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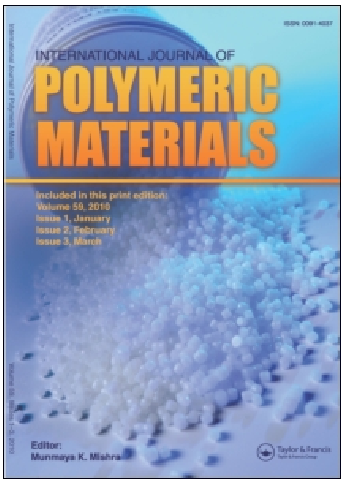

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U. I. Patel[a]; J. S. Parmar[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India

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Polymaleimide Ion Exchange Resin

U. I. PATEL and J. S. PARMAR
Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

(Received October 2, 1995)

New maleimide derivatives, N-(3-hydroxy-4-acetothiosemicarbazonephenyl) maleimide (HATPM) and N-(3-hydroxy-4-acetosemicarbazonephenyl) maleimide (HASPM) have been prepared by condensation of N-(3-hydroxy-4-acetyl phenyl) maleimide with thiosemicarbazide and semicarbazide hydrochlorides respectively. These are homopolymerized and copolymerized with styrene and maleic anhydride to give chelating ion exchange resins. They are analysed by elemental analysis, IR spectral study, TGA, DSC and molecular weight measurements.

KEY WORDS Maleimide, homopolymerization, chelating resins.

INTRODUCTION

Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radio isotopes and find large scale applications in water treatment and pollution control.[1,2]

Various commercial ion exchangers have a polymeric base (styrene, acrylic acid, phenol-formaldehyde etc) with cationic or anionic groups as the site of ion exchange.

The addition polymerization of N-phenyl maleimide is well documented in the literature.[3] It is found that semicarbazone and thiosemicarbazone are very good chelating groups. Ablov and Gerbeleu[4–6] have studied metal complexes formed by salicylaldehyde thiosemicarbazone. R. V. Singh and J. P. Tondon prepared the following compounds[7,8]: (i) salicylaldehyde semicarbazone and thiosemicarbazone, (ii) 2-hydroxy-1-naphthaldehyde semicarbazone and thiosemicarbazone, (iii) O-hydroxy acetophenone semicarbazone and thiosemicarbazone and studied their metal chelates.

Hitherto the addition polymerization of N-phenyl maleimide with such chelating ligands has received no attention in spite of good chelating properties of semicarbazones and thiosemicarbazones. The present communication deals first time with synthesis, characterization and preliminary ion exchange study of polymers from N-(3-hydroxy-4-acetothiosemicarbazonephenyl) maleimide (HATPM) and N-(3-hydroxy-4-acetosemicarbazonephenyl) maleimide (HASPM).

RESULTS AND DISCUSSION

The monomer A,2-hydroxy-4(2,5-dioxo-3-pyrolin-1-yl) acetophenone has been synthesised and polymerized in our laboratory earlier. The thiosemicarbazone (C) is

TABLE I

C, H, N, S analysis data

Compound	C %	H %	N %	S %
A	62.33 (61.21)*	3.89 (3.75)	6.06 (5.91)	-
B	62.33 (61.20)	3.89 (3.81)	6.06 (5.85)	-
C	51.31 (50.53)	3.94 (3.76)	19.42 (17.52)	10.52 (10.50)
D	54.16 (53.10)	4.16 (4.10)	19.44 (18.40)	-
E	51.31 (50.10)	3.94 (3.70)	18.42 (17.52)	10.52 (9.67)
F	54.16 (53.82)	4.16 (3.96)	19.44 (19.01)	-
G	61.76 (60.32)	4.90 (3.79)	13.72 (12.05)	7.84 (6.72)
H	64.28 (62.58)	5.10 (4.92)	14.28 (13.60)	-
A_1	58.35 (56.65)	3.34 (3.02)	4.25 (4.02)	-

* Calculated from formula weight.

prepared by reacting (A) with thiosemicarbazide (A.R.). It is soluble in N,N-dimethyl formamide (DMF) and acetic acid and insoluble in $CHCl_3$, dioxane, cyclohexanone, CCl_4 and decomposes at 230°C. The formation of C was confirmed by Lassaign test in which presence of N and S was clearly detected. It was also characterized by IR and elemental analysis. IR absorption of C shows νOH at 3325 cm^{-1} and ethylenic double bond at 3080 and νC=N stretching is observed at 1620 cm^{-1} and νC=S stretching frequency at 830 cm^{-1}. It also shows characteristic maleimide absorption peaks at 1760 cm^{-1}. Similarly compound D has been prepared and characterised. The elemental analysis data (Table I) for C, H, N, S agrees quite well with the calculated values. All these features suggest the formation of compound C. The polymerization was carried out by free radical initiator AIBN at 70°C. The polymer of appreciable molecular weight ($[\eta] = 0.11$ $dl \cdot g^{-1}$) was obtained after 72 hrs compared to the polymer A which required only 6 hrs.[9] This clearly shows the hindrance effect of long side group of thiosemicarbazone. Alternatively thiosemicarbazide and semicarbazide hydrochloride was reacted with homopolymer, B; to give polymer E and F containing these functional groups. This is found a more useful route since it gives 65% yield within 4 hours. The polymer E&F are insoluble in common organic solvents and soluble only in DMF. This may be due to partial cross linking reaction

TABLE II

IR spectral analysis data (cm^{-1})

Compound						
C	D	E	F	G	H	Probable Assignment
3080 (b)	3070 (b)	—	—	—	—	ν—CH stretching of 1,2-ethylenic double bond
3325	3540	3540	3580	3530	3540	ν—OH stretching of phenol
3400 (b)	3400 (b)	3400 (b)	3410 (b)	3410 (b)		
1760 (s)	1780 (s)	1770 (s)	1780 (w)	1785	1780	ν—C—O stretching of cyclic
		1710 (w)	—	1710 (s)	1710 (s)	imide ring
1620 (s)	1610 (b)	1610 (w)	1610 (w)	1600 (s)	1600 (s)	νC=N stretching
1370 (s)		1370 (s)				frequency
1525 (s)	1530 (s)	1520 (s)	1510 (w)	1504 (s)	1505 (s)	νC=N + νNH_2
1410 (s)	1410 (s)	1390 (s)	1425 (s)	1400 (s)	1390	νC=N + αNH_2 + νC=S
1140	1150 (w)	1175 (s)	1140 (b)	1160 (s)	1160 (s)	
1210 (s)	1230 (w)	1260 (s)	1240 (w)	1205 (s)	1210 (w)	νC=N + νC=S
—	—	—	—	3050 (s)	3040 (s)	ν—CH stretching of —CH_2 of styrene
1080 (s)	1010 (s)	1070 (w)	1020 (s)	1015 (s)	1020 (s)	αNH_2 + βNH_2
1020 (w)						
790 (s)	810 (s)	805 (s)	810	800 (s)	790 (s)	-*p*-disubstituted phenyl ring
830 (s)	—	850 (s)	—	840 (s)		νC=S group frequency

s = sharp, b = broad, w = weak.

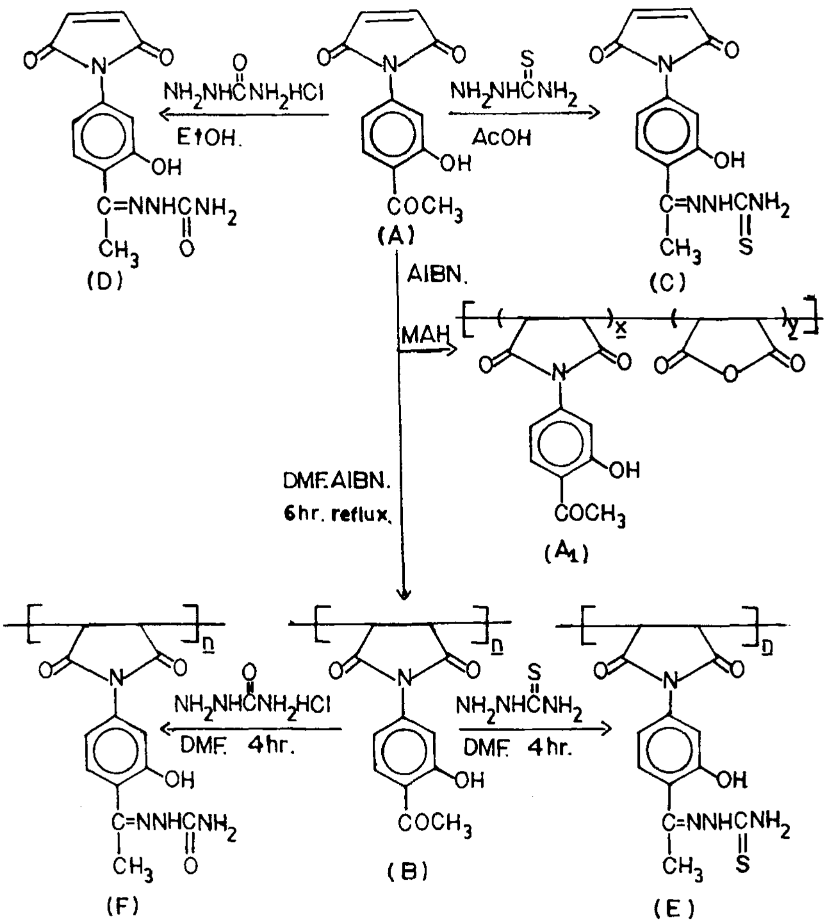
taking place during their preparation because of second —NH_2 group in thiosemicarbazone and semicarbazone.

IR spectra of the monomer with that of poly[HATPM] (E) and poly[HASPM] (F) (Table II) reveals a discernible difference in terms of a band due to —C=C— (ethylenic group). Such a band appeared at 3080 cm^{-1} and gets almost disappeared in the spectrum of polymer E&F and similarly other compounds were also characterised and respective structures are shown in Schemes I and II. The TGA thermograms show certain trends, some polymers degrade in single step whereas others in two steps (Table III). It is reported that N-phenylmaleimide-styrene copolymer shows excellent thermal stability than maleic anhydride styrene co-polymer.[10] The observations in the present case with polymer G&H which are stable upto 300°C show good agreement with these findings.

EXPERIMENTAL

Materials

The maleic anhydride was recrystallized from chloroform prior to use, the amines, viz 4-amino-2-hydroxy acetophenone and thiosemicarbazide (A.R.) were obtained from Chiti Chem Corporation, Baroda (India) and semicarbazide (German product from Sisco-Chem Industries, Bombay (India). The solvents acetic anhydride, DMF, Methanol, Benzene, DCE are purified by distillation. Styrene was freed from inhib-



SCHEME-I

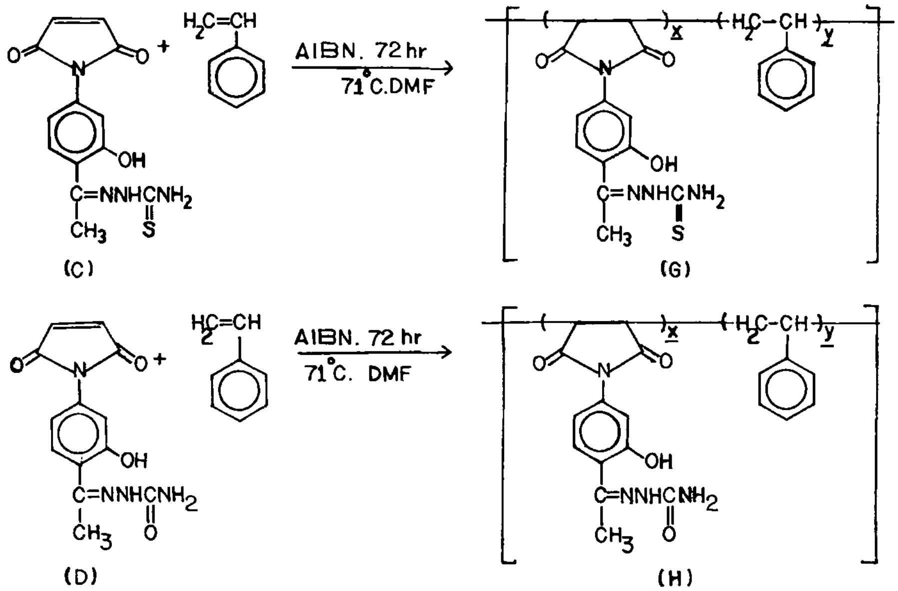
itor by washing thrice with 2% aq. NaOH solution followed by several washings with distilled water and finally dried using anhydrous calcium chloride.

Preparation of Monomers HATPM and HASPM

The monomers HATPM and HASPM have been prepared by condensation of HAPM(A) with thiosemicarbazide (TSC) and semicarbazide hydrochlorides (SC) by known standard procedure.[11,12] The contents were refluxed in ethanol: acetic acid 1:1 molar ratio for about 4–6 hrs. Product filtered and dried in oven at 50°C, yield 82% and 71% respectively.

Preparation of Homopolymers and Co-Polymer with Styrene and Maleic Anhydride

The homopolymers of HATPM, (E) and HASPM, (F) and copolymer with styrene and HAPM (A) with maleic anhydride have been prepared according to the procedure



SCHEME II

TABLE III

Thermogravimetric analysis of polymer sample

Polymer sample	Weight loss (%) at temperature, T°C						
	100	200	300	400	500	600	700
E	7.5	7.5	15.0	35	53.5	78.0	85.0
F	10.0	17.5	22.5	37.5	80.0	96.0	--
G	6.5	7.5	9.5	85.0	96.0	--	--
H	1.0	2.0	4.5	70.0	91.0	--	--
A_1	10.0	12.0	12.5	15.0	45.0	70.0	75.0

described in our earlier publication.[13] After proper purification they were labeled as B, E, F, G, H and A_1 as shown in Schemes I and II.

Measurements

The C, H, N, S contents of all the compounds were estimated using Heraeus, Germany CHNSO elemental Analyser. The IR-spectra were scanned in KBr pellets on a Perkin Elmer 983 spectrophotometer. TGA thermograms were recorded on DuPont 950 thermogravimetric analyser in air at a heating rate 10°C/min.

CONCLUSIONS

1. The cation exchange resins prepared are stable at room temperature and insoluble in common organic solvents.
2. These polymers and copolymers were characterised by various techniques.
3. Primary chelating properties of these polymers are also studied by formation of transition metal chelates with homopolymers.

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