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Copolymerization via zwitterion of methacrylic acid and ethyleneimine

Part 17

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SUMMARY

The copolymerization without initiator of methacrylic acid (MA) as nucleophilic monomer with ethyleneimine (EI) as electrophilic monomer in solution at 35°C was investigated. Copolymers are insoluble in water and in common organic solvents as $CHCl_3$, DMF, MeOH and they were characterized by IR spectroscopy and elemental analyses. Six copolymers were examined as resins with retention properties for copper(II), iron (III) and uranium (VI).

INTRODUCTION

The process of copolymerization usually requires an initiator, catalyst or high energy radiation but there have been reports on zwitterion copolymerization which occur spontaneously between a pair of nucleophilic (MN) and electrophilic (ME) monomers forming alternating or statistical copolymers (1-13). The interaction between these monomers generate an ionic species $^{+}MNME^{-}$ which is the key intermediates responsible for initiation and for propagation.

$$\mathrm{MN} + \mathrm{ME} \longrightarrow \underset{\textbf{1}}{{}^{+}\mathrm{MNME}^{-}} \rightleftharpoons \underset{\textbf{2}}{{}^{+}\mathrm{MN}\left(\mathrm{MEMN}\right)_{n}\mathrm{ME}^{-}}$$

According to our series of studies on the noncatalyzed copolymerization via zwitterion intermediates (7-13), the copolymerization between methacrylic acid(MA) as electrophilic monomer with ethyleneimine (EI) as nucleophilic monomer is now reported. The retention properties for uranium, copper and iron are examined.

EXPERIMENTAL

Materials: Ethyleneimine (Fluka) was distilled from KOH (pellets) under N_2; Methacrylic acid (Merck) was distilled under N_2. Acetonitrile was distilled over P_2O_5 under N_2.

Copolymerization reaction: A typical procedure for the copolymerization is as follows: the mixture of EI and MA (total amount: 0.04 mole) was placed in a polymerization flask under N_2 in the presence of a p-methoxyphenol(1mg) as radical polymerization inhibitor. The system was kept at 35°C for 48 h.

The copolymers were precipitated in diethyl ether. The copolymer was separated by centrifugation and purified by reprecipitation and dried under vacuum.

Measurements: The IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. Iron (III) and copper(II) were determined on a Perkin Elmer atomic absorption spectrophotometer and uranium on a PMQ II Carl Zeiss spectrophotometer.

RESULTS AND DISCUSSION

The copolymerization between EI and MA was carried out under various experimental conditions. Seven copolymerizations were carried out with different feed ratios and solvents. The conditions are summarized in Table 1.

Table 1. Copolymerization conditions for ethyleneimine (EI) with methacrylic acid (MA) at 35°C for 48 h.

Copolymer	EI (mol)	MA (mol)	Solvent (5ml)	Initial ratio EI:MA	Yield (%)
1	0.030	0.010	CH_3CN	1.00:0.33	98
2	0.027	0.013	CH_3CN	1.00:0.50	90
3	0.020	0.020	CH_3CN	1.00:1.00	92
4	0.013	0.027	CH_3CN	1.00:2.00	70
5	0.010	0.030	CH_3CN	1.00:3.00	61
6	0.020	0.020	C_6H_6	1.00:1.00	90
7	0.020	0.020	CH_3COCH_3	1.00:1.00	78

All the copolymers are insoluble in water and organic solvents such as chloroform, ethanol, dimethylformamide.

The copolymerization yield increased as the feed became richer in EI. For the EI/MA ratio of 1.00:0.33 the yield was 98%.

The IR spectra of the 7 copolymers are the same; they exhibited characteristic absorption bands at 1640 and 1730 cm^{-1} corresponding to $\nu_{C=O}$ (amide) and $\nu_{C=O}$ (ester) respectively.

The copolymer compositions were determined by elemental analyses (see Table 2). The N/C ratio is unaffected by the occluded water in the copolymer was determined.

Table 2.- Elemental analyses of the copolymers.

Copolymer	Experimental values		
	%C	%H	%N
1	54.63	9.46	15.87
2	54.39	9.00	15.44
3	54.98	8.93	11.99
4	56.46	8.58	7.44
5	57.21	8.09	6.78
6	56.00	8.93	13.39
7	57.39	7.85	12.36

Some theoretical composition values:

$(EI)_{2.0}(MA)_{1.0}(H_2O)_{0.2}$; C=54.59; N=15.92; H=9.32
$(EI)_{1.4}(MA)_{1.0}(H_2O)_{0.1}$; C=55.74; N=13.38; H=9.02
$(EI)_{1.2}(MA)_{1.0}(H_2O)_{0.1}$; C=55.02; N=12.03; H=8.74
$(EI)_{0.85}(MA)_{1.0}(H_2O)_{0.0}$;C=55.74; N=9.69; H=8.35
$(EI)_{0.60}(MA)_{1.0}(H_2O)_{0.0}$; C=55.74; N=7.50; H=8.04

Table 3.- Copolymer compositions

Copolymer	EI (mol)	MA (mol)	Initial ratio EI/MA	N/C[a] ratio	Copol.Compos. EI/MA	Incorporation water (in mol)
1	0.030	0.010	1.00:0.33	0.2905	1.00:0.51	0.194
2	0.027	0.013	1.00:0.50	0.2839	1.00:0.53	0.230
3	0.020	0.020	1.00:1.00	0.2181	1.00:0.84	0.106
4	0.013	0.027	1.00:2.00	0.1318	1.00:1.72	0.000
5	0.010	0.030	1.00:3.00	0.1185	1.00:1.96	0.000
6	0.020	0.020	1.00:1.00	0.2391	1.00:1.38	0.000
7	0.020	0.020	1.00:1.00	0.2153	1.00:1.20	0.000

[a] Determined from elemental analyses.

The copolymer compositions were calculated without considering the crosslinking reaction, although it occurs.

According to the data in table 3 the copolymer structure is influenced by the initial composition of the comonomer mixture.

These copolymers contain nitrogen which is a good ligand for ions such as copper, uranium and iron (14-22); thus the following assays by batch method were carried out for the copolymers 1 to 6.

pH dependence for copper. The adsorption of this ion was analyzed as follows: A mixture of 0.1 g of the resin and 50 ml of an aqueous solution containing 1g/l in Cu^{++} from $CuSO_4 \times 5H_2O$ was shaken for 2 h. The adsorption experiments were carried out in the pH range from 0 to 3. The resin was filtered and copper was analyzed on the filtrates. (See Table 4).

Table 4. Percent of copper (II) adsorbed

Resin	pH			
	0	1	2	3
1	6.5	4.4	17.9	26.0
2	0.6	3.4	22.7	35.7
3	3.3	9.4	41.9	44.2
4	1.4	2.3	35.5	16.2
5	3.9	4.4	23.3	24.3
6	4.9	5.0	32.5	34.4

pH dependence for uranium. These experiments were carried out in a similar way as for copper. The solution contained 1.0g/l in uranium (from uranyl-acetate). Uranium was determined by spectrophotometric method (See Table 5).

Table 5. Percent of uranium (VI) adsorbed.

Resin	pH			
	0	1	2	3
1	52.3	78.9	85.1	100.0
2	98.5	98.8	100.0	100.0
3	94.0	80.6	100.0	100.0
4	82.1	100.0	100.0	100.0
5	88.0	81.6	80.6	100.0
6	68.3	100.0	100.0	79.9
IRA-400	14.2	31.9	70.9	28.5

All the copolymers show retention for both copper and uranium. There is a very low retention of copper particularly at pH 0 and 1. Uranium retention at these pH is high.

Copolymers 4 and 6 adsorb 100% of uranium and only 2.3 and 5.0% of copper at pH=1.0, respectively. All copolymers show a better adsorption behaviour than IRA-400 a commercial resin under these experimental conditions.

The six copolymers adsorb less than 8% of iron (III) at pH 2.0. This observation is relevant as iron is an important interferent in copper minerals.

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