63	180–195
P-3	P(8-QMA-co-S) 30 : 70	0.0141	3	30	0.0673	7	70	35.00	52	134–152
P-4	P(8-QMA-co-S) 20 : 80	0.0094	2	20	0.0769	8	80	59.00	42	150–162
P-5	P(8-QMA-co-S) 10 : 90	0.0047	1	10	0.0865	9	90	41.24	34	145–158
P-6	P(8-QMA)	0.0470	10	100	–	–	–	–	97	240–263
P-7	PS	–	–	–	0.0962	10	100	–	92	120–140

Solvent: dimethyl formamide (DMF): 50% w/v
Initiator: Azobisisobutyronitrile (AIBN): 1% w/w of total monomer weight
Reaction size : 10 g
Reaction temperature : 70 ± 2°C
Reaction Time : 5 h

The IR spectra of monomer, homo and copolymers were recorded on Nicolet-400D FT-IR spectrophotometer in the KBr dispersed pellet form. The ^1H NMR spectrum of 8-QMA was recorded on Hitachi-R-1500 FT-NMR spectrometer (60 mHz) in $CDCl_3$ using TMS as an internal standard. The purity of 8-QMA was checked on Water's HPLC system using methanol as a mobile phase at 1 mL/min. Foss-Hareaus CHN-O rapid automatic analyzer was used for the elemental analysis of the monomer. UV spectra of the homo- and copolymer were recorded on a Shimadzu-160A UV-visible spectrophotometer using calibration curve of absorbance of 8-QMA solution in chloroform at 281 nm *vs.* its concentration. GPC analysis was performed on a Water's GPC system using THF as a mobile phase at 1 mL/min flow rate. The GPC system was calibrated using eight different polystyrene standards having reported peak molecular weight. The solution viscosity was determined by Schott-Garett viscometer system at 25°C using DMF as a solvent. Thermal analyses were performed at 10°C/min heating rate on Du Pont 951 thermogravimetric analyzer and 910 differential scanning calorimeter using static air atmosphere for TG and nitrogen atmosphere for DSC.

RESULTS AND DISCUSSION

The new monomer 8-QMA obtained in a light yellow coloured powder form showed m.p. at 49°C. The practical values of elemental analysis are very close to those calculated theoretically. The ^{1}H NMR spectrum of 8-QMA shows all expected signals. The signal at δ 2.14 ppm is due to the methyl protons. For each non-equivalent methylene protons, there is a signal centred at δ 6.53 ppm and δ 5.61 ppm[14]. This is due to ester to ester bonding of the quinolinyl moiety with the vinyl group. The integration values of signals confirm the assignment and number of protons in the ester. IR spectrum of the ester, 2910 cm^{-1} $\nu(CH_3)$, 1730 cm^{-1} ν(C=O), 1635 cm^{-1} ν(C=C), 1230 and 1160 cm^{-1} ν(C—O—C), 970 and 950 cm^{-1} ν(= CH$_2$—CH out of plane bonding mode of vinyl group). The three absorption bands at 1590, 1500 and 1470 cm^{-1} may be assigned as the characteristic absorption of 8-*o*-substituted quinolinyl ring[15, 16]. The HPLC analysis of monomer gives 99.47% product purity. The homo and copolymers are soluble in common organic solvents like acetone, benzene, toluene, chloroform, DMF, THF, etc. The IR spectrum of homopolymers shows the absence of bands for C=C and vinyl methylene group (=CH$_2$), which are characteristic of monomeric ester. The ν(C=O) at 1730 cm^{-1} and ν(C—O) at 1310 cm^{-1} of monomer is shifted to 1750 and 1300 cm^{-1} respectively after the polymer is formed. Due to the presence of =CH$_2$ and C=O group, there is an extensive conjugation in the monomer. This conjugation, however is broken in the polymer thereby resulting in slight decrease in C—O bond order and increase in C=O and C—O stretching frequencies after the polymerization. IR spectra of copolymers shows all the characteristic bands of both the segments, *i.e.*, P(8-QMA) and styrene. The relative intensities of the bands due to each segment change according to change in their composition in each copolymer. GPC analysis of the copolymer show that number average molecular weight ($\overline{M}_n$) varies between 3058 to 4885 whereas weight average molecular weight ($\overline{M}_w$) varies between 16404 to 31908. The molecular weight distribution was broad with values varying between 4.60 to 10.43, as is typical in free radical polymerization.

Thermal behaviour of the homo and copolymer was studied by TGA and DSC. The natures of thermograms are found to be similar in general shape and show one step degradation. The thermal data and various kinetic parameters of thermal degradation are presented in Table-2. It is observed that polystyrene and P(8-QMA) start degrading at 250–300°C. The activation energy for the thermal degradations E_A was calculated by Brodio method[17] which ranges from 137 to 173 kJ mol^{-1}. The values of characteristic integral procedural degradation temperatures (IPDT) were calculated by Doyle's method[18]. IPDT expresses the overall thermal stability of the polymer which varies between 351 to 381°C. The heat of fusion (ΔH_f) evaluated from DSC thermograms ranges from 0.29 to 1.64 kJ mol^{-1}.

TABLE-2
CHARACTERISTIC TEMPERATURES AND KINETIC PARAMETERS FOR THERMAL DEGRADATION OF THE COPOLYMERS OF 8-QMA AND STYRENE EVALUATED FROM TGA AND DSC

Sample code No.	% Weight loss at various temperatures (°C)				Decomposition Temperature range (°C)	T^a_{max} (°C)	T^b_{50} (°C)	IPDT[c] (°C)	Activation Energy[d] E_A (kJ mol^{-1})	Heat of fusion[e] (ΔH_f) (kJ mol^{-1})
	250	350	450	550						
P-1	3.5	34.5	92.5	97.5	275–475	359	360	362	137	1.05
P-2	2.0	19.0	92.5	97.5	275–475	368	367	367	152	0.80
P-3	2.5	28.0	97.0	99.5	300–475	361	362	359	169	1.64
P-4	1.0	12.5	92.5	97.5	300–475	375	375	381	173	0.72
P-5	1.5	20.0	91.0	95.5	275–500	376	375	377	141	0.79
P-6	4.0	61.0	95.0	98.0	300–475	348	345	351	147	0.29
P-7	2.5	55.5	95.5	98.0	225–400	348	347	351	145	0.81

(a) Temperature for maximum rate of decomposition. (b) Temperature for 50% weight loss. (c) Integral procedural decomposition temperature by Doyle's method. (d) By Brodio's method (Ref. 17). (e) From DSC thermograms

TABLE-3
EFFECT OF pH ON Cu^{2+}, Ni^{2+} and Co^{2+} METAL ION BINDING CAPACITY OF 8-QMA HOMO AND COPOLYMERS

Metal ion (0.1 M, 2.0 mL)	Sample No	Metal ion uptake (me qg^{-1})					
		pH of the medium					
		3.0	3.5	4.0	5.0	5.5	6.0
$Cu(NO_3)_2$	P-1	0.70	0.75	0.82	1.44	2.06	2.23
	P-2	0.66	0.72	1.08	1.32	1.95	2.08
	P-3	0.35	0.38	0.68	0.92	1.06	1.12
	P-4	0.50	0.57	0.74	1.02	1.79	1.82
	P-5	0.57	0.96	1.25	1.72	1.85	1.98
	P-6	0.96	1.62	2.10	2.92	3.04	3.52
$Ni(NO_3)_2$	P-1	0.28	0.48	0.78	1.02	2.02	2.28
	P-2	0.32	0.40	0.48	0.80	1.90	2.04
	P-3	0.18	0.35	0.67	1.01	1.04	1.12
	P-4	0.31	0.59	1.17	1.70	1.76	1.78
	P-5	0.21	0.41	0.80	1.18	1.22	1.38
	P-6	0.52	1.00	1.98	2.88	2.98	3.10
$Co(NO_3)_2$	P-1	0.38	0.46	0.52	0.72	2.08	2.38
	P-2	0.36	0.38	0.40	0.56	1.90	2.10
	P-3	0.26	0.54	0.74	1.02	1.05	1.24
	P-4	0.44	0.90	1.25	1.72	1.78	1.89
	P-5	0.30	0.62	0.87	1.20	1.24	1.36
	P-6	0.74	1.52	2.12	2.92	3.02	3.38

Wight of Polymer : 50 mg, Electrolyte : 1.0 M $NaNO_3$ (40 mL)

The polymers show capacity to adsorb metal ion due to the presence of pendant quinolinyl group. Table-3 shows the result of pH on the metal binding capacity of synthesized polymers. It is observed that the relative amount of metal ion adsorbed by the polymer increases with inereasing pH of the medium. The result of distribution ratios (Table-4) also indicates that at equilibrium, the distribution of each metal between the polymeric phase and aqueous phase increases with increasing pH of the medium.

Tables 5–7 show the results of the effect of type and concentration of an electrolyte adsorption by the polymer from their solution at room temperature. It is observed that the amount of Cu^{2+}, Ni^{2+} and Co^{2+} ions adsorption increases with increasing concentration of NO^- and Cl^- ions. But in case of SO_4^{2-} ions, it may be explained in terms of the stability constant of the complexes of studied metal ions with NO_3^-, Cl^- and SO_4^{2-} anion[19]. Table 8 shows the results of the rate of metal ion uptake by 8-QMA homo- and copolymers as a function of time. A percentage attainment of equilibrium is with respect to 100% equilibrium after 24 h.

TABLE-4

DISTRIBUTION RATIO OF Cu^{2+}, Ni^{2+} and Co^{2+} IONS ADSORBED BY THE POLYMER AND REMAINED IN THE SOLUTION AT EQUILIBRIUM

Metal ion (0.1 M, 2.0 mL)	Sample No.	Distribution ratio (K_D)					
		pH of the medium					
		3.0	3.5	4.0	5.0	5.5	6.0
$Cu(NO_3)_2$	P-1	81	87	96	185	292	325
	P-2	76	83	131	166	271	295
	P-3	39	42	78	109	128	137
	P-4	56	65	86	123	142	248
	P-5	65	115	156	230	152	277
	P-6	115	213	299	480	515	661
$Ni(NO_3)_2$	P-1	31	54	91	123	284	335
	P-2	35	44	54	93	262	288
	P-3	19	38	79	121	126	137
	P-4	34	67	144	226	137	240
	P-5	23	45	95	154	151	175
	P-6	58	120	276	473	499	532
$Co(NO_3)_2$	P-1	42	51	58	83	295	356
	P-2	40	42	44	63	261	299
	P-3	28	61	86	123	127	154
	P-4	49	106	156	230	240	260
	P-5	32	71	102	145	154	172
	P-6	86	197	303	482	509	614

Wight of polymer : 50 mg
Electrolyte : 1.0 M $NaNO_3$ (40 mL)

TABLE-5
EFFECT OF ELECTROLYTE CONCENTRATION IN METAL ION ADSORPTION CAPACITY OF 8-QMA HOMO- AND COPOLYMERS

Sample No.	Electrolyte concentration (mol. L^{-1})	Metal ion uptake (me qg^{-1})		
		Cu^{2+}	Ni^{2+}	Co^{2+}
P-1	0.05	0.48	0.50	0.33
	0.10	0.52	0.56	0.30
	0.50	0.66	0.72	0.22
	1.00	0.70	0.80	0.18
P-2	0.05	0.24	0.28	0.08
	0.10	0.26	0.34	0.14
	0.50	0.60	0.54	0.24
	1.00	0.68	0.60	0.30
P-3	0.05	0.18	0.20	0.10
	0.10	0.22	0.24	0.16
	0.50	0.28	0.32	0.20
	1.00	0.30	0.36	0.24
P-4	0.05	0.08	0.12	–
	0.10	0.12	0.14	–
	0.50	0.16	0.20	0.04
	1.00	0.18	0.24	0.10
P-5	0.05	–	–	–
	0.10	–	0.04	–
	0.50	0.06	0.04	0.06
	1.00	0.08	0.08	0.06
P-6	0.05	1.08	2.08	0.62
	0.10	1.42	2.40	1.14
	0.50	1.64	2.88	1.92
	1.00	2.60	3.02	2.06

Wight of polymer : 50 mg
Electrolyte : 1.0 M NaCl solution (40 mL)
pH of the medium : 5.5

TABLE-6
EFFECT OF ELECTROLYTE CONCENTRATION IN METAL ION ADSORPTION CAPACITY OF 8-QMA HOMO- AND COPOLYMERS

Sample no	Electrolyte concentration (mol L^{-1})	Metal ion uptake (m.e. q.g.$^{-1}$)		
		Cu^{2+}	Ni^{2+}	Co^{2+}
P-1	0.05	1.40	1.30	1.28
	0.10	1.32	1.26	1.20
	0.50	1.02	0.92	0.82
	1.00	0.98	0.84	0.76
P-2	0.05	1.08	0.92	0.72
	0.10	0.98	0.86	0.56
	0.50	0.62	0.50	0.28
	1.00	0.54	0.42	0.22
P-3	0.05	1.00	0.88	0.60
	0.10	0.92	0.80	0.48
	0.50	0.42	0.44	0.20
	1.00	0.36	0.38	0.12
P-4	0.05	0.72	0.42	0.22
	0.10	0.58	0.30	0.18
	0.50	0.18	0.14	0.08
	1.00	0.12	0.12	0.04
P-5	0.05	0.20	0.08	0.08
	0.10	0.18	0.06	0.04
	0.50	0.10	–	–
	1.00	0.08	–	–
P-6	0.05	3.22	2.94	2.72
	0.10	2.98	2.52	1.88
	0.50	2.42	2.04	0.90
	1.00	2.08	1.78	0.86

Weight of polymer : 50 mg
Electrolyte : 1.0 M Na_2SO_4 solution (40 mL)
pH of the medium : 5.5

TABLE-7
EFFECT OF ELECTROLYTE CONCENTRATION IN METAL ION ADSORPTION CAPACITY OF 8-QMA HOMO- AND COPOLYMERS

Sample No.	Electrolyte concentration (mol L^{-1})	Metal ion uptake (m.e. q.g.$^{-1}$)		
		Cu^{2+}	Ni^{2+}	Co^{2+}
P-1	0.05	0.36	0.50	0.18
	0.10	0.42	0.58	0.26
	0.50	0.86	0.96	0.76
	1.00	1.98	1.98	1.96
P-2	0.05	0.22	0.32	0.12
	0.10	0.30	0.42	0.18
	0.50	0.54	0.78	0.84
	1.00	1.72	1.74	1.83
P-3	0.05	0.20	0.28	0.10
	0.10	0.24	0.30	0.15
	0.50	0.42	0.72	0.61
	1.00	0.96	1.12	1.10
P-4	0.05	0.08	0.12	0.10
	0.10	0.19	0.20	0.17
	0.50	0.81	0.84	0.81
	1.00	1.68	1.82	1.72
P-5	0.05	0.12	0.32	0.04
	0.10	0.30	0.36	0.16
	0.50	0.52	0.78	0.54
	1.00	1.82	1.20	1.18
P-6	0.05	1.76	1.82	0.82
	0.10	1.92	2.04	0.98
	0.50	2.68	2.80	1.46
	1.00	3.04	3.12	2.92

Wight of polymer : 50 mg
Electrolyte : 1.0 M $NaNO_3$ solution (40 mL)
pH of the medium : 5.5

TABLE-8

RATE OF Cu^{2+}, Ni^{2+} and Co^{2+} METAL ION UPTAKE BY 8-QMA HOMO- AND COPOLYMERS AS A FUNCTION OF TIME

Metal ion (0.1 M, 2.0 mL)	Sample No.	% Attainment of equilibrium						
		Time (h)						
		1.0	2.0	3.0	4.0	5.0	6.0	7.0
$Cu(NO_3)_2$	P-1	26.8	40.2	49.2	71.5	76.0	84.9	93.1
	P-2	33.3	46.7	66.7	80.0	86.7	93.3	100.0
	P-3	21.4	42.9	64.3	71.4	78.0	85.8	92.3
	P-4	30.0	32.8	48.8	70.0	80.1	90.1	–
	P-5	22.2	44.4	54.8	77.8	88.9	100.0	–
	P-6	31.1	46.7	68.9	75.6	80.0	86.7	93.9
$Ni(NO_3)_2$	P-1	30.2	34.8	48.6	76.0	82.5	88.4	89.5
	P-2	32.8	38.4	46.5	65.8	76.6	80.1	86.5
	P-3	38.6	50.2	61.4	76.8	80.2	84.5	90.0
	P-4	30.2	42.8	58.5	70.8	82.5	89.0	91.0
	P-5	28.6	32.5	48.6	58.8	72.5	86.5	92.5
	P-6	22.4	38.2	62.5	78.4	84.2	88.9	90.2
$Co(NO_3)_2$	P-1	22.2	26.2	40.5	60.5	72.5	81.5	85.9
	P-2	24.5	28.4	30:5	60.6	78.9	88.9	89.0
	P-3	18.9	25.2	40.5	50.6	68.9	82.5	90.8
	P-4	20.5	24.8	38.4	62.5	78.4	80.1	86.2
	P-5	25.6	38.5	44.5	53.5	70.2	83.5	90.2
	P-6	15.8	25.6	38.5	50.8	70.5	78.8	88.5

*With respect to 100% equilibrium after 24 h

Weight of polymer	: 50 mg
Electrolyte	: 1.0 M $NaNO_3$ solution (40 mL)
Metal ion	: 0.1 M
pH of the medium	: 5.5

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