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Sulfonated copolymers of acrylamide synthesized by plasma-initiated copolymerization in order to obtain polymers for enhanced oil recovery

Cristofor I. Simionescu* and Carmen Chelaru

"P. Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica-Voda 41A,
6600 Jassy, Romania

SUMMARY

High molecular weight acrylamide (AAM, M1)-co-2-acrylamido-2-methyl propane sulfonic acid (AAMPS,M2) copolymers were obtained by plasma-initiated copolymerization in water solutions. The reactivity ratios, determined by Kelen-Tudos method, were shown to be $r_1 = 1.04$ and $r_2 = 0.41$. Some microstructural aspects of the obtained copolymers are presented. In order to test a special use (mobility control in polymer flooding technology), the rheological and thermal behaviour were investigated.

INTRODUCTION

In some previously published papers, plasma-initiated polymerizations (PIP) and copolymerizations were reported (1-5). Experimental data showed that a "living" radical mechanism of polymerization has to be considered (6,7) to explain this new approach to polymer synthesis. Some results (8-10) pointed out the possibility to direct the synthesis towards very low polydispersity ultra high molecular weight polymers.

In order for a polymer to be economical in Enhanced Oil Recovery (EOR), it must produce a large viscosity increase at low concentration. To be used as good viscosity modifiers in displacement fluids for EOR, the polymer molecules must have very large dimensions in water (11).

Copolymers of acrylamide and sulfonated monomers are promising due to their large dimensions in water solutions even in the reservoirs with large calcium and sodium contents, of their good thermal stability and resistance to the biological degradation (12).

Sulfonated copolymers of acrylamide were synthesized by classical radical polymerization (13), but in order to obtain ultrahigh molecular weights we used for synthesis of AAM/AAMPS copolymers the method of PIP.
The objectives of this work were to prepare AAM/AAMPS copolymers and to investigate some characteristics of the obtained products.

EXPERIMENTAL

The experimental apparatus and procedure of PIP used in the present synthesis was essentially the same as that already reported earlier (1-5).
Monomers were purified prior to use. AAM, reagent grade from Merck-Schuchardt, and AAMPS were twice recrystallized from methanol and vacuum dried at room temperature.

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*Corresponding author

The comonomers mixtures in water solutions were introduced in polymerzation ampoules, degassed by repeated freezing and thawing at 10^{-3} -10^{-4} torr, and finally frozen in liquid nitrogen and sealed. Electrical discharge was then operated between two electrodes situated on each ampoule at 2.0 and 3.0 cm respectively from the frozen sample and coupled to a high frequency generator (2.5 MHz, 100W), the discharge duration being 60 seconds. Following initiation, the ampoules were kept in dark at 25° C. The postpolymerization time was 3 hrs for the samples used to obtain the copolymerization data and 72 hrs for the samples with maximum polymer yield. After opening the ampoules, the samples were diluted with distiled water and precipitated in methanol for several times.
The copolymer compositions were determined by elemental analysis and H-NMR spectroscopy, the spectra being registered in D_2O solutions at 60° C on a JEOL-C60HL spectrometer.

The solutions of copolymers were prepared by very gentle mixing and no mechanical stirring was applied to prevent shear degradation. Intrinsic viscosities were measured in 1M NaCl solutions, at 30° C, on a standard Ubbelhode viscometer. The data here reported were not corrected for the shear rate effect on the viscosity, which is expected to be small, but significant for high molecular weight polymers such those used in this work. The most important limiting condition in EOR is the porous media flow.

For testing the virtual activity of these copolymers in EOR, it was determined (in the same conditions like intrinsic viscosities) "the screen factor" (Fs), which make evident the relationship between polymer size and pore size of the reservoir rock, as indicator of polymer effectiveness (14). Fs is defined as the ratio of the flow time of a given volume of polymer solution through a relatively open porous medium, to the flow time for the appropriate solvent (water or brine). A simple instrument was designed to measure Fs. The "screen viscometer" that we used has a measured fluid volume of about 35 ml and consists of a pack of five 10 mm diameter 100 mesh stainless steel screens. The solutions were first filtered to avoid plugging the viscometer.

The thermal behaviour of the copolymers synthesized was analyzed by DSC and TGA. DSC was performed on the V40B (Du Pont) 2000 instrument and TGA was performed on the V51A (Du Pont) 2000 instrument.

RESULTS AND DISCUSSION

1.Copolymerization Data

The IR spectra (Figure 1) make evident the formation of the AAM/AAMPS copolymers.
Copolymerization and structural data obtained from 1HNMR spectra (Figure 2) are summarized in Table 1 and the copolymerization diagram is presented in Figure 3.
Monomer feed ratios and experimentally determined values of copolymer composition were used to evaluate monomer reactivity ratios for the sulfonated copolymers. The Kelen-Tudos method (15) were used to determine reactivity ratios at low conversion. In Figure 4 the Kelen-Tudos plot for the copolymerization of AAM (M1) and AAMPS (M2) is represented. The obtained reactivity ratio values are r_1=1.04 and r_2 =0.41. The experimental data lie on a straight line, indicating that no penultimate effect seems to exist for these copolymers and that the terminal model of copolymerization could be considered to describe this system.

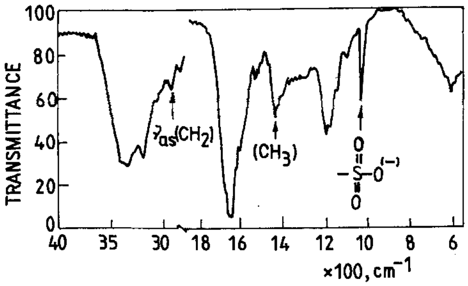

Figure 1. IR spectrum of AAM/AAMPS copolymer.

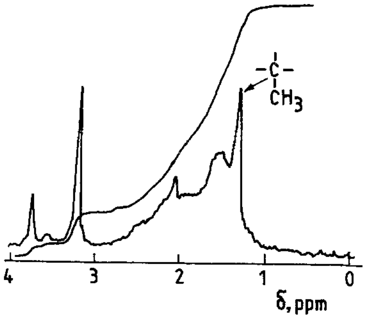

Figure 2. 1HNMR spectrum of AAM/AAMPS copolymer.

Table 1. Copolymerization* and structural** data for AAM(M1)/AAMPS(M2) copolymers obtained by PIP.

Sample	Feed composition (M1)/(M2)***	Conversion %(g)	Copolymer d(M1)/d(M2)	Contact type (probability) f_{1-1}	f_{2-2}	f_{1-2}
S1	0.111	4.18	0.232	0.0200	0.6430	0.3370
S2	0.250	2.10	0.479	0.0670	0.4203	0.5127
S3	0.428	4.62	0.709	0.1379	0.2881	0.5740
S4	0.666	5.43	1.000	0.2046	0.2054	0.5900
S5	1.000	7.60	1.381	0.2976	0.1340	0.5684
S6	1.500	6.15	1.821	0.4060	0.0760	0.5180
S7	2.333	5.76	2.773	0.5206	0.0401	0.4393
S8	4.000	8.16	4.555	0.6570	0.0172	0.3258
S9	9.000	8.72	9.63	0.8198	0.0062	0.1740

* from 1HNMR spectra,

** statistically calculated from the reactivity ratios.

*** for 5% wt monomers in water

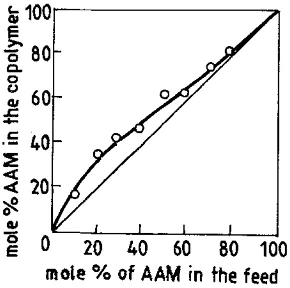

Figure 3. Copolymerization diagram for the system AAM/AAMPS.

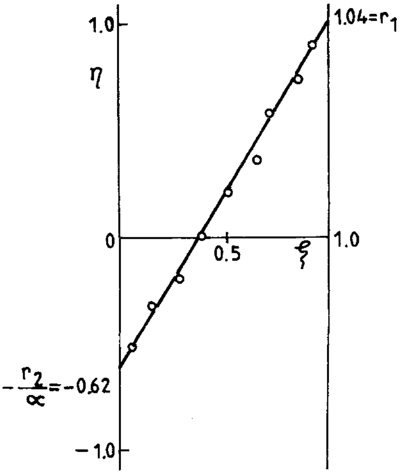

Figure 4. The Kelen-Tudos plot.

The obtained values for the reactivity ratios are in agreement with the steric and electrostatic factors (16-18).

2.The Rheological Behaviour

The high values obtained for the intrinsic viscosity [η] and the screen factor Fs indicate that it is possible to synthesize, by PIP, ultrahigh molecular weight copolymers AAM/AAMPS.
Figure 5 shows that introducing AAMPS (strong acid) units into the macromolecular chain of PAAM (a nonionic polymer) a remarkable increase both in [η] and Fs occurs.

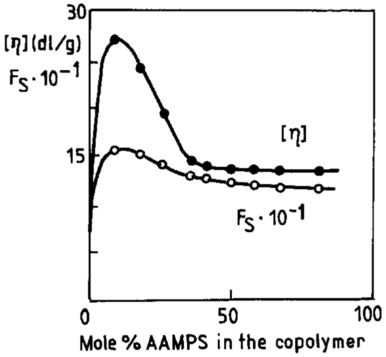

Figure 5. The intrinsic viscosities and "screen factor" for different compositions of AAM/AAMPS copolymers

The intrinsic viscosity and "screen factor" increased as consequence of an expansion of the polymer coil in solution, due to the repulsive forces (both the intramolecular coulombic repulsion from the ionic groups and steric repulsion).
Taking into account the fact that these values are obtained in 1M NaCl, and AAM/AAMPS copolymer, like any polyelectrolyte has sensitivity to brine, it appears that the effect is stronger (19).

The [η] and Fs measurements were performed immediately after the solutions preparation, in accordance with Kulicke's observations (20,21) about the conformational change that can occurs at ultrahigh molecular weight polymers and that can lead to either an increase or a decrease in viscosity.

The results of [η] and Fs measurements as function of copolymer composition indicate an optimum corresponding to 9.4 % mole AAMPS in copolymer (a maximum in [η] - and Fs-composition responses). Up to 9.4 % AAMPS in copolymer, the increase of the amount of sulfonic acid groups leads to a strong rising both of [η] and Fs, because of the increase in coil dimensions After this point [η] and Fs continuously decreases up to aprox. 30% AAMPS in copolymer, after this they remaining at constant values.

3.The Thermal Behaviour

The DSC curve (Figure 6) makes evident two endotherm processes: the first beginning at 115°C, with a maximum at 131.9°C, and the second starting at 273.13°C, with a maximum at 297.5°C.

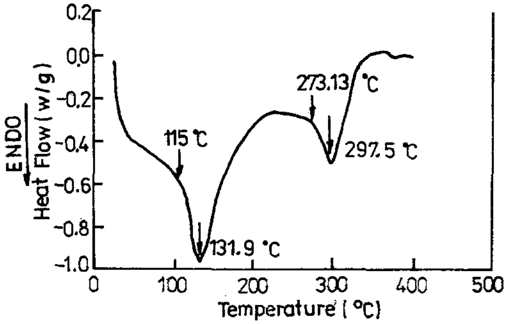

Figure 6. DSC curve of AAM/AAMPS copolymer (S9): sample size 28.377 mg; heating rate 10 °C/min, nitrogen purge.

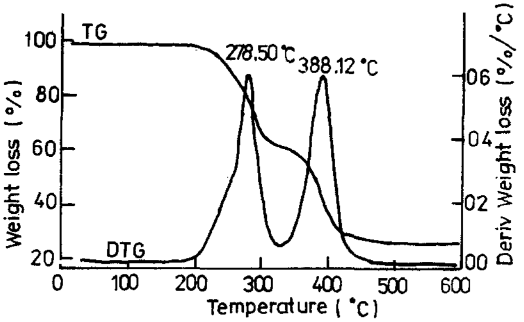

Figure 7. TG and DTG curves of AAM/AAMPS copolymer (S9): sample size 6.315 mg, heating rate 10°C/min, nitrogen purge.

We can attribute the first transition to the melting process of the copolymer, while the second peak could be attributed to an endotherm degradation process, which can be correlated with the TG data.
The TG curve (Figure 7) shows two stages of the weight loss, the first between 200°C and 330 °C, with a weight loss about 38%, and the second between 330°C and 460°C, with a weight loss about 34%, respectively.

CONCLUSIONS

1. Using the experimentally determined reactivity ratios and classical statistical relationships, it is possible now to synthesize by plasma-initiated polymerization model copolymers AAM/AAMPS, with controlled structure.

2. The intrinsic viscosity and "screen factor" data determined for the brine solutions of the copolymers of AAM with AAMPS obtained by PIP indicate ultrahigh molecular weights for these products.

3. The DSC and TG data indicate a good thermal stability for these copolymers.

4. From the rheological behaviour and thermal behaviour we can conclude that using plasma-initiated copolymerization of AAM and AAMPS it is possible to obtain copolymers with characteristics that make they very interesting for the suggested purpose.

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