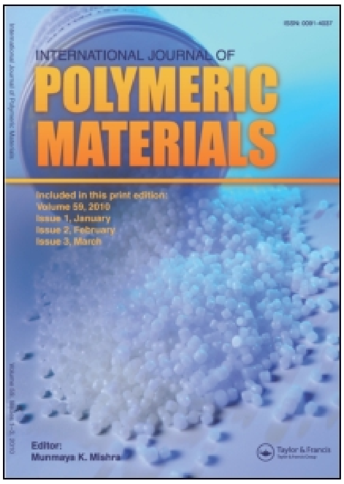

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I. A. Golubeva[a]; V. F. Gromov[a]; Ye. V. Bune[a]; O. N. Tkachenko[a]; R. H. Almaev[a]
[a] Academy of Oil and Gas, Moscow

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Stabilization of Cationic Acrylamide Polymers Designed to Enhance Oil Recovery

I. A. GOLUBEVA, V. F. GROMOV, Ye. V. BUNE, O. N. TKACHENKO and R. H. ALMAEV

Academy of Oil and Gas Moscow-117236, Leninsini Prospect 65.

Synthesis and stabilization of high molecular weight water soluble cationic acrylamide are investigated to develop products that enhance oil recovery.

KEY WORDS Oil recovery, acrylamides

To enhance oil recovery, water-soluble acrylic polymers have been increasingly used. Their principal purpose is to compensate for the heterogeneity of the producing formation and to extend flooding sweep area. That can be achieved by means of water thickening, by addition of a certain amount of polymer into the process of conventional flooding of oil-bearing formation, as well as by limiting water influx by producing a plugging agent owing to the focculating properties of the polymers. These polymer properties can be utilized in solving ecological problems—by treatment of oil-containing waste water.

The authors have studied possible means to synthesize and stabilize high-molecular weight water-soluble cationic acrylamide (HA) polymers designed to enhance oil recovery processes.

Synthesis of cationic polymers was carried out by means of radical copolymerization of acrylamide with dimethyldiallylammonium chloride (DMDAAC) or dimethylaminoethylmethacrylate sulfate (AM.HA) under isothermic conditions or at adiabatic heating-up of the reaction mixture. The adiabatic mode of polymerization was chosen because it most closely corresponded to industrial production conditions. It was difficult to maintain constant temperature in large reactors during synthesis of the polymers due to substantial heat evolution and the high viscosity of the reaction mixture which developed in these systems during previous process stages.

Technical solutions of DMDAAC of specific concentration (~40% by weight) were used in the study.

It was found that addition of acrylamide to DMDAAC caused an increase in polymer molecular weight (Table I). High-molecular weight copolymers of acryl-

TABLE I

Copolymerization of acrylamide with DMDAAC

Polymerization conditions	AA/DMDAAC mol.%	[M] mol/l	[PK] mol/l	$T_{init.}$ °C	[η] dl/g
Isothermal	30/70	3,7	I.IO^{-2}	30	2,9
	30/70	3,7	I.IO^{-2}	60	I,7
	0/IOO	2,6	I.IO^{-2}	60	0,44
	30/70	3,7	I.IO^{-3}	30	2,9
	30/70	3,7	I.IO^{-3}	60	2,I
	0/IOO	2,6	I.IO^{-3}	30	0,39
	0/IOO	2,6	I.IO^{-3}	60	0,49
Adiabatic	48/52	4,3	0,8.IO^{-3}	25	4,I
	48/52	4,3	2,9.IO^{-3}	25	3,7
	48/52	4,3	7,9.IO^{-3}	45	3,7
	I6/84	3,0	2,9.IO^{-3}	25	I,9

amide with DMDAAC were produced both in isothermic and adiabatic regimes. Variations in initiator concentration and reaction temperature only insignificantly affected molecular weight and the properties of the polymers, apparently, because of the controlling influence of chain transfer reactions through the DMDAAC molecules.

Copolymerization of acrylamide with AM.SA was studied for a wide range of monomeric mixture compositions, at different total concentrations of monomers, initiator and chain transfer agents. The reaction was carried out in the presence of potassium persulfate, at an initial temperature 25–30°C.

It is known that in order to produce high-molecular weight polymers the reaction should be performed in concentrated solutions. However, in the process of copolymerization of acrylamide with AM.SA under adiabatic conditions, variation of total concentration of monomers in the range of 1.5 to 4.5 mL/l has little effect on the molecular weight of the copolymers produced or on their properties. Measured by the light scattering method, the values of M_w for copolymer samples which were produced at monomer concentrations of 1.5–4.5 mL/l were nearly constant and equaled 3.10^6 (Table II).

As we may suppose, the unusual dependence of polymer molecular weight upon monomer concentration is a specific peculiarity of radical adiabatic polymerization. In these conditions the molecular weight of the polymer is subject to such contrary factors as (1) increase of monomer concentration which would elevate molecular weight of the polymer, and (2) increase the maximum temperature of reaction mixture which is more pronounced at high monomers concentrations and induces

TABLE II

Effect of total monomer concentration on molecular weight of AA-DM.SA copolymers (AA/DM.SA = 60/40, [PK] = $2.5 \cdot 10^{-3}$ mol/l, initial temperature 35°C)

[M] mol/l	[η] dl/g	$M_w \cdot 10^{-6}$
4,5	4,6	3,6
3	4,5	3,0
2	4,1	2,6
I,5	5,1	3,5

TABLE III

Effect of monomeric mixture composition on molecular properties of AA-DM.SA copolymers ([Butanol] = 0.1 mol/l, [PK] = $1.0 \cdot 10^{-3}$ mol/l, T_{init} = 25°C)

AA/DM.SA	[M] mol/l	[η] dl/g	$M_w \cdot 10^{-6}$
90/10	3,0	15,0	6,4
80/20	4,5	11,8	5,3
60/40	4,0	12,8	5,8
30/70	4,0	5,4	6,3
70/30[a)]	3,0		4,8
30/70[a)]	3,0		5,6
0/100[a)]	3,0		4,3

an increase in the rate of initiation and chain transfer reactions, and, consequently, causes a decrease in the molecular weight of the polymer.

When the acrylamide content in the monomeric mixtures increased, an increase in the intrinsic viscosity of the copolymers is observed (Table III). Taking into consideration the fact that the molecular weight of these polymers is practically the same, it may seem that this effect is associated with structural difference in the macromolecules produced from different monomer compositions.

The insignificant dependence of copolymer molecular weight upon monomeric mixture composition during copolymerization of acrylamide with AM.SA correlates with the kinetic data for acrylamide copolymerization with dimethylaminoethylmethacrylate salts in diluted aqueous solutions. Indeed, the rate of acrylamide homopolymerization is higher than that of the second co-monomer. However, for the monomeric mixture composition AA: aminoether salt in the range of 80:20 to 30:70, the total rate of copolymerization is approximately constant and close to the rate of the aminoether salt homopolymerization.

In some cases, during the process of copolymerization of monomeric mixtures with high acrylamide content, and, especially, when processing such polymers into powder, water insoluble polymers are produced. Loss of solubility in such a case may be controlled both by a physical factor (particularly, by entanglement of high-molecular weight chains resulting in an extremely slow dissolution rate), and by chemical cross-linking of the polymer under the impact of mechanical stress during the process of grinding. Insoluble polymer generation during processing may also be affected by traces of monomer and/or initiator retained in the powdery polymer.

To produce completely soluble products by the process of copolymerization, the reaction was performed in the presence of a chain-transfer agent; butanol and glycerin were used for this purpose. Introduction of such additives into the reaction mixture provided for lower molecular weight polymer generation with decreased branching and, consequently, with superior solubility. Besides, the decreased branching of polymer chains imparted to their higher stability. The addition of 0.16 mL/l of glycerin to the reaction mixture produced soluble co-polymer with an intrinsic viscosity 10 dl/g. To produce a completely soluble polymer in the presence of butanol, its concentration should be at least 0.5 mol/l.

To prevent polymer cross-linking during the grinding process, a number of stabilizing agents were studied, including: phenoxane (potassium salt of phenozanic acid—PhA), phenozane (composition of phenozanic acid and potassium carbonate—PhZ), mercaptobenzimidazole (MBI), sodium dimethyldithiocarbamate (DDC), thiourea (ThU) and phosphoric acid. The stabilizing effect of PhA and PhZ is based on their interaction with peroxide radicals RO_2^-, the effect of MBI is based on its destruction of hydroperoxides, while DDC displays a complex effect, in particular, the destruction of hydroperoxides and interaction with peroxide radicals.

Stabilizing additives were introduced into the polymer before its grinding. The amount of the additive introduced was from 0.3–10% (to the polymer) and was determined by its water solubility.

It was found that PhA and PhZ not only failed to improve polymer solubility but their introduction into the polymer during processing stage was also accompanied by cross-linking of the polymer chains. In the presence of DDC, polymer solubility improved, however, this effect was possibly associated with a decrease in the molecular weight. Substantial stabilizing activity is peculiar to MBI and ThU. Polymers do not lose their solubility during processing in the presence of these compounds. As a rule, the intrinsic viscosity of such polymers is higher than that of polymers processed in the absence of stabilizing agents. Higher as well were the screen-factor values (used to characterize the viscoelastic properties of aqueous polymer solutions) of the polymers which had been processed in the presence of MBI or ThU (Table IV). Sometimes the introduction of stabilizing agents prevented the formation of insoluble polymer during its processing into powder.

TABLE IV

Effect of stabilizing agents on viscoelastic properties of aqueous polymer solutions (polymer concentration 0.1%)

AA/DM.SA monomeric mixture composition, mol.%	Powdered polymer properties									
	Without stabilizing agent,		MBI 3%		PhZ 1,5%		DDC 10%		ThU 1%	
	[η]	SF	[η]	SF	[η]	SF	[η]	SF	[η]	SF
80/20	9,3	I8	I0,I	32	-	-	4,9	-	I2,2	3I
80/20	7,4	I8	8,0	22	3,6	-	2,5	-	-	-
80/20	5,6	7	6,5	9	H.p.		-	-	-	-
60/40	4,3	6	6,3	9	4,7	8	3,7	-	-	-
60/40	2,5	2	9,2	I9	-	6	I,0	-	-	-

To ascertain the possible synergistic effect of mixtures of individual stabilizers, the system MBI + PhA was studied. The results obtained revealed that, concerning its efficiency, mixtures of these stabilizers did not differ much from the stabilizing effect of the individual components.

An investigation of the effect of stabilizers on viscous and viscoelastic properties of aqueous polymer solution, was based on copolymers of acrylamide with DM.SA of different compositions used. Analysis of the results obtained revealed that the relationships found were valid for all the samples investigated. Acrylamide content in these samples varied over the range of 80 to 30 mol.%.

Cationic polymers produced in this work and processed in the presence of stabilizers were able to improve significantly the solution viscoelastic properties, and in this respect they may in practice be used as water thickeners, e.g., in oil production processes. The products synthesized are peculiar for their relatively high screen-factors values.

Flocculation properties of the stabilized polymers synthesized were also studied. The flocculation effect was estimated by means of the settling into of a bentonite suspension in mineralized water. It was shown that, unlike the completely cationic industrial polymer WPC-402 which did not affect settling rate, the addition of only small amounts of AA-DM.SA copolymer to the suspension was accompanied by a sharp increase in flocculation rate. As to their efficiency in such systems, cationic AA-DM.SA copolymers containing 60–80 mol.% of acrylamide moieties and with a molecular weight of about 7.10^6 also surpassed acrylamide homopolymer of the same molecular weight.

Thus, techniques to produce completely water-soluble powdered cationic acrylamide polymers with high functional performance were found in this study.