

RADICAL GRAFTING REACTIONS ONTO STARCH AND OTHER WATER-SOLUBLE COPOLYMERS IN ISOLATED GEL DROPLETS

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ABSTRACT

A novel radical grafting copolymerization process has been designed for water-soluble polymers which avoids the problems of conducting grafting reactions in highly viscous polymerization media. A variety of water-soluble graft copolymers having starch or dextran as the backbone chain with grafted side chains of polyacrylamide ($-\text{AM}-$), poly (acrylic acid) ($-\text{AA}-$), poly (acrylamide-co-acrylic acid) ($-\text{AM}-\text{NH}_4\text{AA}-$) or poly (acrylamide-co-2-acrylamido-2-methyl-1-propanesulphonic acid) ($-\text{AM}-\text{AMPS}-$) have been synthesized in gel droplets using a ceric sulphate redox initiator, and their properties compared. The reaction conditions were optimized taking into account reaction kinetic data and the observed properties of the products produced under different reaction conditions. The effects of the ratios of [backbone]/[graft monomer], $[\text{AM}]/[\text{AA}]/[\text{AMPS}]$, $[\text{Ce}^{4+}]/[\text{S}_2\text{O}_8=]$ and pH value on the reaction rate, conversion, grafting degree, grafted chain length and the product molecular weight have been investigated.

INTRODUCTION

Water-soluble polymers which produce highly viscous aqueous solutions, such as polyacrylamide and partially hydrolysed polyacrylamide, are currently widely used in both secondary and tertiary oil recovery, techniques which are often described as enhanced oil recovery (EOR) methods.

A series of graft copolymers of acrylamide and/or its derivatives onto starch or dextran have already been designed for obtaining high molecular weight linear, grafted or slightly crosslinked copolymers with large hydrodynamic volume (HDV) in solution^[1-6].

Unfortunately, however, the graft copolymers could only be synthesized at low concentrations of polymer in the reaction medium since at high concentrations the system became too viscous to be handled. The low concentration polymerisation procedure led poor productivity.

This paper describes a novel polymerization process which allows the use of high concentration of backbone polymer and graft-monomer in the reaction medium, high rates of polymerization, and which gives rise to products with high molecular weights. The process uses an acid to foam or gelate reaction medium containing the polymeric backbone, monomers and initiator, followed by the addition of carbonate salt. The reaction between the carbonate salt and the acid

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generates CO_2 which foams the solution prior to the formation of the backbone radicals which ensures that reaction takes place in the auto-acceleration leads to rapid polymerisation. The evolved CO_2 not only acts as an efficient cooling agent but also helps to remove water from the reaction mixture giving rise to products with a low water content.

The mol ratios of [backbone]/[monomer], [AM] (Acrylamide)/[AA] (Acrylic acid)/[AMPS] (2-acrylamido-2-methyl-1-propanesulfonic acid)/[Ce^{4+}]/[$\text{S}_2\text{O}_8^{2-}$] were used to control the polymerization reaction rate and the composition of the final product. The percentage total monomer conversion ($RC\%$), the degree of grafting, ($DG\%$), the rheology properties and the 30 minutes fruit loss were used to evaluate the products.

The chemical structures of the graft copolymers were studied by selective hydrolysis of the carbohydrate backbone of the graft copolymers and the carboxyl content assessed by conductometric titration for both the graft copolymer and the grafted side-chain.

EXPERIMENTAL

1. Materials

The following reagents were used as supplied;

Water-soluble starch (BDH), dextran standards (Sigma), potassium persulphate (BDH), ethylenediaminetetra-acetic acid disodium salt (BDH), 2-acrylamido-2-methyl-1-propanesulfonic acid (Aldrich). Acrylic acid monomer (Allied Colloids) was distilled at reduced pressure (40mm Hg) b. p. 65°C . Acrylamide monomer (Allied Colloids) was recrystallized from acetone three times prior to use.

2. Synthesis of graft copolymers

Graft-copolymerizations were conducted at 40°C in a 1 l glass resin flask equipped with stirrer and thermometer. Typically, the desired amount of acrylamide was added to a relatively small amount of concentrated aqueous solution of starch or dextran. Then acrylic acid and AMPS were added in quantities equal to or less than the amount of acrylamide in order to make the concentration of monomers more than or equal to 50% (by weight). When the acrylamide and AMPS were dissolved, the solution was partially gelled by decreasing pH value or by dissolving excess acid monomers therein. Sodium carbonate was then added to produce carbon dioxide which foamed the gel and neutralized the excess acid monomers. In this way backbone material was well distributed gel droplets. Then a calculated amount of acid solution of persulphate mixed with ceric salt was added and the pH adjusted with carbonate or acid. For approximately 30 minutes polymerization occurs at 40°C after which the reaction mixture heats up as a result of the heat of polymerisation, a reaction which can be violent and give rise to large temperature increase. The reaction exotherm is short-lived and the decrease in the temperature of the reaction mixture indicates that the reaction is complete.

3. Optimization of the reaction conditions

A. The reactant ratios [backbone]/[monomer], [AM]/[AA]/[AMPS],

[Ce⁴⁺]/[S₂O₈⁼] were optimized in order to achieve the conversions, degree of grafting and final properties required. The ratio of [S₂O₈⁼]/[backbone] was changed systematically to affect the number of the grafted side chains (*Ng*) and the degree of polymerization of the grafted side chains (*DP*). The values for *RC%*, *DG%*, *Ng* and *DP* were calculated as follows:

$$RC\% = ((Wt.G + Wt.H - Wt.B) / Wt.M) \times 100 \tag{1}$$

$$DG\% = ((Wt.G) / (Wt.G + Wt.H)) \times 100 \tag{2}$$

$$Ng = ([Ce^4] / [Backbone]) \times N \tag{3}$$

$$DP = [Monomers] / [Ce^4] \tag{4}$$

where *Wt. G*, *Wt. H*, *Wt. B* and *Wt. M* stand for the weight of graft copolymers, homopolymers, backbones and monomers and *N* is the number of repeat units which is 1982 (molecular weight is about 321, 000) for starch and 18520 (molecular weight is about 3,000,000) for dextran. The values of *RC%* were checked by determination of residual monomers in the alcohol solution using a gas chromatograph fitted with a capillary column (Perkin Elmer Model). The rheological properties of the polymers were measured using a four-speed rotameter viscometer. The ratios of the reagents used in the polymerization studies are summarized in Table 1.

Table 1 The systematically varying reaction conditions

No.	[Bac] / [Mon]	[AM]/[AA] / [AMPS]	[Initi]	Ce ⁴⁺ /S ₂ O ₈ ⁼	L-H-Time	pH
I-1	0.1/0.9	0.7/0.2/0.1	1.5E-4	0.1/0.9	13-18	12-7.4
I-2	0.1/0.9	0.7/0.2/0.1	1.5E-4	0.2/0.8	25-11	12-7.5
I-3	0.1/0.9	0.7/0.2/0.1	1.5E-4	0.3/0.7	45-10	12-7.4
B-1	0.2/0.8	0.7/0.2/0.1	1.5E-4	0.1/0.9	22-13	12-7.4
B-2	0.4/0.6	0.7/0.2/0.1	1.5E-4	0.1/0.9	20-15	12-7.4
B-3	0.5/0.5	0.7/0.2/0.1	1.5E-4	0.1/0.9	15-17	12-7.5
M-1	0.1/0.9	0.8/0.2/0.0	1.5E-4	0.1/0.9	17-16	12-7.5
M-2	0.1/0.9	0.7/0.3/0.0	1.5E-4	0.1/0.9	17-15	12-7.5
M-3	0.1/0.9	0.5/0.5/0.0	1.5E-4	0.1/0.9	18-14	12-7.4
M-4	0.1/0.9	0.3/0.7/0.0	1.5E-4	0.1/0.9	18-13	12-7.4
M-5	0.1/0.9	0.9/0.0/0.1	1.5E-4	0.1/0.9	65-29	12-7.4
M-6	0.1/0.9	0.6/0.0/0.4	1.5E-4	0.1/0.9	72-30	12-7.4
H-1	0.1/0.9	0.7/0.2/0.1	1.5E-4	0.1/0.9	60-40	7.8-4
H-2	0.1/0.9	0.7/0.2/0.1	1.5E-4	0.1/0.9	95-55	13.5-9

Note:

L-H-Time stands for the low temperature polymerization period and the high temperature polymerization period in mins.

pH is the pH value from the initial time to the end of the polymerization.

B. Selective hydrolysis of the graft copolymer backbone

The method employed for the hydrolysis of polysaccharides using NaIO₄ and NH₄OH^[8] makes use of the absorbance which occurs at 630 nm in the visible spectrum absorbance of the sample after hydrolysis^[9]. Selective hydrolysis was performed in the dark at 35 °C for 1.5h after which the solution was dialysed using

a cellulose membrance against water at room temperature for 24 hrs, when the solution inside the membrance turned to blue, the membrance was discarded and the blue solution with the grafted side chain was collected and was then freeze-dried. The weight fraction of the polymeric side-chain W_{psc} , was calculated as follows.

$$W_{psc} = (Wt. \text{ Polymeric Side-Chain}) / (Wt. \text{ Sample}) \quad (5)$$

C. Carboxyl content measurement by conductometric titration

The fraction of $-\text{NH}_4 - \text{AA}$ or $-\text{NH}_4 - \text{AMPS}$ in the polymeric side-chain was determined by conductometric titration (WPA M35 conductometer connected to a pen recorder). Each sample solution was adjusted by adding 0.01N of sodium hydroxide, then was titrated with 0.01N hydrochloric acid at 25 °C. The unit fraction of $-\text{NH}_4 - \text{AA}$ or $-\text{NH}_4 - \text{AMPS}$, F_{aa} or F_{amps} can be calculated by Eq. 6 and Eq. 7.

$$F_{-aa} = (N_{\text{HCl}} V_{\text{HCl}} 71.08) / (W(g) - N V (89.08 - 71.08)) \quad (6)$$

and

$$F_{-amps} = (N_{\text{HCl}} V_{\text{HCl}} 71.08) / (W(g) - N V (207.24 - 71.08)) \quad (7)$$

Where N_{HCl} is the concentration of HCl titrant, V_{HCl} is the volume of HCl titrant, $W(g)$ is the weight of the sample in grams, and 71.08, 89.08 and 207.24 are the molecular weights of acrylamide, acrylic acid and AMPS respectively.

D. Evaluation of solution properties and phase behaviour

The solution properties and phase behaviour of the graft copolymers were carried in two ways : a) Intrinsic viscosity measurements were performed with a Ubbelohde suspended-level dilution capillary viscometer at 30 °C in aqueous solutions containing 1.0 M NaNO_3 . The molecular weights of the copolymers were obtained^[1] by the equation:

$$[\eta] = 3.73 \times 10^4 \times M^{0.6}$$

b) In order to examine the behaviour of the solution of the graft copolymers, a series of the intrinsic viscosity measurements were performed in varying ionic strength solutions.

RESULTS AND DISCUSSION

The reaction conditions were systematically varied (as described in Table 1) in order to assess the influence of each reaction parameter on the degree of grafting of the resulting graft copolymers. Thus four series of reactions were conducted in which one reaction parameter was varied while keeping the other parameter constant. The results are shown in Table 2.

Figure 1 is the conversion percent vs. time the curve can be divided into two regions. The first describing the initial low-temperature polymerisation with the conversion region from 0 to 40%, the second the high-temperature polymerization with the conversion region from 40% to 90%. The low-temperature polymerization period will be described as "grafting time" (T), in which grafting copolymerization takes place mainly. The magnitude of T can be adjusted by varying the ratio of the ceric sulphate to persulphate. The effect of the ratio of $\text{Ce}^{4+} / \text{S}_2\text{O}_8^{2-}$ on the conversion with time is shown in Figure 2.

Table 2 The different characters of the products

No.	RC %	DG%	N _g	DP	M _n	[η] (dl/g)	[η] _g (dl/g)
I- 1	94	88	297	26900	8.31E6	10.4	1.5
I- 2	95	93	446	18000	8.35E6	10.8	1.2
I- 3	96	96	892	8500	7.90E6	9.9	0.8
B- 1	94	88	149	18000	3.10E6	7.4	1.2
B- 2	88	82	74.5	18000	1.66E6	3.8	1.1
B- 3	86	77	59.4	18000	1.39E6	3.0	1.3
M-1	95	82	297	26900	8.31E6	9.8	1.6
M-2	96	76	297	26900	8.31E6	10.5	1.8
M-3	96	78	297	26900	8.31E6	8.7	1.1
M-4	98	80	297	26900	8.31E6	7.3	—
M-5	98	72	297	26900	8.31E6	8.3	—
M-6	98	74	297	26900	8.31E6	6.5	—
H- 1	90	87	297	26900	8.31E6	9.5	—
H- 2	95	76	297	26900	8.31E6	10.6	1.6

Note:
[η]_g stands for the intrinsic viscosity of the grafted side chains.

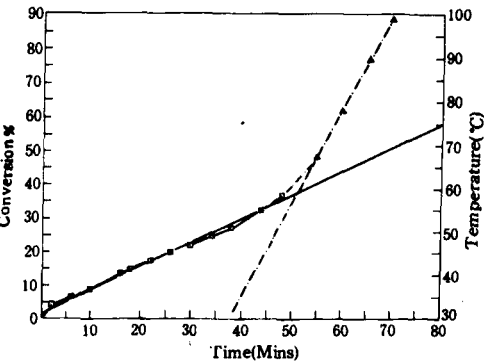


Fig. 1 The conversion percent vs time in mins
(□)Conversion 0— 40%; (△) Conversion 40— 90%
[MO]=0.84 mol/L; [CMC]=3.3×10⁻³mol/L
[Ce⁴⁺]=1.0×10⁻⁴mol/L;
[S₂O₈²⁻]=5×10⁻³mol/L
[AM]/[AA]/[AMPS]=0.7/0.2/0.1

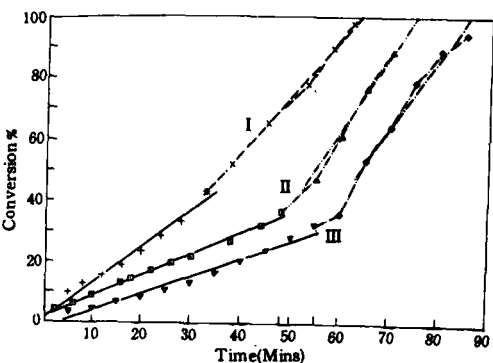


Fig. 2 The effect of the ratio of [Ce⁴⁺] to [S₂O₈²⁻] on the conversion percent with time
1. [Ce⁴⁺]/[S₂O₈²⁻]=1.0×10⁻⁴/1.0×10⁻³(mol),
T=32.60; 2. [Ce⁴⁺]/[S₂O₈²⁻]=1.0×10⁻⁴/5.0×10⁻⁴
(mol), T=48.04; 3. [Ce⁴⁺]/[S₂O₈²⁻]=1.0×10⁻⁴/
2.5×10⁻⁴(mol), T=55.22. [MO]=0.84mol/L;
[AM]/[AA]/[AMPS]=0.7/0.2/0.1;
[Bac]/[Mon]=0.1/0.9.

The onset of auto-acceleration is controlled by the total monomer concentration remaining after the initial grafting period. When *T* is large, the residual concentration of the monomers is small and the product is composed of mainly grafting copolymer which has good properties for additives of the drilling mud. but the product contains of more water component. When little grafting takes place the large temperature rise is observed as the more residual monomers are consumed. Under these conditions the amount of water component in the product is low and the grafted copolymer as well. The effect amount of remaining monomer on the water content in the products for series B is shown in Figure 3.

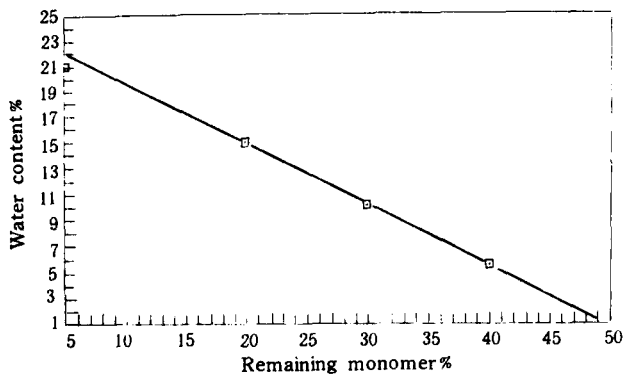


Fig. 3 The effect of the remaining monomer on the water content in the products

No.	[Bac]/[Mon]	[AM]/[AA]/[AMPS]	[Initi]	[Ce]/[S ₂ O ₈]	L-H-time
B-1a	0.2/0.8	0.7/0.2/0.1	1.5E-4	0.1/0.9	22-13(mins)
B-1b	0.2/0.8	0.7/0.2/0.1	2.5E-4	0.1/0.9	15-11(mins)
B-1c	0.2/0.8	0.7/0.2/0.1	4.0E-4	0.1/0.9	12-8 (mins)

Increasing ceric concentration while holding the total concentration of initiator for series I resulted in a slight increase in conversion as well as an increase in Ng, as can be seen in Figures 4A and 4B.

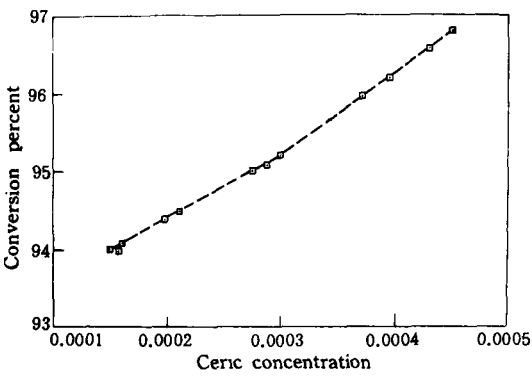


Fig. 4A The Ceric concentration vs the conversion percent see series I in Table 1

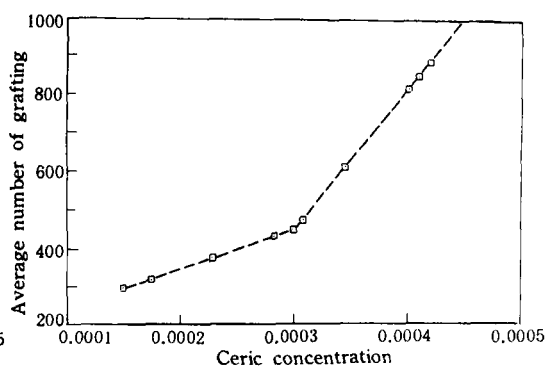


Fig. 4B The Ceric concentration vs the number of grafting see Series I in Table 1

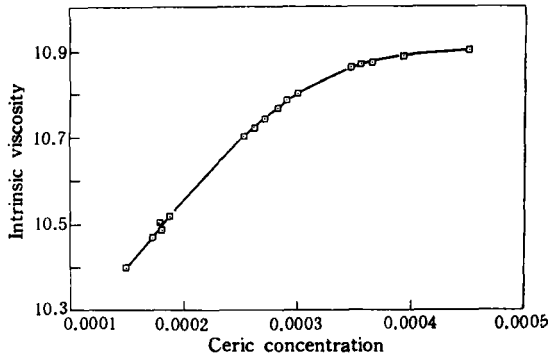


Fig. 5 The Ceric concentration vs the intrinsic viscosity The condition can be seen in Table 1

An increase in the degree of grafting was observed with increasing $[Ce^{4+}]$ as can be seen from the data in Table 2. The effect of changing the concentration $[Ce^{4+}]$ on the intrinsic viscosity of the grafted copolymers is shown in Figure 5.

The intrinsic viscosity of the grafted copolymers decreased with increasing ratios of the $[Backbone]/[Monomer]$ as shown in Figure 7.

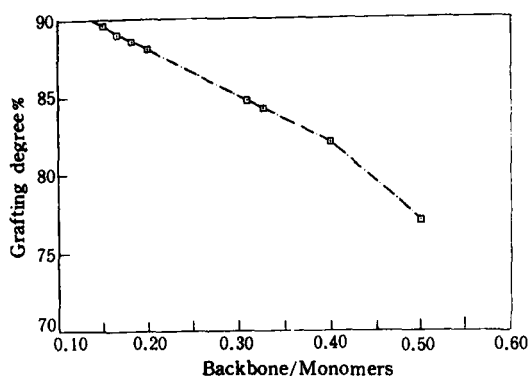


Fig. 6A $[Bac]/[Mon]$ vs grafting degree
I-1, I-2, I-3, B-1, B-2, B-3; H-1, H-2

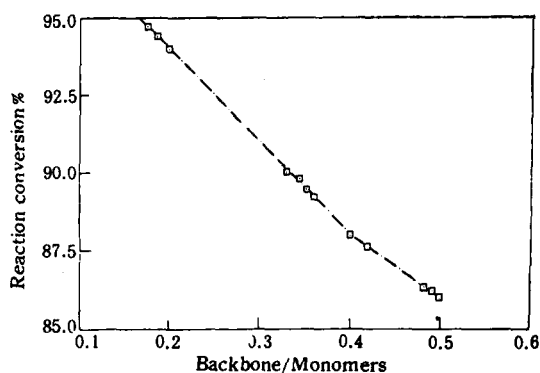


Fig. 6B $[Bac]/[Mon]$ vs the Reaction Conversion
I-1, 2, 3; M-1, 2, 3, 4, 5, 6; B-1, 2, 3.

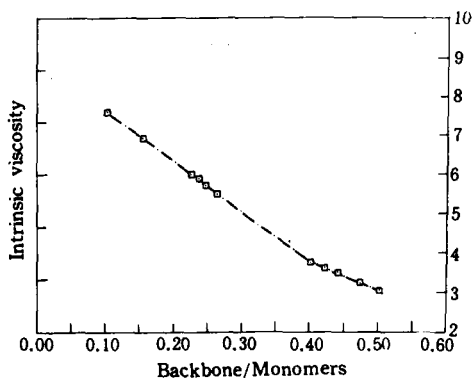


Fig. 7 $[Bac]/[Mon]$ vs intrinsic viscosity

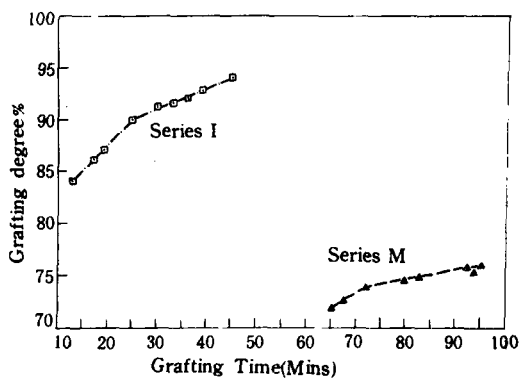


Fig. 8 Grafting time T vs the grafting degree

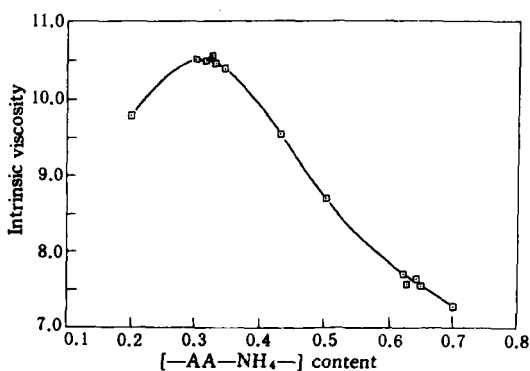


Fig. 9 $-AA-NH_4-$ Content vs intrinsic viscosity

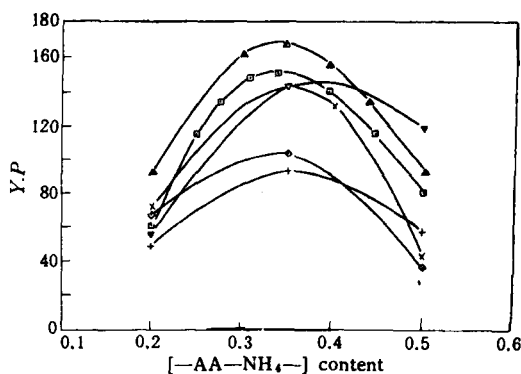


Fig. 10 $-AA-NH_4-$ Content vs yield point
 Δ 9-22-7 $\square$ 9-23-7 ∇ 9-25-1 $\diamond$ 9-23-4
+ 9-23-3 $\times$ 9-23-3

The relationship between $DG\%$ and grafting time T is shown in Figure 8.

The effect of the content of $-AA-NH_4-$ in the grafted copolymers on intrinsic viscosity, yield point and plastic viscosity are shown in Figure 9 to 11.

Linear relationships between intrinsic viscosity and the inverse square root of ionic strength are observed in aqueous sodium nitrate solutions for all graft

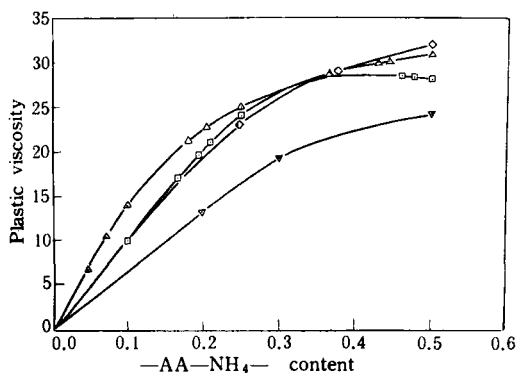


Fig. 11 — AA — NH₄ — Content vs plastic viscosity
 □ 9-23-6 ◇ 9-22-6 Δ 9-22-8 ▽ 9-23-1

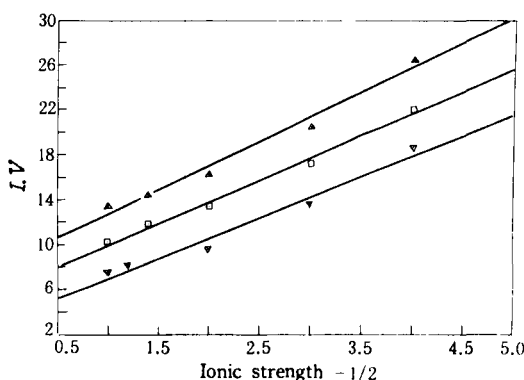


Fig. 12 The square root of the ionic strength vs
 intrinsic viscosity

copolymer types. The slopes of the lines and the magnitudes of $[\eta]$ are measures of salt sensitivity and are dependent on polymer structure as shown in Figure 12. At high ionic strengths, charge-charge repulsions along the macromolecular backbone are minimized and chain dimensions become smaller and the intrinsic viscosity becomes lower.

Since the concentration of monomers was very high, the polymerization rate was fast and a large number of gel droplets were converted into viscous polymeric beads very quickly. Initially the heat of polymerization is dissipated through the escape of carbon dioxide and the loss of water vapour ensuring that the temperature of polymerization mass remains constant for a period. With increasing conversion of the monomers, the viscosity of the gel phase increases and heat transfer by the mechanism described becomes more difficult. The temperature of polymerization medium then increased sharply and the polymerization enters the auto-acceleration stage. The activation energy of the reaction between the oxidant portion (Ce^{4+} and $\text{S}_2\text{O}_8^{2-}$) of the redox initiating system and the backbone (which is the reducing portion) is only 36 — 41 kJ/mol which is similar to the activation energy of the chain propagation reaction such as 20 — 32 kJ/mol. Under these specific conditions, the effect of the temperature on the value of $kp/kt^{1/2}$ was very small and could be ignored. Since the value of $kp/kt^{1/2}$ was roughly constant during the period of the reaction when the temperature was essentially constant, the average degree of polymerization did not decrease but subsequently does increase due to the auto-acceleration effect. The effect was caused by using prior gelation of the polymeric backbone which makes the polymerization system so viscous at the beginning of the polymerization that the effect of Norrish-Trommsdorf occurred early. The nature of the effect of Norrish-Trommsdorf is that the propagating polymeric chains were isolated partially or entirely, which causes an simultaneous increase in the concentration and average life-time of the chain radicals. This leads to two results:

(1) The rate of polymerization increased markedly with the increase of the concentration of the monomers in the polymerization system (due to $R_p = K_p [M] \cdot [R - M']$);

(2) The average kinetic chain length, L_{kin} , or the average degree of

Table 3 The applied properties of the products

No	AV	YP	PV	GEL	LOSS
I-1	92/76/86	166/104/56	10/24/28	70/94/147	12.0/10.5/8.5
I-2	73/82/61	122/124/62	12/20/30	85/94/142	12.5/11.0/9.0
I-3	87/74/51	146/88/52	14/30/25	68/86/147	12.5/10.5/8.0
B-1	14/20/32	6/10/30	11/15/20	5/11/20	11.0/10.3/9.0
B-2	19/25/35	12/13/22	13/19/24	5/9/11	10.3/9.5/8.3
B-3	14/17/23	4/10/14	12/13/16	6/7/9	10.3/10.0/8.5
M-1	66/57/73	112/68/79	10/23/32	60/115/80	13.5/10.0/8.5
M-2	80/49/32	144/85/24	8/20/20	93/162/93	13.0/9.3/8.0
M-3	64/55/46	96/63/40	16/23/24	55/142/118	12.5/9.5/8.5
M-4	63/30/36	96/30/24	14/15/24	67/103/37	13.5/10.5/10
M-5	78/37/40	117/46/28	19/14/26	46/93/58	14.0/10.5/9.0
M-6	61/24/23	94/20/14	14/16/16	72/132/44	12.3/10.3/8.8
H-1	94/76/82	157/96/85	15/28/39	82/86/115	11.5/9.5/8.5
H-2	76/47/72	112/91/83	14/23/30	79/84/102	10.5/9.0/8.0

Notes for Table 3:

A.V.=1/2 S. A.V. is the apparent viscosity and S is the reading at 600 RPM. Y.P.=T-P.V., is the yield point. T is the reading at 300 RPM. P.V.=S-T, is the plastic viscosity.

In all cases the three readings correspond to having 0.1, 0.25 and 0.5g polymer in 370g mud.

Loss is the amount of fluid lost in 30 minutes. The lower the value the better the polymer as a fluid retainer in the system.

polymerization, DP , increased with the increasing rate of polymerization and with the decreasing rate of termination (due to $L_{kin} = R_p/R_t$). There are two ways to form the graft copolymers in this process by the evaluation of the content of the products.

1. By reacting molecules of initiator with molecules of polymeric backbone. The most important feature of the oxidation of polymeric backbone with Ce^{4+} in that it proceeds via a single electron transfer with the formation of a free radical on the backbone;

2. By transferring the chain radicals to the molecules of the backbone. Since the temperature of polymerization is high and in these conditions persulphate can individually initiate polymerization of the monomers, the second way of the formation of graft copolymers becomes relatively more important. The products were therefore slightly cross-linked and formed a mixture of random homopolymers and graft copolymers.

Keywords:

Radical grafting copolymerization; Isolated gel droplets, Acrylamide; Starch; Kinetics

REFERENCES

- [1] Hester, R. D. and Michell, P. H., *J. Polym. Sci. Polymer Chem.*, **1980**, 18, 1727—1738.
- [2] Butler, G. B. and Hogen-Esch T. E., *U.S.P.* 4, 400, 496, **1983**.
- [3] McCormick, C. L. and Park, L. S., *J. Polym. Sci., Polym. Chem. Ed.*, **1984**, 22, 49.
- [4] McCormick, C. L., Park, L. S. and Hester, R. D., *Polym. Eng. Sci.*, **1984**, 24 (2), 163.
- [5] McCormick, C. L., *J. Macromol. Sci. Chem.*, **1985**, A22 (5—7), 955.
- [6] Young, T. S., Willhite, G. P. and Green, D. W., *SPE/DOE 17343*, **1988** 257—266.
- [7] Arthur Jett C. and Baugh, Peter J., *J. Appl. Polym. Sci.*, **1966**, 10, 1591.
- [8] Jermyn, M. A., *Anal. Biochem.*, **1975** 68, 332.
- [9] McCormick, C. L. and Lin Kaoching, *J. Macromol. Sci. Chem.*, **1981** A16(8), 1441.