ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 7, pp. 1721–1724. © Pleiades Publishing, Ltd., 2015.
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Synthesis and Properties of Copolymers of *N,N*-Dimethyl-*N,N*-bis(β-chloroallyl)ammonium Chloride with Acrylamide

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Received March 17, 2015

Abstract—A method of synthesis of cationic polyelectrolites is suggested based on *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride prepared from organochlorine wastes from epichlorohydrin production and acrylamide. Flocculating ability of the copolymer was studied.

Keywords: organochlorine wastes, *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride, flocculating ability

DOI: 10.1134/S1070363215070257

Copolymers with cationic functional groups find wide application in wood products and pulp-and-paper industry, biotechnology, medicine, purification of sewage and drinking water, therefore the expansion of their assortment is a state-of-the-art problem. Among a rather limited number of most thoroughly studied polyelectrolytes are the synthesis and properties of polymers and copolymers of *N,N*-dimethyl-*N,N*-diallylammonium chloride which is prepared from dimethylamine and allyl chloride [1, 2]. However, the principal method of preparation of allyl chloride by gas-phase high-temperature chlorination of propylene is followed by the formation of a number of by products, in particular, 1- and 2-monochloropropenes, polychloropropanes and -propenes, and other compounds [3]. Therefore, the attempt of synthesis of cationic polyelectrolyte from industrial organochlorine wastes can simultaneously solve two problems: designing a water-soluble copolymers with valuable properties and utilization of organochlorine wastes by their conversion into polymeric compounds. The production of one ton of epichlorohydrin results in the formation of ~500 kg of organochlorine wastes, 80–85% of which is 1,2,3-trichloropropane [4, 5]. Organochlorine wastes are specific in that they do not have natural analogs, so there are no strains of microorganisms capable of transforming them into nontoxic products. Besides, a high photochemical activity of organochlorine compounds and their enhanced ability to penetrate in living organisms make them highly toxic and ecologically harmful. The existing methods of their utilization by combustion or by high-temperature chlorination are followed by the formation of secondary toxicants [5]. With this in mind, the only promising way of rendering them harmless is the conversion into compounds which could find wide application.

The goal of the present study was to develop a method of synthesis of cationic polyelectrolyte on the basis of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride from organochlorine wastes of epichlorohydrin production and the investigation of its flocculating ability.

1,2,3-Trichloropropane is isolated from the mixture of organochlorine wastes by extraction of water-soluble admixtures (epichlorohydrin, dichloropropanols, chloroethers) with water containing 2–3 g/L of sodium carbonate or sodium hydroxide at pH of 7–8. After removal of water-soluble admixtures, the mixture is subjected to azeotropic drying, and then 1,2,3-trichloropropane is isolated by rectification in ≥99 % yield, which after treatment with alcoholic NaOH solution gives 2,3-dichloropropene-1.

$$ClCH_2CHClCH_2Cl + NaOH \xrightarrow[-NaCl,\ -H_2O]{} H_2C{=}CHCl{-}CH_2Cl.$$

Table 1. Copolymerization of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride (M_1) and acrylamide (M_2)

Exp. no.	Composition of starting mixture, mol %		Composition of copolymer, mol %		Yield, %
	M_1	M_2	m_1	m_2	
1	90	10	25.7	74.3	12.6
2	70	30	22.6	77.3	34.7
3	50	50	21.6	78.4	56.2
4	30	70	8.7	91.3	64.9
5	10	90	3.9	96.1	78.3

Table 2. Comparison of flocculating ability of the copymer on the basis of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride–acrylamide and industrial VPK-402

Disperse system	Flocculation rate, mm/s	
	copymer[a]	VPK-402
Phosphorite	4.8	3.6
Golden ochre	5.0	4.0

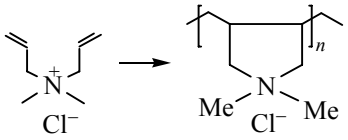
[a] Content of acrylamide units is 77.3 mol %.

By the reaction of 2,3-dichloropropene-1 with dimethylamine at 40ºC *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride was obtained in 80% yield. The structure and composition of this salt were proved by the IR and NMR spectroscopy and elemental analysis.

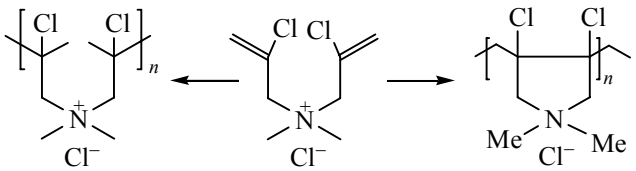
$$H_2C{=}CHCl{-}CH_2Cl + Me_2NH \longrightarrow Me_2\overset{+}{N}(CH_2CCl{=}CH_2)_2\ Cl^-.$$

Homopolymerization of the synthesized salt gives rise to solid polymer powder, readily soluble in water, in the yield of ~25%. The increase of the temperature, concentration of ammonium persulfate, or duration of the reaction did not lead to increase in the yield.

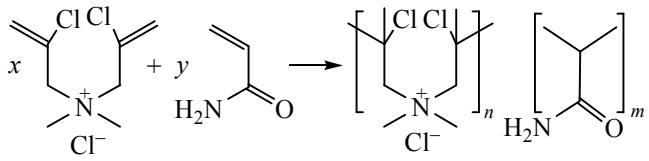
Numerous studies of polymerization of *N,N*-dimethyl-*N,N*-diallylammonium chloride, which is close in structure to the aforementioned salt obtained by us, have shown that the reaction gives rise to the formation of five-membered pyrrolidinium fragments [1]:



Therefore, we also do not exclude the possibility of formation of cyclic structures upon polymerization of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride:



By copolymerization of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride and acrylamide we obtained solid compounds readily soluble in water (Table 1). In the IR spectra of the synthesized copolymers the absorption bands of the stretching vibrations of the C–N bond (1230, 1030 cm^{-1}) and acrylamide units (1690, 1600, and 1420 cm^{-1}) appear, but the absorption bands characteristic of the vinyl group are lacking.



With the increase in the content of ammonium salt in the mixture the yield of the product decreased. The maximum content of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride in the copolymer is 25.7 mol % when the starting mixture contains 90 mol % of the dichloro-containing monomer.

From the dependence of the copolymer composition on the composition of the starting mixture the constants of copolymerization were calculated: r_{salt} = 0.06, $r_{acrylamide}$ = 3.36.

The values of relative constants of copolymerization are indicative of a larger activity of acrylamide as compared to that of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride, so with the increase of the amount of the latter in the starting mixture the yield of the product decreased.

The industrial cationic polyelectrolyte poly-*N,N*-dimethyl-*N,N*-diallylammonium chloride (VPK-402) from "Kaustik" is produced as 30% aqueous solution and is an effective flocculant. We have prepared 30% aqueous solution of the copolymer on the basis of *N,N*-

dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride and acrylamide and compared the flocculating ability of polyelectrolytes (Table 2). As follows from the data of Table 2, the flocculating ability of the copolymer of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride and acrylamide is practically as good as that of VPK-402.

Therefore, a new way of utilization of organochlorine wastes of epichlorohydrin production is found by converting them into cationic polyelectrolytes and possible ways of their application are proposed.

EXPERIMENTAL

Acrylamide of "pure" grade was several times crystallized from benzene and dried in a vacuum at 40°C. Ammonium persulfate was crystallized from bidistilled water at the temperature no higher than 30–40°C and dried in a vacuum dessicator over P_2O_5. Elemental analysis was performed on gas analyzer Thermo Finnigan Flash EA 1112 Series. IR spectra were taken on a Specord 75IR spectrophotometer in KBr. NMR spectra were registered on a Varian VXR-500S spectrometer in C_2D_5OD with HMDS as an internal reference.

Flocculating ability of polyelectrolytes was determined as follows: graduated cylinder was charged with suspension prepared from the mixture of 40 g of ochre or phosphorous sludges, added 1 L of water was added and 3 mL of working solution of flocculant. After active shaking for 5 min the time of full sedimentation of suspended particles or the time of reaching of deep cleaning of water was measured.

Isolation of 1,2,3-trichloropropane. Water soluble admixtures (epichlorohydrin, dichloro-propanol, chloroethers) contained in wastes with 1,2,3-trichloropropane were removed by washing with water with added 2–3 g/L of Na_2CO_3 or NaOH to maintain pH of 7–8. From the residue, 1,2,3-trichloropropane of ≥99% purity (according to GC) was isolated by azeotropic distillation and rectification.

Preparation of 2,3-dichloropropene-1. 147.5 g (1 mol) of 1,2,3-trichloropropane was treated with 10% alcoholic NaOH solution at room temperature for 4 h. The precipitated NaCl was filtered off and from the filtrate 115 g (80%) of the target product was isolated by fractional distillation.

Synthesis of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl) ammonium chloride. To 68.2 g (0.5 mol) of 33% aqueous solution of dimethylamine at 40ºC and vigorous stirring 55 mL (0.5 mol) of freshly distilled 2,3-dichloropropene-1 and 50 g (0.625 mol) of 50% aqueous NaOH was added in the course of 20 min. The obtained mixture was kept for 4–6 h at 60ºC. After completion of the reaction the organic layer was separated and stored at room temperature till the precipitation of the crystals of quaternary salt. Yield 58.0 g (80%). IR spectrum, ν, cm^{-1}: 1030, 1230 (C–N), 1648, 2975, 3080 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.18 d (4H, $=H_2C$, *J* 96.7 Hz), 4.70 s (4H, $2CH_2$), 3.41 s (6H, $2CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 126.12 ($=CH_2$), 125.33 (=CCl), 66.51 (CH_2), 47.33 (CH_3).

Homopolymerization of *N,N*-dimethyl-*N,N*-bis-(β-chloroallyl)ammonium chloride. Homopolymerization was performed in aqueous solution under the action of ammonium persulfate (0.5 wt %) at 30°C. Ampules were filled by the gravimetric method. After polymerization was completed (7 h) the polymer was purified from the monomer and initiator by dialysis (solvent water). After dialysis the solution of polymer was precipitated by the mixture acetone–ether. The formed precipitate of the polymer was filtered, washed with water, acetone, and dried in a vacuum at 40°C to a constant mass. Found, %: C, 41.71; H, 6.35; Cl, 46.07; N, 5.87. $C_8H_{14}NCl_3$. Calculated, %: C, 41.65; H, 6.07; Cl, 46.21; N, 6.08.

Copolymerization of *N,N*-dimethyl-*N,N*-bis(β-chloroallyl)ammonium chloride and acrylamide. Copolymerization was carried out in aqueous solution by the action of ammonium persulfate (0.5 wt %) at 30°C. Ampules were filled by the gravimetric method. After completion (7 h) of the reaction the product was dissolved in water, the copolymer was precipitated by the mixture acetone–ether. Copolymers were twice reprecipitated from aqueous solution by the mixture acetone–ether and dried in a vacuum to a constant mass. The composition of the copolymer was calculated from the data of elemental analysis on chlorine by standard procedure [6].

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Education and Science, project no. 37.

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