

Macromolecular Systems in Heat-Resistant Drilling Fluids; Advantages of Gels on Linear Polymers

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SYNOPSIS

The degradation process of linear water-soluble vinyl polymers was followed in aqueous medium at temperatures higher than 150°C. We found that, for any chemical structure, thermal oxidative degradation of the longest chains always occurs, leading to moieties of lower molecular weight (20,000–60,000). The behavior of swollen tridimensionnal networks was tested under the same conditions, and it appeared that rheological and fluid loss properties of the system could be maintained in that case for an optimum number of crosslinks. The corresponding gels were used in simple formulations containing some other drilling fluid components. The first results concerning the thermal stability of the latter are very encouraging. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A consequence of the increase in well depth is the need for drilling fluids that exhibit their basic requirements at higher and higher temperatures.¹ The properties that characterize drilling muds are too extensive to be listed here, but some of them have greater relevance, e.g., rheological behavior and fluid loss (i.e., when filtrate escapes into a permeable formation).² In water-based muds, which are the most used in deep wells, those properties are generally controlled thanks to addition of clay colloids and water-soluble polymers.³ Therefore, the thermal stability of these additives is of major importance since drilling fluids must often be operative for long periods of time at elevated temperature. Many types of formulations are stable under such conditions up to 150°C, but higher temperatures are very detrimental to the flow properties and filtration control of the muds.⁴ This is mainly due to hydrolysis, depolymerization or other chemical degradation of the polymer⁵ and to flocculation or irreversible transformations of the clays.⁶

The purpose of this work was to investigate a new high-temperature-resistant polymeric additive that would stabilize drilling fluid properties up to 200°C without addition of clay. The requirements for such a compound at a given application temperature include: (1) good chemical stability for a sufficiently long time, (2) high viscosity with ability to control the fluid loss, and (3) compatibility with all other components involved, especially in alkaline medium, with the occurrence of divalent ions and negatively charged clay particles from the formations.

So, first of all we followed the behavior of various currently available polymer structures in aqueous solution as a function of temperature and time. Then, from the results of this study, we developed a new macromolecular structure that could answer most of the above requirements.

MATERIALS AND METHODS

Polymers

Commercial-grade polymers were mostly used: (1) polyacrylic acid (PAA, molecular weight $\bar{M}_w = 6 \times 10^5$), (2) polystyrene sulfonic acid (PSS1 $\bar{M}_w = 2 \times 10^5$, PSS2 $\bar{M}_w = 7 \times 10^5$), (3) polyvinylsulfonic

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acid (PVS, $\bar{M}_w = 10^4$), (4) polyacrylamido-2-methyl-2-propane sulfonic acid (PAMPS, $\bar{M}_w = 8 \times 10^5$), (5) copolymer of vinylacetamide and vinylsulfonic acid (Co-PVAMVS, $\bar{M}_w = 2 \times 10^6$). In addition, three samples of high \bar{M}_w polystyrene were prepared in the laboratory by emulsion polymerization.⁷ Complete sulfonation of the samples was achieved using a complex of sulfur trioxide (SO₃) with triethylphosphate (TEP) giving three samples of polystyrene sulfonic acid.⁸ Their molecular weights were determined from intrinsic viscosity data,⁹ (PSS3: $\bar{M}_w = 2 \times 10^6$, PSS4: $\bar{M}_w = 5 \times 10^6$, PSS5: $\bar{M}_w = 9 \times 10^6$).

Gels

Gels were obtained either from direct copolymerization of styrene and divinylbenzene or from reticulation of semidilute polystyrene solutions with dichloromethylbenzene,¹⁰ the second method appeared to be more reproducible and to give more homogeneous networks.¹¹ Considerations on the gelation process and on the physico-chemical characteristics of the final gels have been given elsewhere,^{7,12} and we will just report here in Table 5 values of X , which is the initial molar percent of reticulating agent introduced in the reaction batch. These organic gels were powdered, swollen in dichloroethane and sulfonated, with the SO₃/TEP complex.^{7,8}

The resulting hydrophilic gels were finely ground ($\cong 40 \mu\text{m}$) before use. For such charged hydrogels, the swelling ratio (i.e., the quantity of solvent absorbed per mass unit) depends not only on their reticulation degree but also on the ionic strength of the medium; however, when the salt concentration is above 0.5M (3%), the screening of the network charges is sufficient to cancel the polyelectrolyte effect, and there is no more dependence of the swelling ratio on the ionic strength.

Degradation Tests

Degradations were run in a 100-cm³ stainless steel autoclave containing a glass cartridge filled with 50 cm³ of an aqueous polymer solution or swollen gel at pH 10 in the presence of NaCl. The samples were heated at different fixed temperatures between 100 and 200°C during 1–60 h.

In case of soluble polymers, reduced specific viscosities of the solutions were measured before ($[\eta_{sp}/C_p]_0$) and after ($[\eta_{sp}/C_p]$) degradation with a low-shear viscometer (Contraves LS 30, 30°C, shear rate

1–5 s⁻¹). Results were generally expressed as the relative specific viscosity loss, VL

$$VL = \frac{[\eta_{sp}/C_p]_0 - [\eta_{sp}/C_p]}{[\eta_{sp}/C_p]_0}$$

Rheological and fluid loss properties of swollen gel particles were checked before and after degradation by using the same standard instruments and tests as those commonly designed for drilling fluids.

Rheological measurements were achieved with a six-speed Fann viscometer: we found that all our samples behaved as Bingham fluids, i.e., that the shear stress (τ)/shear rate ($\dot{\gamma}$) relation can be expressed by the following equation:

$$\tau = \tau_0 + \mu_p \dot{\gamma}$$

where τ_0 is the yield stress and μ_p the plastic viscosity. According to the American Petroleum Institute (API) norm,¹³ rheological characteristics of drilling fluids are evaluated from τ_0 , μ_p , and an effective viscosity μ_e (defined as the shear stress–shear rate ratio at shear rate $\dot{\gamma} = 1020 \text{ s}^{-1}$). Rheological properties of a drilling fluid will be considered as appropriate if $\mu_e > 20 \text{ cP}$, $\mu_p > 15 \text{ cP}$ [(1 cP = 1 mPa s)] and $\tau_0 > 35 \text{ lb}/100 \text{ ft}^2$ [16.8 Pa].

The filtration properties of drilling fluids are generally determined by means of a standard filter press: the test requires 100 psi pressure for 30 min according to the API standardized procedure.¹³ The volume of collected liquid V_{API} is an indication of the fluid loss properties which are considered to be good for $V_{\text{API}} < 15 \text{ cm}^3$, excellent for $V_{\text{API}} < 10 \text{ cm}^3$.

DEGRADATION OF POLYMERS IN AQUEOUS SOLUTION

Many water-soluble polymers and copolymers have been claimed to give good temperature stability to drilling fluids.^{5,14–19} They are generally vinylic or acrylic derivatives whose chains are well-known to exhibit rather good resistance to hydrolysis. Various compositions of anionic and nonionic units in copolymers and terpolymers have been proposed in order to decrease the polyelectrolyte sensitivity to salts. Performances of formulations including these compounds have generally been evaluated from the result of an API filtration test after standing 15 h at 200°C. Some corresponding data have been gathered from literature in Table I. This kind of test gives good global indications as to the fluid-loss be-

Table I Fluid Loss (cm³) from API Test for Various Copolymers in Different Media

Copolymer Composition ^a	Before Thermal Treatment $C_p = 1\%b$			After 15 h Thermal Treatment at 200°C and Cooling $C_p = 2\%b$		
	I	II	III	I	II	III
AMPS (65%)						
VMA (20%), AM (15%) ¹⁴	8.5	9	4.8	8.8	10.4	5.5
AMPS (80%), VMA (20%) ¹⁴	8.3	6.6	4.5	9.1	8.1	5.4
VS (45%), VMA (55%) ¹⁵	9.2	14	8.5	12	44	21.6
VS (20%), AM (70%), VPy (10%) ¹⁵	8.9	7.4	27	9.3	30	100
VS (50%), VMA (50%) ¹⁶	8.5	9	4.8	8.8	10.4	5.5
AM (60%), AA (40%) ¹⁵	9	8.8	100	9.2	46	> 100

^a AMPS, aminomethylpropane-sulfonate sodium salt; VMA, vinyl-methyl acetamide; AM, acrylamide; VS, vinyl-sulfonate sodium salt; VPy, vinyl-pyrrolidone; AA, acrylic acid.

^b I, bentonite 4%; II, bentonite 4%, NaCl 25%; III, bentonite 4%, NaCl 10%, CaCl₂ 10%.

havior of the drilling mud but does not inform us about the effect of high temperature on the macromolecular chains themselves in solution.

We tried to investigate more carefully this last parameter in comparing the thermal stability, in water solution, of polymers whose main chains were chosen as those of the main components of the above co- and terpolymers. The effects of temperature, degradation time, molecular weight, ionic strength of the medium, and polymer concentration were systematically investigated.

Effect of Temperature

Degradations of PAA, PSS1, PVS, PAMPS, and Co-PVAMVS were achieved at different temperatures during 15 h. The resulting values of VL and pH are reported in Table II. A large pH drop is observed in the case of the highly sulfonated derivatives. This is due to the degradation of sulfonate groups, which gives rise to the occurrence of sulfuric acid in the medium.⁸ Elementary analysis, potentiometry and spectroscopy confirm this assumption and allow a quantitative evaluation of the phenomenon: e.g., for PSS, less than 5% of the sulfonate groups are lost after 60 h at 200°C and at initial pH = 10. From other data of Table II it appears that the relative percent of VL is between 50 and 80% after 15 h at 180°C. This can only be explained by rupture of the macromolecular chains since no evidence of new compounds could be found in final solutions from spectroscopic techniques.

Effect of Degradation Time

In Figure 1 is reported the percent of viscosity loss versus degradation time for PSS at 200°C. Same

kinds of curves are found for other polymers, and their features are characteristic of thermal-oxidative degradation.²⁰ After an induction period of about 10 h (3 h for PAA due to simultaneous decarboxylation) VL reaches 95% in usual conditions. The viscosity loss can be limited in the presence of a more inert atmosphere, e.g., when argon is bubbled through the sample prior to test. Addition of various antioxidants was found to be inefficient under our degradation conditions.

Effect of Molecular Weight

The results for the series of PSS are displayed on Table III together with the average number of broken bonds per chain

Table II Effect of 15 h Thermal Treatment at Different Temperatures on VL and pH ($C_p = 1\%$, $C_{NaCl} = 3\%$)

Polymer	25°C	100°C	150°C	180°C
PAA				
VL %	0	15	58	85
pH	10	9.5	9	9
PSS1				
VL %	0	10	50	84
pH	10	9.5	9	8
PVS				
VL %	0	0	34	50
pH	10	8.5	6	5
PAMPS				
VL %	0	5	15	73
pH	10	9.5	9	9
Co-PVAMVS				
VL %	0	13	34	67
pH	10	10	9	9

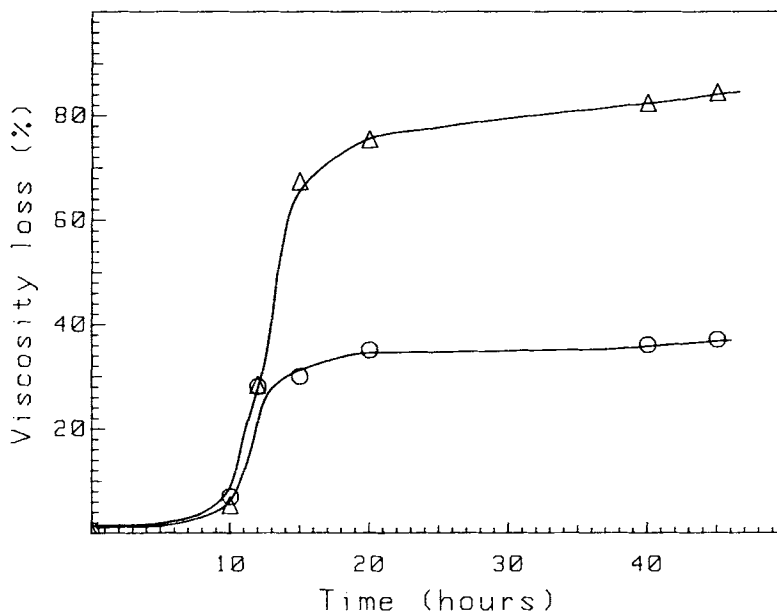


Figure 1 Viscosity loss vs. degradation time at 200°C (PSS1: $C_P = 1\%$, $C_{NaCl} = 3\%$, pH = 10): (Δ) oxidant atmosphere (air) and (O) after treatment by argon bubbling prior to test.

$$\alpha = \frac{M_{w0}}{M_w} - 1$$

where M_{w0} is the initial molecular weight of chains and M_w is the final molecular weight of chains; α values show that for any initial molecular weight, degradation always leads to $20,000 < M_w < 60,000$ (this was measured on the final samples by size exclusion chromatography).

Effect of Ionic Strength of the Medium

The data of Table IV show that when the screening of the polyelectrolyte charges by the salt is high enough ($C_{NaCl} > 3\%$) there is little influence of C_{NaCl} on VL percent.

Effect of Polymer Concentration

Viscosity loss percent of PSS2 and PSS3 are reported on Figure 2 as a function of polymer concentration.

Table III Viscosity Loss and Average Number of Chain Ruptures for PSS of Various Molecular Weights (15 h, 200°C, $C_P = 1\%$, $C_{NaCl} = 3\%$, pH = 10)

\bar{M}_w	2.10^5	7.10^5	2.10^6	5.10^6	9.10^6
VL%	72	78	89	93	96
α	6	11	30	60	140

tration C_P . Notice that the increase in VL percent at low C_P is artificial and only depends on the effect of initial concentration since the final degradation state of the polymer is always the same as shown from size exclusion chromatography.

For higher C_P , formation of microgels (probably here from radical recombination) is observed in the medium, which becomes more turbid, and thanks to these microgels, initial viscosity can be partly recovered. There is an optimal C_P value (3.2% for PSS2 and 2.6% for PSS3) at which the viscosity loss appears minimum. Above that concentration, the initial viscosity is so high that microgel formation cannot compensate for chain degradation and the VL again increases.

Discussion of Results

In drastic conditions of time, temperature and medium such as those required for drilling muds in very deep wells, thermal-oxidative degradation of linear macromolecules always occurs, leading to the loss

Table IV Effect of Salt Concentration on Viscosity Loss (PSS2, 15 h, 200°C, $C_P = 1\%$, pH = 10)

C_{NaCl} %	0.6	3	6	12
VL%	90	78	76	75

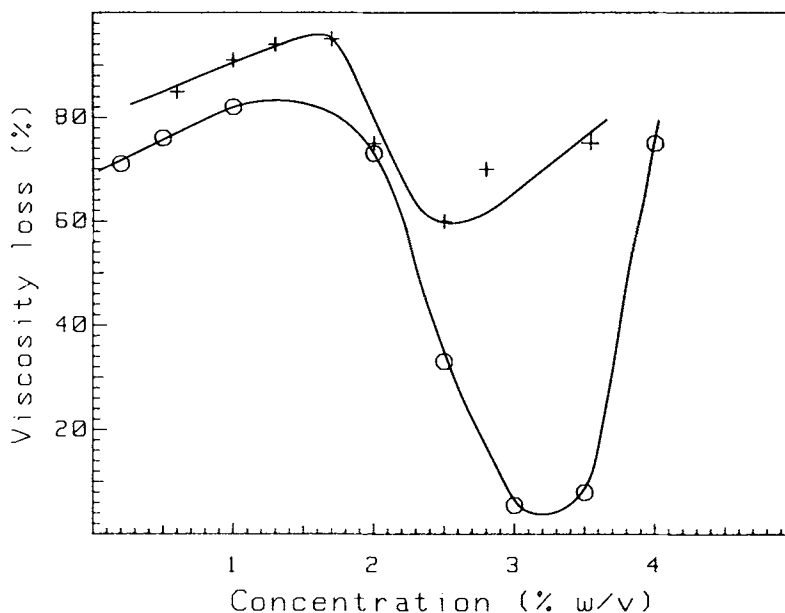


Figure 2 Viscosity loss vs. polymer concentration (15 h, 200°C, $C_{\text{NaCl}} = 3\%$, pH = 10):
 O PSS2 ($\bar{M}_w = 7 \cdot 10^5$), +PSS3 ($\bar{M}_w = 2 \cdot 10^6$).

of their viscosity-enhancing properties. However, formation of microgels may confer a macroscopic apparent viscosity to the system. In such tridimensional structures, the macromolecular behavior can be kept even when bonds are broken if the maximum molecular weight between two reticulation points corresponds with the final molecular weight of the linear chains after degradation (about 40,000 for PSS as seen above). So the resistance of those species to thermal-oxidative degradation obviously increases with the number of crosslinks. Conversely, one must bear in mind that the swelling degree of finely divided gel particles, which controls the apparent viscosity of their suspensions at a given concentration, decreases with the number of crosslinks.

Therefore, if tridimensional networks can answer our initial problem, the crucial role of their reticulation ratio is emphasized. Then, the next step of our study deals with finding a good compromise between thermal resistance and rheological properties of swollen gel systems.

HIGH-TEMPERATURE BEHAVIOR OF SWOLLEN GELS

Choice of Chemical Structure

The use of a polystyrene skeleton appeared suitable for many reasons. Besides its good resistance to thermal-oxidative degradation and its reasonable

cost, this polymer offers a lot of other advantages for our problem: (1) several ways of reticulation have been previously described and compared.¹¹ (2) The physico-chemical process of gelation has been largely studied in this case and, thanks to model gels and theoretical considerations, structural information on the network and prediction of mechanical properties are directly available from the swelling rate.^{7,12} (3) Such organic gels can be easily made hydrophilic by sulfonation and compatibility of sulfonate groups with clay formations and with divalent ions is well known.

Influence of the Reticulation Degree on Thermal Stability of Swollen Gels

The thermal stability of sulfonated gels swollen in aqueous medium was estimated from the effect of a 48-h high-temperature (200°C) treatment on their swelling ratio Q (in gram of solvent per gram of gel), effective viscosity μ_e , and fluid loss properties (V_{API}). Data of Table V show that gels with cross-linking agent content per styrene unit X higher than 1.5% display good thermal stability but bad rheological properties (see experimental part for criteria) at least for a concentration $C = 2\%$. These disadvantages would only be partly offset if such gels were used at slightly higher concentrations than their maximum swelling (i.e., about $C = 4\%$ for $X = 1.5\%$ and $C = 7\%$ for $X = 2\%$) but values of τ_0 are then out of specification and anyway such concentrations

Table V Effect of a Thermal Treatment on the Swelling, Rheological, and Fluid-Loss Properties of Gels with Various Contents of Reticulating Agent in Aqueous Medium ($C_{\text{NaCl}} = 3\%$)

X%	$C_{\text{gel}} = 1\%$		$C_{\text{gel}} = 2\%$			
	Q g/g		$V_{\text{API}} \text{ cm}^3$		$\mu_e \text{ cP}$	
	(a)	(b)	(a)	(b)	(a)	(b)
0.5	45	Solubilization	8	> 100	24	2
1	40	45	9	8	20	22
1.5	30	35	20	18	13	14
2	26	28	40	39	5	5
2.5	15	15	> 100	> 100	—	—

^a Initial properties at room temperature.

^b Properties after 48 h standing at 200°C and cooling at room temperature.

are not suitable for economical reasons. Less reticulated gels have the advantage of absorbing a greater volume of solvent and then can give good results for convenient concentrations at room temperature. However, the structure with $X = 0.5\%$ is completely destroyed at high temperature because the number of crosslinks in the network is not sufficient to overcome the breaking of certain bonds. For our synthesis conditions, only networks with $X \cong 1\%$ appear to display the right balance between all the requirements. In what follows, these last gels will be tested in a few simple formulations in order to know if their use in drilling fluids is realistic or not.

Performance of a Few Simple Formulations

First of all, in practical applications, operating procedures have to be carried out in a reasonable time, and it is generally admitted that for a newly prepared drilling fluid, the characteristic parameters must

Table VI Swelling Kinetics of a Gel With $X = 1\%$ in 3% Aqueous NaCl ($C_{\text{gel}} = 3\%$)

Time (h)	$\mu_e \text{ cP}^a$	$\mu_p \text{ cP}^a$	$\tau_0 \text{ lb}/100 \text{ ft}^2 \text{ b}$
2	55	37	36
3	56	37	38
5	61	42	39
7	63	41	45
9	64	43	40
24	78	54	48
26	78	52	52
29	78	52	52

^a 1 cP = 1 mPa s.

^b 1 lb/100 ft² = 0.48 Pa.

reach half of their final values after standing 2 or 3 h. The swelling kinetics of our gel perfectly meets this specification (Table VI).

Four formulations have been described (Table VII). Their compositions have been chosen in order to test the behavior of the gel in various conditions. Their rheological and fluid loss properties before and after a 48-h thermal treatment at 200°C are reported in Table VIII. All formulations display excellent characteristics; formulation I has even been kept one week at 200°C without modification of its properties.

The gel can be used with or without addition of bentonite (compare I and III) and is perfectly compatible with divalent ions (II and IV). The viscosity drop between 20 and 80°C is not so important compared with what is observed for linear polymers and the overall gel concentration never exceeds 3% even in a medium of high salinity (II). At low ionic strength (IV) or in presence of bentonite (III), this concentration can be lowered to 2.5%.

CONCLUSION

Although high-temperature performances of some drilling fluid formulations are increased by addition of certain high-molecular-weight vinyl polymers,

Table VII Composition of the Formulations

Formulation	$C_{\text{gel}} \%$	$C_{\text{NaCl}} \%$	$C_{\text{CaCl}_2} \%$	$C_{\text{bentonite}} \%$
I	3	2.9	0	0
II	3	5.8	1.1	1.2
III	2.5	2.9	0	0
IV	2.5	0.58	0.5	0

Table VIII Rheological and Fluid-Loss Properties of Four Formulations

Formulation	I		II		III		IV	
	20°C	80°C	20°C	80°C	20°C	80°C	20°C	80°C
μ_e cP								
(a)	65	60	18.5	21	64	58	48	45
(b)	50	38	21	26	57	40	46	40
μ_p cP								
(4)	41	38	14	15	30	28	33	32
(b)	33	23	17	19	26	16	32	20
τ_0 lb/100 ft ²								
(a)	48	42	43	38	68	54	30	26
(b)	34	24	8	14	62	48	28	40
V_{API} cm ³								
(a)	9	—	7	—	9	—	9	—
(b)	7	—	7	—	10	—	8	—

^a Initial properties.

^b Properties after 48 h standing at 200°C and cooling.

this behavior is obviously not inherent to the thermal resistance of the macromolecular chains themselves. We have shown here, that for any water-soluble synthetic polymer, rupture of the longest chains always occurs at temperatures higher than 150°C, always leading to compounds of lower molecular weight (20,000–60,000), which can no longer provide the required rheological and fluid loss properties. However, the effect of polymer concentration on the viscosity loss suggested that the overall apparent stability of such fluids might be due to some gelation process by radical recombination or by secondary reaction with other components of the fluid giving rise to tridimensional networks. In such networks, crosslinks between chains act as a statistical distribution of strengthening bonds, but high degrees of crosslinking are unfavorable to good rheological and fluid loss properties. In fact the efficiency of drilling fluids containing crosslinked species has already been claimed²¹ but without systematic investigation.

Thus, controlling the gel structure from the beginning of the process seemed a more rational approach to improve these assumptions and to avoid unexpected behavior of the fluid in practice. So we prepared a series of well-characterized hydrophilic gels of rather low crosslink content. We studied the effect of high temperature on their structural, rheological, and fluid-loss properties when they are swollen in aqueous medium and it appeared that only gels with a content of about 1% of crosslinking

agent were convenient for the considered application. Their performances are much better than those of the previous systems.

Some simple formulations made with these gels have exhibited very good stability for a rather long time (at least one week). Their cost/price is very reasonable, nevertheless their development is being subjected to more elaborate tests (e.g., high-temperature, high-pressure tests, etc.).

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Received October 14, 1993

Accepted December 12, 1993