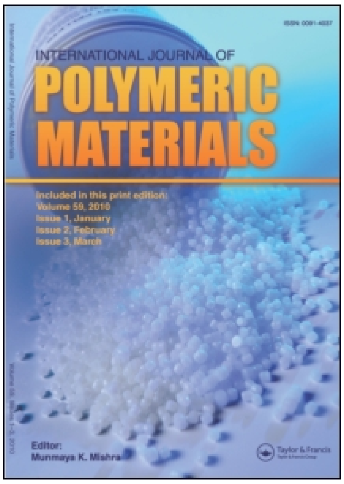

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Methyl Methacrylate-8-Quinolinyl Acrylate Copolymers-I: Synthesis and Characterization

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The monomer, 8-quinolinyl acrylate (8-QA) was synthesized and characterized by IR and ^{1}H-NMR spectroscopy, high performance liquid chromatography (HPLC) and elemental analysis. The homopolymer, poly (8-QA) and its copolymers with methyl methacrylate (MMA) in different monomer feed ratio were prepared by free radical polymerization using dimethyl formamide (DMF) as a solvent and 2,2′-azobis-isobutyronitrile (AIBN) as an initiator. The resulting polymers were characterized by IR spectroscopy, UV-visible spectrophotometry, gel permeation chromatography (GPC), solution viscosity and thermal analysis (TG and DSC). It was observed from the GPC results that as the 8-QA content in the copolymer increases, the molecular weight decreases whereas polydispersity increases with increasing 8-QA content in the copolymers. It was also observed from the TG data that the initial decomposition temperature (IDT) of the copolymers decreases with increasing 8-QA content in the copolymers.

Keywords: Copolymer; 8-quinolinyl acrylate; feed ratio; thermal analysis; GPC

INTRODUCTION

8-hydroxyquinoline (8-HQ) and its derivatives are widely used as a complexing agent in varieties of applications due to their good complex forming ability [1–3]. Patel *et al.* [4, 5] reported the synthesis and

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*Corresponding author.

ion-exchange properties of the 8-HQ-formaldehyde condensation polymers. There are some reports for the synthesis of acrylic polymers with pandent quinolinyl group. Pittman *et al.* [6] reported the synthesis and fungicidal properties of 8-QA-vinyl acetate copolymers. Bankova *et al.* [7, 8] synthesized the copolymers of 5-chloro-8-quinolinyl (meth)acrylate with (meth)acrylic acid and *N*-vinyl pyrrolidone and studied their antibacterial properties.

The present work describes the synthesis and characterization of 8-QA monomer, its homopolymer and copolymers with MMA. The effect of 8-QA content in the copolymers on molecular weight, molecular weight distribution and thermal properties of the resulting copolymers has been discussed.

EXPERIMENTAL

Materials

Acrylic acid, benzoyl chloride, 8-HQ, absolute alcohol, DMF and AIBN used were of analytical grade reagents.

Synthesis of 8-Quinolinyl Acrylate [9]

Acryloyl chloride was prepared as per the reported process [10] and used for the further reaction. The monomeric ester, 8-QA, was prepared by dropwise addition of equimolar quantity of acryloyl chloride to the sodium salt of 8-HQ 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 reaction scheme for the synthesis of 8-QA is shown in Figure 1. The recrystallized product yield was 62%, melting point 49°C. Elemental analysis was as given below:

	C	H	N	O
Theoretically calculated (%)	72.36	4.52	7.04	16.08
Practically obtained (%)	72.37	4.53	7.00	16.10

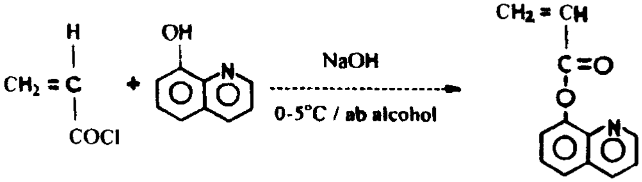

FIGURE 1 Reaction scheme for the synthesis of 8-QA.

Homo- and Copolymerization of 8-QA and MMA

The homopolymer was prepared by free radical polymerization of 8-QA using DMF as a solvent and AIBN (1% w/w of the monomer) at 70°C for 5 hr 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-QA and MMA were prepared by the same procedure using different monomer feed ratio (Tab. I). Figure 2 shows the reaction scheme for the synthesis of homo and copolymers.

Measurements

The IR spectra of monomer, homo- and copolymers were recorded on Nicolet-400D FT-IR spectrophotometer in KBr. The ^{1}H-NMR spectrum of 8-QA was recorded on Hitachi-R-1500 FT-NMR spectrometer (60 MHz) in $CDCl_3$ using TMS as an internal standard. The purity of 8-QA was checked on Waters 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 copolymers were recorded on a Shimadzu 160A UV-VIS spectrophotometer using chloroform as a solvent. 8-QA content in the copolymers was determined using calibration absorbance of 8-QA solution in chloroform at 281 nm *versus* its concentration. GPC analysis was performed on a Waters GPC system using THF as a mobile phase at 1 ml/min flow rate. The GPC system was calibrated using eight polystyrene standards having reported peak molecular weight 2.70×10^6, 4.02×10^5, 2.33×10^5,

TABLE I Reaction parameters and GPC data for the solution (co)polymerization of 8-quinolinyl acrylate (8-QA) and methyl methacrylate (MMA)

Sample code no.	*Designation of polymer/copolymer*	*Monomer feed composition*				*Composition of 8-QA in copolymer (%)*	*Yield (%)*	*Softening range (°C)*	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$	*Viscosity* [η] *dl/gm*
		8-QA		*MMA*								
		Mol.	*% Wt.*	*Mol.*	*% Wt.*							
P-1	P(8-QA)	0.0503	100	–	–	–	93	232–258	–	–	–	0.017
P-2	P(8-QA-co-MMA) 50:50	0.0252	50	0.05	50	47.32	90	211–226	5647	39094	6.92	0.023
P-3	P(8-QA-co-MMA) 40:60	0.0201	40	0.06	60	36.19	91	200–218	5862	32757	5.59	0.017
P-4	P(8-QA-co-MMA) 30:70	0.0151	30	0.07	70	29.56	94	198–208	7321	31586	4.31	0.014
P-5	P(8-QA-co-MMA) 20:80	0.0101	20	0.08	80	19.29	92	192–212	8812	43531	4.94	0.028
P-6	P(8-QA-co-MMA) 10:90	0.0050	10	0.09	90	09.85	94	190–209	8991	44657	4.97	0.019
P-7	PMMA	–	–	0.10	100	–	98	192–214	14848	60146	4.05	0.014

Solvent: Dimethyl formamide (DMF) (50% w/w).
Initiator: Azobisisobutyronitrile (AIBN) (1% w/w of total monomer(s) weight).
Reaction temperature: 70 ± 2°C; Reaction time: 5 hr.

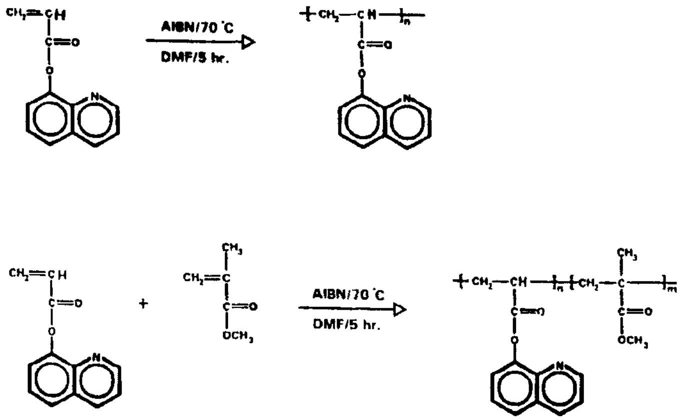

FIGURE 2 Reaction scheme for the synthesis of homo- and copolymers.

1.06×10^5, 3.03×10^4, 7.50×10^3, 4.00×10^3 and 2.70×10^3. 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 monomer, 8-QA, obtained in a light yellow coloured powder form showed melting point 49°C. The practical values of elemental analysis are very close to those calculated theoretically. The NMR spectrum of 8-QA shows all the expected signals (Fig. 3). The signal at δ 5.957–6.270 ppm is attributed to the Hc proton of the vinyl group. The signal at δ 6.553–6.689 ppm is attributed to the two non-equivalent protons (H_A and H_B) of the methylene group. For six aromatic protons of the quinolinyl moiety there are three different signals observed in the aromatic region. The multiplet between δ 7.266–7.803 ppm may be attributed to four equal protons *i.e.*, H_3, H_4, H_5 and H_6 whereas two doublets of nearly equal intensities at δ 8.076–8.203 and 8.877–8.926 ppm are due to H_7 and H_2 protons respect-

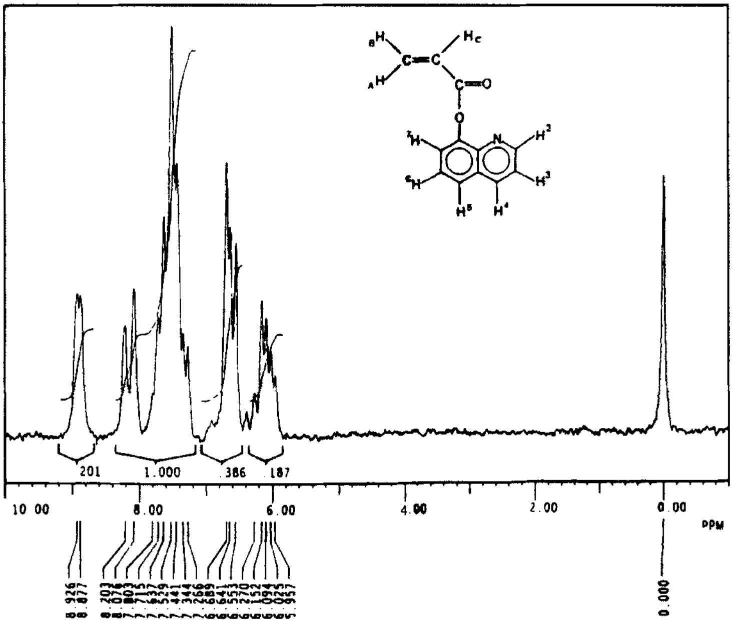

FIGURE 3 NMR spectrum of 8-QA.

ively. The resonance signals of the aromatic protons were shifted towards the lower field compared to those of 8-HQ due to ester bonding of quinolinyl group with the vinyl group [12]. IR spectrum of monomer, shows the following absorption bands confirming the structure of the ester (Fig. 4): 1730 cm^{-1} ($\nu_{C=O}$), 1635 cm^{-1} ($\nu_{C=C}$), 1230 and 1164 cm^{-1} (ν_{C-O-C}) and 970 cm^{-1} ($\nu_{=CH_2}$). The absorption bands at 1590, 1500 and 1470 cm^{-1} may be attributed as a chracteristic of 8-O substituted quinolinyl ring [13, 14]. The HPLC analysis of monomer gave 99.90% product purity.

The homo- and copolymers obtained in a light yellow colour amorphous powder form. The copolymers are soluble in common organic solvents like acetone, toluene, benzene, chloroform, DMF, THF *etc.*, whereas P(8-QA) homopolymer is soluble only in DMF and DMSO. The IR spectrum of homopolymer shows the absences of bands for $C=C$ and vinyl methylene group ($=CH_2$), characteristic of monomeric ester (Fig. 4). The shift in $\nu_{-C=O}$ and ν_{-C-O} bands, after polymerization, is interesting. While the ν_{-C-O} at 1730 cm^{-1} and $\nu_{-C=O}$ at

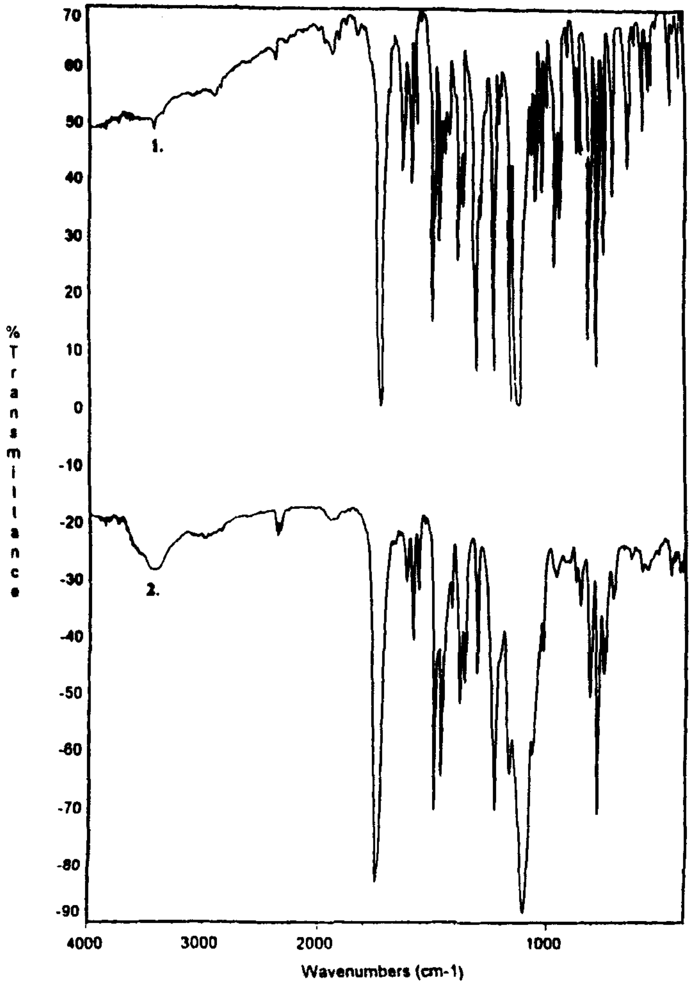

FIGURE 4 FT-IR Spectra of: (1) 8-QA (2) Poly (8-QA).

1310 cm^{-1} of monomer shifts to 1750 and 1300 cm^{-1} respectively after the polymer is formed. Because of presence of $=CH_2$ group, there is an extensive conjugation involving $=CH_2$, C=O and C—O in the monomer. This conjugation, however, broken in the polymer thereby resulting in slight decrease in C—O bond order and increase in C=O and C—O stretching frequencies, of the monomer, observed after the

TABLE II Characteristic temperatures and kinetic parameters for thermal degradation of 8-QA-MMA copolymers evaluated from TGA and DSC

Sample code no.	*% Weight loss at various temperature (°C)*							*Decomposition temperature range (°C)*	T_{max}[a] *(°C)*	T_{50}[b] *(°C)*	*IPDT*[c] *(°C)*	*Activation energy*[d] *Ea* $(kJ \cdot mol^{-1})$	*Heat*[c] *of fusion* ΔH_f $(kJ \cdot mol^{-1})$
	250	300	350	400	450	500	550						
P-1	29	62	71	76	83	98	99	175–525	278	275	304	64.6	0.20
P-2	03	50	78	88	93	99	98	225–510	308	300	313	123.7	0.89
P-3	02	27	77	92	95	96	98	250–450	325	320	321	169.1	1.08
P-4	01	25	76	91	96	98	99	250–500	310	315	315	154.2	2.30
P-5	03	36	86	98	99	99	–	250–400	322	310	294	171.1	0.82
P-6	01	16	81	98	98	99	–	250–400	332	320	315	178.2	0.73
P-7	03	20	55	96	99	99	–	250–425	354	347	336	153.8	0.51

[a] Temperature for maximum rate of decomposition.

[b] Temperature for 50% weight loss.

[c] Integral procedural decomposition temperature by Doyle's method.

[d] From DSC thermograms.

[e] By Broido method.

polymerization. IR spectra of copolymers shows all the characteristic bands of both the segment *i.e.*, P8-QA and PMMA. The relative intensities of the bands due to each segment changes according to change in their composition in each copolymer. GPC analysis of the copolymer shows that number average molecular weight ($\overline{Mn}$) varies between 5,650 – 8,990 whereas weight average molecular weight ($\overline{Mw}$) varies between 31,590 – 44,660. The molecular weight distribution was broad with ($\overline{Mw}/\overline{Mn}$) values varies between 4.31 – 6.92, as is typical of free radical polymerization [15]. It is also observed from the GPC data that the values of $\overline{Mn}$ and $\overline{Mw}$ slightly increases with decrease in P8-QA composition in the copolymer. This may be due to the effect of stearic hindrance of bulky quinolinyl group.

Thermal behaviour of the homo and copolymers was studied by TGA and DSC. The nature of TG thermograms is found to be similar in general shape and showing one step degradation. The thermal data and various kinetic parameters of thermal degradation are presented in Table II. It is observed that PMMA and P8-QA starts degrading at 250 and 175°C respectively whereas copolymers starts degrading somewhere between 225 – 250°C. The activation energy for the thermal degradation, Ea, was calculated by Broido method [16] which is ranges from 123 – 178 $\mathrm{kJ \cdot mol^{-1}}$. The values of characteristic degradation temperatures, integral procedural degradation temperature (IPDT), were calculated by Doyle's method [17]. IPDT express the overall thermal stability of the polymers varies between 294 – 336°C. The heat of fusion (ΔH_f) evaluated from DSC thermograms ranges from 0.73 to 2.3 $\mathrm{kJ \cdot mol^{-1}}$.

CONCLUSION

The monomer, 8-QA was synthesized, characterized and copolymerized with MMA using different monomer feed ratio by solution copolymerization. The resulting copolymers characterized by convensional techniques. The GPC results indicates that incorporation of 8-QA with MMA decreases the overall molecular weight and increases the polydispersity of the copolymers. This may be due to the presence of bulky pandent quinolinyl group in the polymer chain. The TG data reveals that all the homo and copolymers shows single step degradation and moderate thermal stability.

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