Polymer Bulletin 40, 757–764 (1998)

Polymer Bulletin

Polyacrylamide obtained by plasma-induced polymerization for a possible application in enhanced oil recovery

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Received: 18 March 1998/Revised version: 21 April 1998/Accepted: 24 April 1998

Summary

Ultrahigh molecular weight polyacrylamides (PAAM) were obtained by plasma-induced polymerization in water solutions. The influence of monomer concentration, sealing pressure, initiation time and post polymerization period on polymer yield and molecular weight were investigated. The viscosity and “screen factor” measurements, as well as the thermally stimulated depolarization currents spectroscopic data of the synthesized polymers, indicate good properties as efficient viscosity modifiers in displacement of fluids for enhance oil recovery (EOR).

Introduction

Polyacrylamide and its derivatives form a class of water-soluble polymers used extensively through the oil producing industry for a variety of applications: drilling of a well, chemical and hydraulic treatments designed to stimulate production, secondary and tertiary recovery operations, etc. (1). Each application requires specific properties for polymers. In tertiary recovery are of upmoste importance: (i) the complete solubilization of the polymers, (ii) the absence of the branches, in order to diminish the shear degradation, (iii) the achievement of ultrahigh viscosity in dilute solutions; (iv) the achievement of an efficient mobility control in polymer flooding, namely high values for resistance factor (F_R).

A number of different polymerization methods are applied to polymerize acrylamide (AAM) (2). Unfortunately, these methods don’t lead to ultrahigh molecular weight polymers. In some previously published papers, plasma induced polymerization (PIP) was reported, some results pointing out the possibility to direct the synthesis towards very low polydispersity ultrahigh molecular weight polymers (3-7). In order to obtain polyacrylamide (PAAM) satisfying the four above mentioned demands, in our continuing investigations (8,9), we report now the synthesis by PIP of PAAM. Some properties of the obtained polymers were investigated by viscosimetric measurements and thermally stimulated depolarization currents (TSDC) spectroscopic analysis.

Experimental

The experimental apparatus and general technique of PIP are described in previously published papers (5-7). AAM monomer, reagent grade from Eastman Kodak, was recristallized twice from methanol and vacuum dried at room temperature prior to use

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(m.p. 83,5^{0}C). Preweighted amounts of monomer or its solutions in deionized water were introduced in polymerization Pyrex ampoules, degassed by repeated freezing and thawing under vacuum and finally frozen in liquid nitrogen and sealed at different pressures (p_s). Electrical discharge was than operated between two external electrodes, situated on each ampoule at 2.5 and 3,5 cm respectively from the frozen sample and coupled to a high frequency generator (2.5 MHz, 100 W). The discharge was operated during preestablished periods of time (t_i) These initiation periods were followed by predetermined post-polymerization periods (t_p), during that the ampoules were kept in dark, in a constant temperature bath (25^{0}C). After opening the ampoules, the contents were diluted with deionized water, precipitated with methanol and dried at 25^{0}C under vacuum to constant weight. Conversions were determined gravimetrically. IR spectra of PAAM obtained by PIP give the characteristic peaks and absorption bands of classical polyacrylamide, at the same frequencies.

The polymer solutions for intrinsic viscosity ([η]) and "screen factor" (F_s) measurements were prepared with special cautions. We taken into account the fact that the harsh agitation can physically break macromolecules and the rate at which very large polymers go into solution can be so law as require several days of gentle mixing to obtain true *solution equilibrium conditions* If these don't exist, then the polymer aggregates remaining will falsify all characterization results. In order to respect the *dilution conditions* for EOR polymer characterization (10), we used in our determinations polymer solutions at polymer concentrations of maximum 100ppm, for keeping the overlap parameter from Einstein relation (11) less than one.

The viscosity measurements were performed on a standard Ubbelhode viscometer, In 0,1M NaC1 solutions, at 30^{0}C and pH=7. As consequence of nonionic character of PAAM, its viscosity remains constant with a change of pH from 0 to 10, at pH>10, the polymer undergoes hydrolysis and the specific viscosity increase sharply (12). NaCl was used for a complete elimination of any polyelectrolitic effect and for simulates the field conditions. It is found (13) that addition of NaCl to PAAM solutions does not influence their viscosity.

In order to calculate the viscous average molecular weights for the obtained polymers from Mark-Houwink-Sakurada equation:

$$[\eta] = k \cdot \overline{M}_v^{\,a}$$

we used Francois relation (14,15):

$$[\eta] = 9.33x\ 10^{-5}\,\overline{M}_v^{\,0.75}$$

Taking into account that for ultrahigh molecular weight PAAM "k" and "a" values are unknown, like for most EOR polymers, this relation appears like the most close for our needs as application domain ($1.6x\ 10^5 < M \leq 8.1 \times 10^6$). The reported data were not corrected for the shear rate effect on viscosity, which is expected to be small, but in any case, the true molecular weights could be higher than those calculated for our polymers.

The most important limiting condition in EOR being the porous media flow, for testing a virtual activity of the obtained polymers in this domain, it was determined (in the same conditions like intrinsic viscosity) the "screen factor" (F_S), as indicator of polymer effectiveness (16). F_S, 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), is very well correlate with F_R. The experimental technique of F_S determination was described in a previously published paper (9). Both [η] and F_S measurements were performed *immediately* after solutions preparation, in order to respect Haas's (17) and Kulicke's (18,19) observations on the formation, in time, of some supermolecular particles (precipitate-like) in aqueous solutions of high molecular weight polyacrylarnide and, respectively, about the conformational change that occurs at ultrahigh molecular weight polymers in solutions, and that can leads to either an increase or a decrease in viscosity.

TSDC method, which commonly works in ranges of equivalent frequencies of 10^{-4}-10^{-2}Hz, was used like tool for the molecular motions, structure and transitions study of the obtained polymers. Samples used for TSDC measurements were disk-shaped, prepared by compressing the compound powder in a mold under a pressure of 10^5 N/cm^2. The 16mm-diameter disks were provided with vacuum-evaporated silver electrodes of circular form. In order to prevent current leakage on surface, the electrodes had a diameter of only 14mm and were centrally placed on both sides of the disk. TSDC measurements were carried out in dry nitrogen using a device described in a previously published paper (20). The thermal cycles of polarization and depolarization of samples consisted of the following steps. A sample with polarization field E_p=13Kv/cm was warmed up to the polarization temperature T_p= 180^{0}C, which was maintained for a polarization time of 20 min. After cooling to –73^{0}C using liquid nitrogen, E_p was removed and the sample was short-circuited for 5 min in order to eliminate the rapid depolarization currents; then, the depolarization currents were recorded at a heating rate of 3.3^{0}C/min.

Results and discussion

Factors influencing PIP of AAM

1. Influence of monomer concentration on monomer conversion and polymer molecular weight was investigated in a series of eleven experiments with different monomer concentrations in water solutions, performed at p_s=10^{-2}torr, t_i=60sec and t_p=60hours. The obtained data are illustrated in Figure 1.

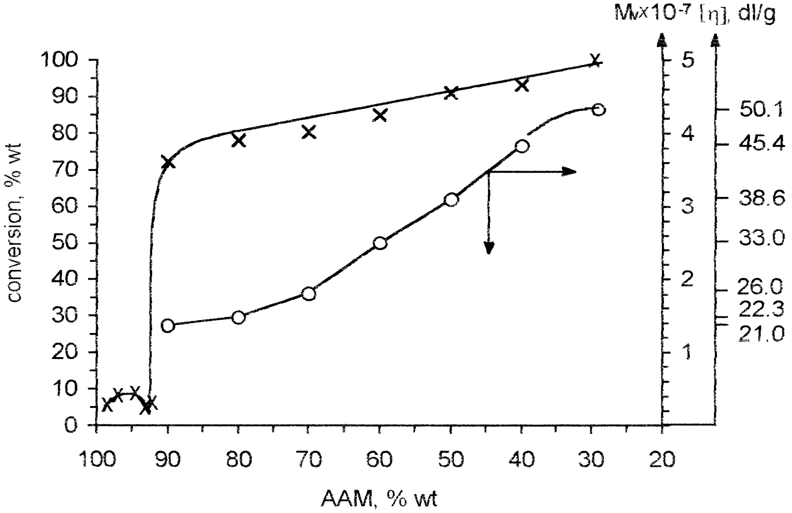

Figure 1. Variation of conversion and polymer molecular weight vs. initial monomer concentration (10^{-2} torr, 60 sec, 60 h)

For samples in which the monomer content ranging between 99-92,5%wt only insoluble (gel-like) polymers were obtained, with very low conversions. We could explain the gel formation by the following: during the discharge, the solid surface of monomer is subjected to a complex bombardment of various plasma species, when some hydrogen atoms are removed. This could leads to free radicals trapped within the growing chain, which can serve as branch and tie points. Relating to the low conversions, these could be explained by the extremely low mobility of the active species. We could not explain the maximum from the conversion curve in the interval of 96-94% wt monomer content.

At approximately 90%wt AAM, the slope of conversion variation curve shows a spectacular increase (Figure 1), that we consider being due to the passing of the system from solid to liquid state. Below 90%wt AAM in the reaction medium, only ultrahigh soluble PAAM are obtained. Both monomer conversion and polymer molecular weights increase with the decreasing of AAM content. This behavior could be due to the increasing of macroradicals mobility as consequence of the monomer concentration decreasing. It is notable the fact that the [η] values of ours polymer solutions are in good agreement with the observations that to be effective and economical EOR candidate, a polymer must have an intrinsic viscosity of about 30dl/g or higher (12).

2. Influence of sealing pressure on molecular weight of the PAAM obtained by PIP, was followed in experiments performed with 50% wt AAM water solutions, at t_i = 60sec and t_p=60 hours, for different sealing pressures. Figures 2 makes evident the increase of the polymer molecular weight with the oxygen quantity increasing.

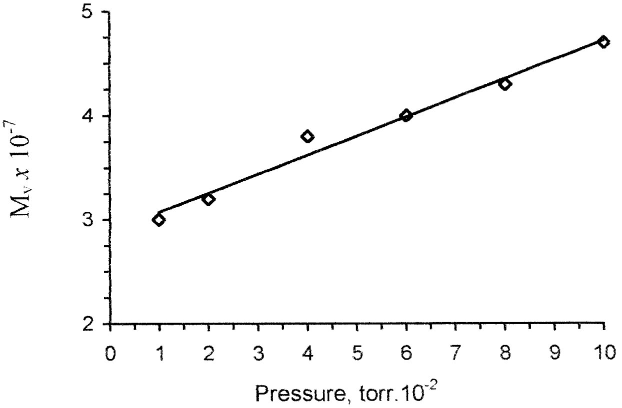

Figure 2. Dependence of molecular weight on sealing pressure (50% AAM, 60s; 60h)

This behavior could be explained by the fact that an increasing of oxygen amount in the reaction medium leads to a higher probability of the O. radicals appearance. The probability of loss by recombination of some “active radicals” increases. As a result, the number of growing macroradicals decreases and the molecular weight: of the polymers increases. Obviously the sealing pressure is limited by the plasma discharge condition.

3. Influence of initiation time on molecular weight of the obtained polymers was investigated in five experiments performed varying the initiation time and keeping constants the rest of operational parameters: 50%wt AAM in reaction medium, 10^{-2} torr-sealing pressure and 60 hours post-polymerization time.

The increasing of discharge (initiation) time leads to an increasing of the number of radicals in plasma, namely to the increasing of the “initiator quantity” and, as consequence, the polymer molecular weights decrease (figure 3).

4. Influence of post-polymerization time on polymer yield and molecular weight were investigated performing experiments with 50%wt AAM in initial mixture, at p_s = 10^{-2} torr, with t_i=60sec and different post-polymerization periods.

Only for monomer conversion they were reiterated the experiments with 70%wt AAM in water solutions.

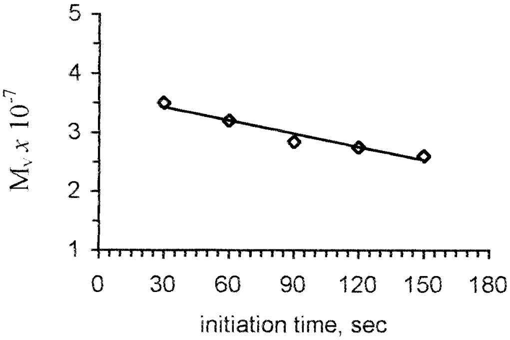

Figure 3. Molecular weight vs. initiation time (50% wt AAM, 10^{-2} torr, 60h)

Both the polymer yield and molecular weight increase with the post-polymerization time, but in different manners (figure 4). For t_p ranging between 10 and 70 hours, the experimental data for polymer yield lie on a straight line, indicating a constant rate of polymerization, while the strong increase of M_v make evident a self acceleration process abated after 40-45 hours

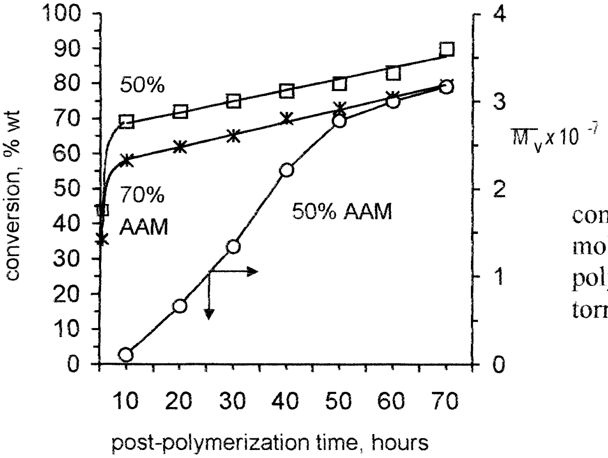

Figure 4. Monomer conversion and polymer molecular weight vs. post-polymerization time (10^{-2} torr; 60 sec)

This behavior is in good agreement with previously published data on the mechanism and the kinetic of different PIP (6-8). It was to be expected that for samples with 70%wt AAM in water the polymer yield values are smaller,

The assessment of a virtual activity for EOR of PAAM obtained by PIP

1. The F_s data were obtained for polymer samples with different M_v, in 100ppm 0,1M NaCl solutions, at 30°C and pH=7. F_S, what is very well correlated with F_R, make evident the relationship between polymer size and pore size.

The considerable rising of Fs values with PAAM molecular weight increase (Figure 5) indicates an efficient behavior of these polymer solutions in porous media flow.

A likeness with polymers that are currently used in polymer flooding (Table 1) make more evident the quality of PAAM synthesized by PIP.

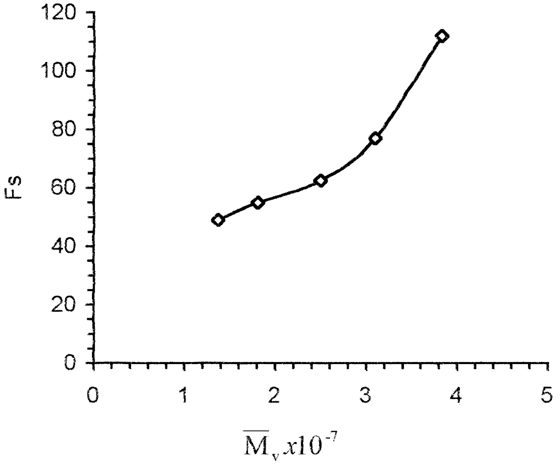

Figure 5. Evolution of F_S with molecular weight

Table 1. Comparative date on F_S for different PAAM samples
(100 ppm AAM in 0.1M NaCl solution)

Polymer	$\overline{M}_v$	F_S	Reference
PAAM *Dow 500 Pusher*	$3.00x10^6$	15	(16)
PAAM *Dow 700 Pusher*	$5.50x10^6$	20	(16)
PAAM -1 *plasma*	$1.37x10^7$	49	
PAAM-2 *plasma*	$3.83x10^7$	112	

2. TSDC spectroscopic analysis was used to ‘investigate the structure of the synthesized polymers. One of the four mentioned fundamental demands for an efficient polymer in EOR is the linearity of the chain. The complete solubilization of ours polymers is an argument that they are not crosslinked. Now, from TSDC spectra we can conclude that they are not branched.

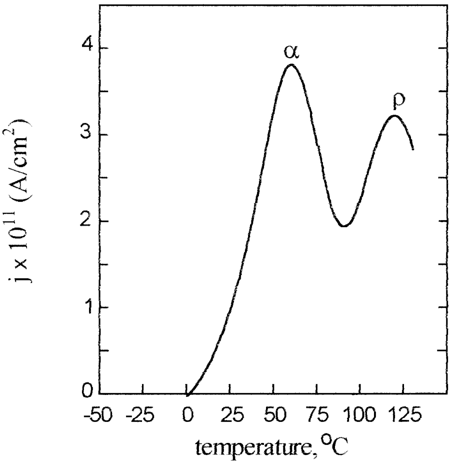

Figure 6. TSDC spectrum of PAAM sample obtained by PIP (M_v=$2.5x10^7$)

A typically example of TSDC spectrum of PAAM synthesized by PIP is presented in figure 6. Two well resolved peaks denoted as α and ρ, located at about 55^{0}C and 120^{0}C respectively were found. The presence of amide and carboxyl groups in the chains of the dry polymer must lead to an intense intermolecular interaction at the expense of hydrogen bonds between the chains. On the basis on our data and literature data (21), α peak could be related to the orientation and redistribution of the hydrogen bonds, which involve conformational rearrangements of the chain segments in amorphous phase. The ρ peak is related to the space charges polarization.

In a comparative TSDC study on linear and branched polyacrylamides, Aras and Baysal (22) found two relaxations in high temperature range at 60^0C and 125^0C for linear polymer and three relaxations at 45^0C, 100^0C and 175^0C for the branched one.

TSDC spectra of PAAM obtained by plasma initiation are similar to that reported for the linear PAAM. The small differences regarding the peak temperature location could be attributed to the different heating rates used in the TSDC cycles.

Conclusions

1. From our experimentally data on the synthesis of PAAM by PIP as well as on the correlation of several operational parameters and polymer properties, it is possible now to select the optimum reaction conditions for the process.
2. Both the viscosimetric and TSDC spectroscopic data motivate a possible use of the obtained PAAM polymers in EOR. They satisfy the four most important demands for those applications where it is desirable for the polymer solutions to penetrate the rock matrix:

- they are completely soluble in water or brine;
- they are not branched;
- their molecular weights are ultrahigh, achieving ultrahigh viscosity in dilute solutions;
- they are able to achieve an efficient mobility control, the obtained values for F_S, being ultrahigh.

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