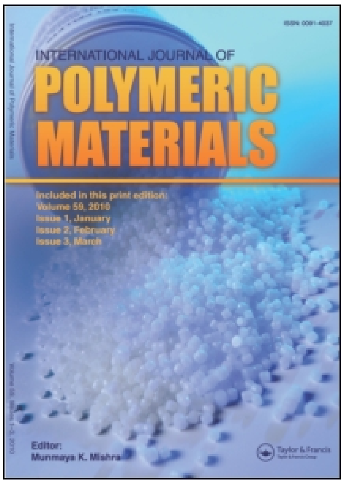


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Aqueous solution polymerization of neutralized acrylic acid using Na 2 S 2 O 5 /(NH 4) 2 S 2 O 8 redox pair system under atmospheric conditions

H. Omidian[a]; M. J. Zohuriaan-Mehr[a]; H. Bouhendi[a]
[a] Adhesive and Resin Department, Iran Polymer Institute (IPI), Tehran, Iran

To cite this Article Omidian, H. , Zohuriaan-Mehr, M. J. and Bouhendi, H.(2003) 'Aqueous solution polymerization of neutralized acrylic acid using Na 2 S 2 O 5 /(NH 4) 2 S 2 O 8 redox pair system under atmospheric conditions', International Journal of Polymeric Materials, 52: 4, 307 — 321

To link to this Article: DOI: 10.1080/00914030304914

URL: http://dx.doi.org/10.1080/00914030304914

International Journal of Polymeric Materials, 52: 307–321, 2003

0091-4037/03 $12.00 +.00
DOI: 10.1080/00914030390119424

AQUEOUS SOLUTION POLYMERIZATION OF NEUTRALIZED ACRYLIC ACID USING $Na_2S_2O_5/(NH_4)_2S_2O_8$ REDOX PAIR SYSTEM UNDER ATMOSPHERIC CONDITIONS

H. Omidian
M. J. Zohuriaan-Mehr
H. Bouhendi
Adhesive and Resin Department, Iran Polymer Institute (IPI),
Tehran, Iran

Thickening is one of the main attributes of high molecular weight poly(sodium acrylate) as a water-soluble polymer. The acrylate polymer was prepared through polymerization of NaOH-neutralized acrylic acid in aqueous solution. The reaction mixture was open to the atmosphere, providing unrestricted access to oxygen. The sodium metabisulfite/ammonium persulfate redox system was used as an initiator in the free-radical polymerization. After prevailing on a few synthetic practical problems, certain parameters affecting the reaction and product characteristics were studied. The parameters were the initiator and monomer concentration, reaction temperature, pH, and chain transfer agent (i.e., isopropanol). As-synthesized polymers were purified and evaluated viscometrically by a Brookfield viscometer (0.5 Wt% polymer solution in distilled water at 25°C). Intrinsic viscosity, [η], was also measured to calculate the viscosity average molecular weight (M_v) based on the corresponding Mark-Hawink-Sakurada equation. Changes of the isolated polymer yield, viscosity, M_v, and a couple of indirect kinetic factors including gelation/reaction times and temperature were investigated according to the mechanism and known kinetic relationships of the free-radical addition polymerization. Finally, a useful Brookfield viscosity-M_v curve was obtained and suggested to use for facile estimation of the average molecular weight of a typical poly(sodium acrylate) sample having medium to high molecular weight.

Keywords: poly(sodium acrylate), free-radical polymerization, aqueous system, $Na_2S_2O_5/(NH_4)_2S_2O_8$ redox pair, viscosity, thickener

Received 12 January 2001; in final form 19 January 2001.

Address correspondence to H. Omidian, Adhesive and Resin Department, Iran Polymer Institute (IPI), PO Box. 14965-115, Tehran, Iran. E-mail: h.omidian@proxy.ipi.ac.ir

INTRODUCTION

Carboxylic acid-containing polymers like poly(acrylic acid), poly(methacrylic acid) and poly(itaconic acid) are all hydrophilic polymers. These materials, their copolymers with other hydrophilic, hydrophobic monomers and their metallic salts are utilized in variety of applications including superabsorbents, paints, detergents, industrial coatings, cosmetics, ceramics, textiles, ion-exchange resins, paper making, oil-well drilling, industrial adhesives, cements, drug delivery systems and so on [1,2]. Besides, good polymerisability of the monomers allows the preparation of high molecular mass polymers that are useful as flocculent and thickeners in aqueous systems [3].

Polymerizations initiated by the free radicals formed *via* oxidation-reduction (redox) reaction are normally characterized by short induction periods, high polymer yield in a short period of time, and performing the polymerization at or below room temperature [4]. Numerous works that are mostly patents [5–9] have reported on the redox-initiated polymerization of sodium acrylate. Sodium acrylate has been polymerized using the redox pair of $NaHSO_3/K_2S_2O_8$ by Contijoch *et al.* [5], $Na_2S_2O_5/(NH_4)_2S_2O_8$ by Cogne *et al.* [6], $Na_2S_2O_5/Na_2S_2O_8$ by Kurenkoff *et al.* [7], $NaH_2PO_2/K_2S_2O_8$ by Komotsu et al. [8] and triethylamine/$(NH_4)_2S_2O_8$ by Yashida [9]. In addition, persulfate-based thermally initiated sodium acrylate polymerizations have also been performed by others under various conditions [10–24]. To our knowledge based on the Chemical Abstracts, scanty reports are available on sodium acrylate polymerization initiated by sodium metabisulfite (SMBS)/ammonium persulfate (APS) redox pair [6].

Poly(sodium acrylate) is industrially produced mostly *via* neutralization of poly(acrylic acid) with aqueous NaOH solution [25]. However, sodium acrylate monomer can be polymerized directly by aqueous solution and inverse dispersion techniques. On the other hand, purging all solutions to remove dissolved oxygen and flushing of the reactor with oxygen-free nitrogen as well as removing the monomer inhibitor are often stated to be necessary to avoid long induction times before polymerization [2,25]. Since simplicity, facility and brevity are always preferred in industrial processes due to economic reasons, our research activity has been focused on industry-oriented synthesis of water-soluble/swellable polymers in the presence of air [26–31].

In the present work, attempts have been made to directly prepare high viscosity poly(sodium acrylate) using aqueous solution method without attempting to exclude atmospheric oxygen and the monomer inhibitor. SMBS/APS redox pair was used as the initiating system.

Certain parameters affecting the reaction and product characteristics are also investigated.

EXPERIMENTAL

Materials

Glacial acrylic acid (AAc) inhibited with 200 ppm hydroquinone monomethylether (Fluka), NaOH pellets (Merck), ammonium peroxydisulfate (Merck), sodium metabisulfite (Merck), isopropanol (Merck) and technical grade methanol were used as received. The solvent was distilled water prepared in the laboratory.

Procedures

Solution polymerization of sodium acrylate was carried out under a non-isothermal optimized condition as follows. In a 250-mL beaker containing 14.9 g (0.207 mol) glacial acrylic acid, 0.207 mole sodium hydroxide (8.3 g NaOH in 26 mL of water) was added dropwise. The final pH of the solution was determined to be 8.7 as monitored by pH-metric titration [30].

The beaker was held in a thermostated water bath adjusted at 20°C (except for the experiments that were run for evaluating the bath temperature effect). Given amounts of APS (in 3 g of water) and of SMBS (in 3 g of water) were added to the neutralized monomer solution. The mixture was stirred magnetically. At the early seconds of the reaction (*i.e.*, induction period which was 8–25 sec., after the addition of the SMBS solution), the mixture viscosity was significantly enhanced and gelation was observed. The reaction temperature was 24–40°C at the corresponding "gelation time". The maximum reaction temperature (about 60°C) was accordingly achieved after 2–5 min.

The mixture was allowed to cool to room temperature and the high viscous-elastic mass was cut into small pieces and poured into excess amount of methanol. After 24 hr the turbid supernatant was decanted. Fresh methanol was added and the flask was kept aside overnight to extract all the impurities (water, unreacted monomers, initiators, *etc.*) from the polymer particles into methanol. After shaking the translucent supernatant was decanted and polymer particles were dried at room temperature for 18 hr. A hammer-type minigrinder (laboratory scale) was used to grind the particles to 40–60 mesh. The product was stored in dark tightly-stoppered bottles away from moisture.

The *isolated yield* was calculated by the following equation:

$$\text{Yield} = (\text{weight of the dried polymer}/\text{weight of the NaAAc used}) \times 100$$

TABLE 1 Viscosities of 0.5 Wt% Aqueous Solutions of Polymer Samples Withdrawn from the Reaction Mixture at Various Times[a]

Sampling time, min.	Viscosity, cP	Gel content
10	90	No gel
20	90	No gel
40	90	No gel
50	95	No gel
60	98	No gel
90	100	No gel
120	125	No gel
150	145	No gel
180	165	No gel
240	185	Negligible
360	190	[b]
1440	196	[b]

[a] The samples were worked up and purified according to the given experimental procedure.

[b] The gel formed was not measurable due to its very slimy nature.

It should be pointed out that the polymer solution viscosity (0.5 Wt% aqueous polymer solutions) was approximately constant while the jelly-like reaction mixture was kept aside for up to about 60 min. Longer times resulted in higher viscosity samples (Table 1). However, the as-synthesized rubber-like mass became more rigid when it was left for more than ~20 min. Therefore, from a practical point of view, such a rigid sample possesses a couple of work-up problems; difficult to cut, necessity of repeated changes of the turbid methanolic supernatant with fresh methanol and consequently, consuming a large volume of methanol and long time for the extraction operation. As a result, a time as short as 10 min. was accepted as the optimum time after achieving the maximum reaction temperature.

In the experiments evaluating the pH effect, the pH of the neutralized acrylic acid solution was increased by adding a few drops of 2M NaOH aqueous solution to reach a desired pH. So, the volume increase of the solution was negligible and no change in the other reactants concentration occurred.

Viscosity Measurements

0.5 g of the dried polymer powder was dissolved in 99.5 g of distilled water (0.5 Wt%) while stirring. Viscosity of each solution was measured by LV Brookfield viscometer (spindle 2, 60 rpm) at 25°C.

Intrinsic viscosity was measured at 25°C by Ubbelohde viscometry using aqueous 2M NaOH as solvent. The solutions concentrations were 1.00, 0.83, 0.66, 0.59 Wt%. The average molecular weight of the polymers calculated by the known Mark-Hawink-Sakurada equation as follows [32]:

$$[\eta] = 42.2 \times 10^{-3} \mathrm{M}_{\mathrm{v}}^{0.64}.$$

RESULTS AND DISCUSSION

General Discussion of the Redox Aqueous Solution Polymerization of Neutralized AAc under Atmospheric Conditions

Equation (1) is often used for describing the free-radical generation by metabisulfite/persulfate redox pair. However, based on a variety of reports in the literature relating to similar systems [4,33], it is proposed that the reductant in the redox reaction is bisulfite anion, that is in equilibrium with metabisulfite anion in aqueous medium Eq. (2). The end-group studies [33] also support the idea that the reducing part of the redox pair is the bisulfite anion Eq. (3) rather than the metabisulfite anion Eq. (1). If so, in the presence of air, oxygen can react as an oxidant which may compete with the bisulfite anion Eq. (4). Actually, some researchers reported that oxygen could couple with bisulfite anion to form a redox pair [34–36]. The aqueous acrylic acid containing bisulfite anion was successfully polymerized by continuous pumping atmosphere air into the reaction mixture [37]. Acrylamide was also readily polymerised under atmospheric oxygen by using $Na_2S_2O_5/KMnO_4$ redox initiator [38]. Therefore, apart from the well-known function of a free-radical scavenger, chain transfer facilitator, and polymerization retarder [39], at the same time, oxygen might form a redox pair in conjunction with metabisulfite anion to generate free radicals, initiating the polymerization.

$$\mathrm{S_2O_5^{2-} + S_2O_8^{2-} \rightarrow S_2O_5^{-\bullet} + SO_4^{-\bullet} + SO_4^{2-}} \tag{1}$$

$$\mathrm{S_2O_5^{2-} + H_2O \rightleftharpoons 2HSO_3^{-}} \tag{2}$$

$$\mathrm{HSO_3^{-} + S_2O_8^{2-} \rightarrow HSO_3^{\bullet} + SO_4^{-\bullet} + SO_4^{2-}} \tag{3}$$

$$\mathrm{4HSO_3^{-} + O_2 \rightarrow 4SO_3^{-\bullet} + 2H_2O} \tag{4}$$

$$\mathrm{R^{\bullet} + M \rightarrow RM^{\bullet}} \tag{5}$$

$$RM^{\bullet} + nM \rightarrow R(M)^{\bullet}_{n+1} \tag{6}$$

$$RM^{\bullet} + O_2 \rightarrow R\text{-}O\text{-}O^{\bullet} \tag{7}$$

$$R\text{-}O\text{-}O^{\bullet} + M \rightarrow R\text{-}O\text{-}O\text{-}M^{\bullet} \tag{8}$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet} \tag{9}$$

$$RM_n^{\bullet} + H_2O \rightarrow RM_nH + HO^{\bullet} \tag{10}$$

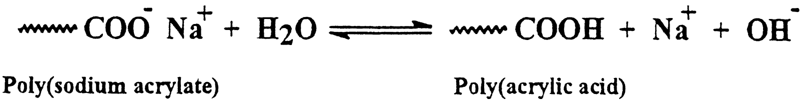
Another probable reaction of oxygen, as shown by Barnes and others [29,40–42], may be the formation of a copolymer with the monomer (M), *i.e.*, a polyperoxide Eqs. (7) and (8).

This reaction may compete with the addition of normal polymer radical ($RM^{\bullet}$) to the monomer. Since addition of monomer to the proxy radical Eq. (8) is much slower than to the normal polymer radical [32] Eq. (6), an inhibition or induction period is often observed.

This period (gelation time, g_t) often led to a jelly-like material (not a real crosslinked gel). The parameter g_t depends strongly on the monomer(s) nature. For instance, under the conditions mentioned in the experimental section, g_t was measured to be 380s, 90s and 20s when the neutralization degree of acrylic acid (by using NaOH) was 25%, 50% and 100%, respectively. During the inhibition period, the degree of polymerization is reported by Flory [43] to be low. Nevertheless, each peroxide link might be a potential source of free radicals to initiate polymerization. Then the concentration of initiating radicals would increase with time, leading to more polyperoxide and to a self-accelerating process. At some point, the concentration of initiating radicals might become high enough to enable significant amounts of normal polymerization to occur, resulting in a rapid increase in viscosity, slowing of oxygen diffusion, and rise in maximum temperature during gelation (T_{max}).

Less probable reactions are the thermal decomposition of the persulfate ion Eq. (9) that is expected to only contribute significantly at high temperatures, and the chain transfer to water Eq. (10). The latter reaction seems a likely contributor, because of the large quantity of water present in aqueous system, although the chain transfer constant for water has been reported to be very low, especially in radical polymerization of acrylic monomers [32].

Another feature of the polymerization of the neutralized acrylic acid arises from the difference in pK_a values for AAc and poly(AAc), *i.e.*, 4.2 and 6.4 respectively [44]. Because the pK_a values of the monomer and polymer differ by 2 to 2.5 units, the monomer may be considered to be a strong acid relative to the polymer. Hence, any dissociated monomer that reacts and becomes part of a polymer chain will develop a more basic character relative to the unreacted monomer molecules, so it may lose the Na^+ ion, upon hydrolysis, and become re-associated with an H^+ ion.



$$\sim\!\sim COO^- Na^+ + H_2O \rightleftharpoons \sim\!\sim COOH + Na^+ + OH^-$$

Poly(sodium acrylate) **Poly(acrylic acid)**

This equilibrium process will result in the dissociation of an additional monomer molecule (if any), due to the generation of OH^-.

All the above-mentioned phenomena make the kinetic relationships too complicated to be able to explain all the empirical results accurately.

Initiator Concentration

A 1:1 (by mol) ammonium persulfate (APS)/sodium metabisulfite (SMBS) redox system was used to initiate neutralized acrylic acid polymerization. This series of experiments was performed with a constant monomer (sodium acrylate) concentration of 9.44 mol% (35 Wt%) at 20°C (Table 2). According to the data (Exps. I1–I5), high initiator concentration resulted in lower time elapsed to reach to T_{max}, that means higher rates of polymerization (R_p) in agreement with the following equation [45]:

$$R_p = k_p[M](k_d[red][ox]/2k_t)^{1/2} \qquad (11)$$

where [M], [red] and [ox] stand for monomer, reductant and oxidant molar concentration, and K_p, Kd and K_t are the corresponding rate constants of propagation, initiator dissociation and termination, respectively. In our work, $[red] = [ox] = [I]$, then, $R_p = K_p(K_d/2K_t)^{1/2}$ $[M][I]$.

On the other hand, higher initiator concentration resulted in shorter gelation time (g_t), *i.e.*, shorter inhibition period. It may be attributed to higher population of generated free radicals that react with monomer Eq. (5). This addition reaction, as mentioned before, is faster than the addition of peroxy radical (having unknown, but constant concentration), to the monomer Eq. (8).

TABLE 2 Effects of the Monomer (Sodium Acrylate) and Redox Initiator (APS/SMBS) Concentration on the Aqueous Solution Polymerization and the Product Yield, Viscosity, and Molecular Weight[a]

Expt. no	Monomer mol%	Initiator mol%	[I]/[NaAAc], (%)	g_t[b]S	ΔTg_t[c]°C	t_{Tmax}[d]S	ΔT_{max}[e]°C	Yield, %	Viscosity[f] cP	M_v[g] (g/mol) × 10^{-3}
I1	9.44	0.0075	0.00079	25	5	150	21	38	432	1058
I2	9.44	0.0224	0.00236	10	7	130	24	67	200	585
I3	9.44	0.0297	0.00314	9	9	100	27	67	91	560
I4	9.44	0.0374	0.0039	8	9	85	30	78	85	542
I5	9.44	0.0561	0.0059	7	17	75	35	79	75	89
M2	6.72	0.0263	0.0039	30	8	110	11	57	41	222
M3	5.24	0.0206	0.0039	60	8	120	10	47	24	44
M4	4.28	0.0165	0.0039	360	6	360	6	41	21	34
M5[h]	3.60	0.0140	0.0039	–	–	–	–	–	–	–
T10	9.44	0.0374	0.0039	12	8	120	20	66	190	563
T30	9.44	0.0374	0.0039	8	10	85	30	81	73	333
T40	9.44	0.0374	0.0039	7	9	90	29	80	71	301
T50	9.44	0.0374	0.0039	7	11	85	32	90	70	283
T60	9.44	0.0374	0.0039	5	11	80	36	92	38	198

[a] In I- and M- series of experiments, starting bath temperature (T_b) was 20°C, while in the experiments T10, T30, T40, T50 and T60; T_b was 10, 30, 40, 50 and 60°C, respectively.

[b] Gelation time.

[c] Reaction temperature increase, from T_b up to gelation point.

[d] Time elapsed to reach from T_b to the maximum reaction temperature (T_{max}).

[e] Reaction temperature increase, from T_b to T_{max}.

[f] Viscosity of 0.5 Wt% solution of purified sample in distilled water at 25°C by Brookfield LV viscometer.

[g] Average molecular weight obtained from capillary viscometry (Ubbelohde, 2M aq. NaOH, 25°C) using the equation of $[\eta] = 42.2 \times 10^{-3} M_v^{0.64}$.

[h] No polymerization occurred within 24 hrs.

As is obvious from the data in Table 2, the polymer with highest molecular weight (I1) was obtained when the lowest initiator concentration was used. The known following relationship [45] clearly explains the observation:

$$X_n = k_p[M]/(fk_d k_t[I])^{1/2} \tag{12}$$

where X_n and f are number average degree of polymerization and initiator efficiency factor, respectively. It was also found that the product with highest viscosity (or M_v) was produced at the expense of a considerable decrease of yield. So, the condition applied in Exp. I4 was selected as preliminary optimum condition (initiator to monomer molar ratio of 0.0039%).

Monomer Concentration

Effect of the monomer concentration, in a constant initiator to monomer mol ratio of 0.0039%, was investigated (Table 2; Exp I4, M2–M5). It can obviously be concluded that ΔT_{max}, as a measure of the reaction rate, decreases with decreased monomer concentration. That is in agreement with Eq. (11). According to the Eq. (12), increased monomer concentration results in higher molecular weight polymer. The M_v variations given in the table are also in good agreement with the equation.

Effect of the Bath Temperature

Because of its strong effect on the reaction rate, bath temperature (T_b), was investigated by conducting the batch polymerizations within the bath temperature range of 10–60°C. Individual reaction temperatures increase to some extent (up to T_{max}) depending on the preset corresponding bath temperatures, heat of polymerization being the source of the temperature increase (ΔT_{max}). The results are given in Table 2, Exp. I4 and T10–T60. It is evident from the table that, with these non-isothermal reactions, increasing of T_b enhances the polymerization rate (*i.e.*, shorter gelation time and t_{Tmax}) and yield, but decreases the polymer molecular weight significantly. These experimental observations are in good agreement with the following known Arrhenius-type equations [45]:

$$\mathrm{Ln}\,R_p = \mathrm{Ln}\,C + \mathrm{Ln}\{[M](f[I])^{1/2}\} - E_R/RT \tag{13}$$

$$\mathrm{Ln}\,X_n = \mathrm{Ln}\,C' + \mathrm{Ln}\{[M](f[I])^{1/2}\} - E_{xn}/RT \tag{14}$$

where C and C′ are constants composed of collision frequency factors of initiation, propagation and termination. E_R and E_{xn} stand for overall activation energy for the rate of polymerization and for the degree of polymerization, respectively. R is the universal gas constant and T is the Kelvin absolute temperature. As a result, since higher molecular weights are achieved at the expense of the lower yields, the temperature of 20°C was recognized to be the optimum starting reaction temperature.

Effect of pH

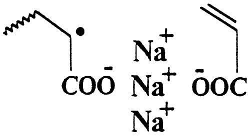
The results obtained through changes in pH from 8.7 to 13 (at 20°C bath temperature) are given in Table 3. Since both sodium acrylate and poly(sodium acrylate) convert to their acid forms at acidic aqueous media, we studied the reactions at $pH > 8.7$ by adding NaOH aqueous solution to the pre-neutralized acrylic acid solution prior to polymerization. In these experiments (P-series), no significant variations were observed with gelation time and temperature. But t_{Tmax} gradually decreased, reached a minimum and then increased. At the same time, product yield and viscosity were affected by pH of 8.7 to 9, and then decreased at higher pH. The initial increase in the rate of polymerization, yield and viscosity (Table 3) may be attributed to the screening or shielding effect of sodium cations between the anionic growing macroradicals and the anionic monomer (Scheme 1). So, decreased electrostatic repulsion makes further growth of the chain more probable. In fact, the conformational state of the chains in the aqueous reacting medium affects the course of polymerization and final properties of the product. The conformational state of polyelectrolyte macromolecules, *e.g.*, poly(sodium acrylate), in aqueous solu-

TABLE 3 Effect of pH on the Aqueous Solution Polymerization, Product Yield, Viscosity and Molecular Weight[a]

Expt. No[b]	g_t (s)	ΔT_{gt} (°C)	t_{Tmax} (s)	ΔT_{max} (°C)	Yield, %	Viscosity, cP	M_v, $g/mol \times 10^{-3}$
P8.7	8	9	85	30	78	85	542
P9	8	12	75	33	82	88	544
P11	7	12	75	34	86	80	610
P13	10	13	85	32	68	80	508

[a] All the parameters have been introduced in the footnote of the Table II, starting bath temperature = 20°C; monomer mol% = 9.44; Initiator mol% = 0.0374.

[b] In P8.7, P9, P11 and P13 experiments, pH was 8. 7, 9, 11 and 13 respectively.



SCHEME 1

tions is recognized to be affected by factors such as pH and the ionic strength of the solution [46]. The conformational state of a growing polyelectrolyte chain must, to a certain extent, be affected by the said factors. Here, in the polymerization of acrylate anion in aqueous solution of NaOH at higher pH range ($pH > 9$), it is reasonable to suppose that an excess of Na^+ in vicinity of the macromolecular chains would diminish the coulombic repulsion of the ionized carboxylic groups, thus making possible the existence of the less-stretched conformation, *i.e.*, collapsing the growing chains, so called "micro-salting-out effect". Hence, conversion and polymerization rate, as well as the product yield and viscosity are decreased (Table 3).

Effect of Chain Transfer Agent

Chain transfer as a chain-breaking reaction is often useful for controlling the polymerization reaction as well as the polymer molecular weight. Isopropanol has a moderate chain transfer constant in radical polymerization [32], so, for instance, it is usually used as a chain transfer agent in polymerization of acrylonitrile for wet spinning of acrylic fiber or Orlon. In the C-series of experiments, isopropanol was used as a chain transfer agent (CTA) and the results were shown in Table 4. All the observations can be explained using the conventional kinetic relationships derived from Mayo equation [45] Eq. (15).

$$1/X_n = (1/X_n)_0 + C_s[S]/[M] \tag{15}$$

where $(1/X_n)_0$ is the value of $1/X_n$ in the absence of CTA, and C_s and [S] stand for chain transfer constant and CTA concentration, respectively. It is obvious that the higher the isopropanol concentration, the lower will be the molecular weight and viscosity. Consequently, since very low molecular weight chains extract by methanol during the purification step (see experimental section), isolated yield also decreases with increased isopropanol concentration. On the other hand, since the propagation can not proceed more at higher [S], the rate of polymerization and the maximum reaction temperature (T_{max}) do decrease.

TABLE 4 Effect of isopropanol as a chain transfer agent on the aqueous solution polymerization, product yield, viscosity, and molecular weight[a]

Expt. No	Isopropanol mol%	t_{Tmax} (s)	ΔT_{max} (°C)	Yield, %	Viscosity, cP	M_v, g/mol × 10^{-3}
C1	0	85	30	78	85	542
C2	0.114	90	30	63	28	231
C3	0.227	95	28	56	25	76
C4	0.454	95	26	53	24	64
C5	0.679	105	24	53	14	62

[a] All the parameters have been introduced in the footnote of the Table III. Starting bath temperature = 20°C; monomer mol% = 9.4; Initiator mol% = 0.037; pH = 8.7. Isopropanol was added to the reaction mixture just after gelation point, so, gelation time and temperature was unchanged in these series of experiments (8 s and 29°C, respectively).

Viscosity-M_v Relationship

Figure 1 displays a plot of Brookfield viscosity of the prepared poly(sodium acrylate) samples *versus* their viscosity average mole-

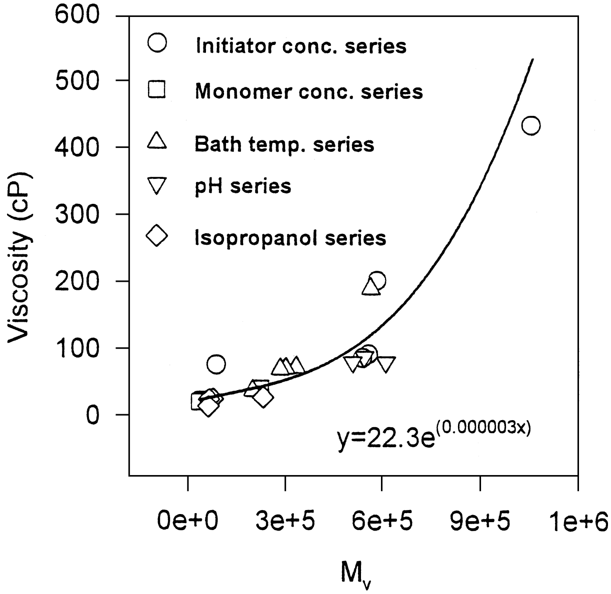


FIGURE 1 Plot of brookfield viscosities of the poly(sodium acrylate) sample (0.5 Wt% in water at 25°C) obtained from different series of experiments *versus* their viscosity average molecular weights. $M_v = 3.3 \times 10^5$ Ln(viscosity, cP/22.3).

cular weights (M_v) obtained from $[\eta] = 42.2 \times 10^{-3} M_v^{0.64}$. Although the two parameters have been measured in different aqueous solutions (*i.e.*, water and 2M NaOH), this plot can be useful in practical and theoretical terms. Such an overall trend has already been reported regarding a $[\eta]$-M_v relationship for sodium salt of poly(acrylic acid) in 1.0 M NaCl at 30°C [47]. Generally speaking, there is a critical rough value of the polymer molecular weight in which the viscosity values diverge from a linear trend to an exponential one. It is clear from the figure, that this appears at polymer molecular weights around 500,000. It seems that polymer chain entanglements appear as a powerful force to increase the viscosity of the polymer solution for polymer molecular weights greater than 500,000.

CONCLUSION

Practical facile conditions were chosen to non-isothermally polymerize NaOH-neutralized acrylic acid and to achieve medium to high viscosity poly(sodium acrylate) thickening agents for aqueous systems. A redox initiator, *i.e.*, $Na_2S_2O_5/(NH_4)_2S_2O_8$ was used for the free-radical polymerization. No attempt was made to exclude atmospheric oxygen from the aqueous solution polymerization mixture. Certain parameters affecting the reaction and the product properties were investigated. The main conclusions may be summarized as follows:

1. Higher initiator concentration resulted in higher polymerization rate and temperature, shorter induction period and higher molecular weight at the expense of lower isolated yield (Table 2, I-series).
2. In a constant initiator to monomer mol ratio of 0.0039%, higher yield and degree of polymerization was achieved at higher monomer concentration (Table 2, M-series).
3. Lower starting bath temperatures, keeping the other variables constant, led to higher product viscosity at the expense of the lower yields (Table 2, T-series).
4. Regarding the pH effect, Na^+ ion concentration showed an appreciable effect on both viscosity and yield, so that, within the pH range of 8.7–9, the mentioned characteristics decreased.
5. Isopropanol, as a moderate chain transfer agent caused a significant decrease in product yield and viscosity.
6. The viscosity and isolated yield of the synthesized thickening agent under the applied practical conditions were found to be

optimum at a particular level of initiator (SMBS = APS = 0.0374 mol%), sodium acrylate (9.44 mol% ≅ 35 Wt%), pH ≅ 9 and starting reaction temperature of 20°C. Total reaction time corresponding to the above conditions was lower than 12 min.

7. An exponential plot of Brookfield viscosity *versus* M_v was proposed to apply for easy rough estimation of the average molecular weight of any poly(sodium acrylate) sample having medium to high viscosities.
8. Overall, the optimum conditions obtained from this work can be used as a starting point to improve larger-scale facile synthesis of poly(sodium acrylate) at atmospheric conditions using non-purified starting materials.

REFERENCES

[1] Buchholz, F. L. (1992). In: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A21, 5th edn., Elvers, B., Hawkins, S. and Schulz, G. (Eds.), VCH: Weinheim, p. 143.
[2] Nemec, J. W. and Bauer, W. Jr. (1985). In: *Encyclopedia of Polymer Science and Engineering*, Vol. 1, Mark, H. F., Bikales, N. M., Overberger, C. G. and Menges, G. (Eds.), Wiley: New York, p. 221.
[3] Shoaf, G. L. and Poehlein, G. W. (1991). *J. Appl. Polym. Sci.*, **42**, 1239.
[4] Liu, Z. and Brooks, B. W. (1999). *J. Polym. Sci.*, *Polym. Chem. Ed.*, **37**, 313.
[5] Contijoch, M. *et al.* (1985). Span Es 54073, *Chem. Abstr.* (106) 96943j.
[6] Cogne, P. *et al.* (1981). Braz PI 8005327, *Chem. Abstr.* (95) 63151j.
[7] Kurenkoff, E. *et al.* (1993). Zh Prick Khim, **66**(7), 1603; *Chem. Abstr.* (120) 135257f.
[8] Komotsu, H. *et al.* (1975). Jpn Kokai 7515881, *Chem. Abstr.* (83) 59926j.
[9] Yashida, E. *et al.* (1976). Jpn Kokai 7668690, *Chem. Abstr.* (85) 109200w.
[10] Dairui, E. *et al.* (1976). Jpn Kokai Tokkyo Koho 7850276, *Chem. Abstr.* (90) 155714z.
[11] Iwashito, A. *et al.* (1977). Jpn Kokai Tokkyo Koho 7796692, *Chem. Abstr.* (86) 7685c.
[12] Tonoka, M. *et al.*, Jpn Kokai Tokkyo Koho 9268304; *Chem. Abstr.* (118) 22819f.
[13] Parizak, R. *et al.* (1993). Czech Rep Cz 278382, *Chem. Abstr.* (122) 32346w.
[14] Parizak, R. *et al.* (1994). Czech Rep Cz 278532, *Chem. Abstr.* (122) 240684g.
[15] Akira, Y. *et al.* (1976). Jpn Kokai 7638378, *Chem. Abstr.* (85) 47318e.
[16] Akira, Y. *et al.* (1976). Jpn Kokai 7637979, *Chem. Abstr.* (85) 33972b.
[17] Akira, Y. *et al.* (1975). Jpn Kokai 7543884, *Chem. Abstr.* (84) 136304u.
[18] Tsubakimoto, E. *et al.* (1975). Jpn Kokai 7543331, *Chem. Abstr.* (81) 121372d.
[19] Beres, J. *et al.* (1979). Pol 100141, *Chem. Abstr.* (91) 141441k.
[20] Cogne, P. *et al.* (1981). Fr Demande 2463780, *Chem. Abstr.* (95) 187911z.
[21] Curnelia, V. *et al.* (1979). Rom 66054, *Chem. Abstr.* (95) 8015v.
[22] Akira, Y. *et al.* (1976). Jpn Kokai 7637978, *Chem. Abstr.* (85) 33973c.
[23] Lu, J. (1994). Hauxue Shijie, **35**(4), 471; *Chem. Abstr.* (123) 145356p.
[24] Manickam, S. P., Venkatarao, K. and subbaratnam, N. R. (1979). *Eur. Polym. J.*, **15**, 483.
[25] Chin, Yu-Ren, *SRI International Report No. 130*, April 1979, Menlo Park, California 94025, p. 119.
[26] Askari, F., Nafisi, S., Omidian, H. and Hashemi, S. A. (1993). *J. Appl. Polym. Sci.*, **50**, 1851.

[27] Omidian, H., Hashemi, S. A., Askari, F. and Nafisi, S. (1994). *J. Appl. Polym. Sci.*, **54**, 241.

[28] Omidian, H., Hashemi, S. A., Askari, F. and Nafisi, S. (1994). *J. Appl. Polym. Sci.*, **54**, 251.

[29] Omidian, H., Hashemi, S. A., Sammes, P. G. and Meldrum, I. (1998). *Polymer*, **39**, 3459.

[30] Omidian, H., Hashemi, S. A., Sammes, P. G. and Meldrum, I. (1998). *Polymer*, **39**, 6697.

[31] Omidian, H., Hashemi, S. A., Sammes, P. G. and Meldrum, I. (1999). *Polymer*, **40**, 1753.

[32] Brandrup, J. and Immergut, E. H. (1989). *Polymer Handbook*, 3rd. edn., Wiley: New York, p. VII/8, II/94-II/133.

[33] Ebdon, J. R., Hunckerby, T. N. and Hunter, T. C. (1994). *Polymer*, **35**(2), 251.

[34] Mukherjee, A. R., Ghosh, P., Chadha, S. C. and Palit, S. R. (1966). *Makromol. Chem.*, **97**, 202.

[35] Konar, R. S. and Palit, S. R. (1961). *J. Indian Chem. Sci.*, **38**, 481.

[36] Palit, S. R. and Mandal, B. M. (1968). *J. Macromol. Sci*: *Rev. Macromol. Chem.*, **C2**, 225.

[37] Igarashi, T., Kondo, A., Tsushima, R. and Aoki, S. (1989). *Makromol. Chem.*, **190**, 2109.

[38] Bajpai, U. D. N., Bajpai, A. K. and Bajpai, J. (1992). *J. Indian Chem. Soc.*, **69**, 841.

[39] Bhanu, V. A. and Kishore, K. (1991). *Chem. Rev.*, **91**, 99.

[40] Barnes, C. E. (1945). *J. Am. Chem. Soc.*, **67**, 217.

[41] Bevington, J. C. (1989). In: *Comprehensive Polymer Science*, Vol. 3, Eastmond, G. C., Ledwith, A., Russo, S. and Sigwalt, P. (Eds.), Pergamon, p. 81.

[42] Bamford, C. H., Barb, W. G., Jenkins, A. D. and Oxyon, P. E. (1958). *The Kinetics of Vinyl Polymerization by Radical Mechanisms*, Butterworth, pp. 101, 103, 185.

[43] Flory, P. J. (1953). *Principles of Polymer Chemistry*, Cornell Univ. Press: New York, p. 168.

[44] Kabanov, V. A., Topchiev, D. A., Karaputadze, T. M. and Mktchian, L. A. (1975). *Eur. Polym. J.*, **11**, 153.

[45] Odian, G. (1981). *Principles of Polymerization*, 2nd. edn., Wiley: New York, Chap. 3.

[46] Kabanov, V. A., Topchiev, D. A. and Karaputadze, T. M. (1973). *J. Polym. Sci., Symposium No. 42*, p. 173.

[47] Welch, G. J. (1975). *Polymer*, **16**, 68.