Polymer Bulletin 2, 147–156 (1980)

Polymer Bulletin

High Molecular Weight Polyacrylamide Prepared by Electron Beam Irradiation

R. Azzam[1] and K. Singer[2]

[1] Department of Chemistry, Nucl. Res. Center, AEE, Cairo, Egypt
[2] Department of Chemistry, Risø National Laboratory, Denmark

Hydrated cations and anions reactive towards precursors of molecular products in radiolytic media constitute favourable solutes for preparing high molecular weight polyacrylamide. The conversion and degree of polymerization are well expressed by the formulated equations:

$$q = q_o(1 + \frac{k2}{k1}[S]^n) \quad \text{and} \quad \overline{DP}_n = \frac{100\,N}{D \cdot G_i}\, q_o(1 + \frac{k2}{k1}[S]^n)$$

The conditions of preparing polyacrylamide having $\overline{M}_w$ of 83.5 mil.§ at q ~ 50 % are described.

High molecular weight (HMW) polyacrylamide has been the subject of very many patents. Hydrolyzing the monomer (ABKIN 1975 & PROFFITT 1962), incorporating acrylate salt (ANDO 1975) and/or salts of inorganic acids (KOLODNY 1965 & SCANLEY 1968) are among the declared methods. However, criticism on these factors and their cooperative effects are not cited in the literature.

Deoxygenated water was prepared by boiling double distilled water for 15 min then cooled and stored under nitrogen gas (KORNEEVA 1973).

Monomers or comonomers dissolved in deoxygenated water were further deaerated by 0.2 l N_2/ml solution at a rate of 550 ml/min.

RISØ'S and RAYCHEM'S linear 10 Mev electron beam accelerators having dose-rates (D_r) of about 5 and 17×10^3 Mrad/s respectively were employed.

Polymer was precipitated in excess methanol, filtered and dried under vacuum at 50°C then 80°C over P_2O_5

§mil. stands for million and r. for rad.

0170-0839/80/0002/0147/$02.00

or SICAPENT to constant weight.

Viscosities of 0.1-0.02 gm/dl polymer in 1 N $NaNO_3$ thermostated at $30 \pm 0.1\,^{\circ}C$ were measured against sodium nitrate blank solution for calculating the weight average molecular weight $\bar{M}_w$ (BARBER 1957):

$$[\eta] = 3.73 \times 10^{-4}\ \bar{M}_w^{0.66}$$

Likewise, the number average molecular weight, $\bar{M}_n$, is determined using aqueous polymer solutions thermostated at $25 \pm 0.1\,^{\circ}C$ (COLLINSON 1957):

$$[\eta] = 6.8 \times 10^{-4}\ \bar{M}_n^{0.66}$$

Acrylamide at 5, 10 & 15 % in water has been irradiated at varying doses under N_2. The data are shown in Figs.1 & 2.

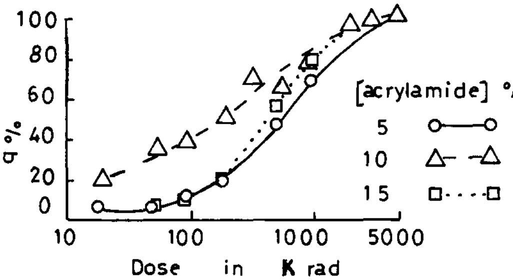

Fig.1
Monomer and dose effect on polyacrylamide yield

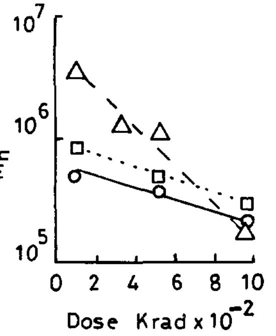

Fig.2
Variation of $\bar{M}_n$ with dose and monomer

It is clear that highest polymer yield (Fig.1) and $\bar{M}_n$ (Fig.2) are associated with 10 % acrylamide. This mostly implies a gel-effect (NORTH 1963). For elucidation, the rate of polymerization has been calculated from the definition:

$$R_p = -\frac{d[M]}{dD} = \frac{q[M_0]}{D} \qquad (1)$$

where $[M_o]$ is the initial monomer concentration and D is the dose.

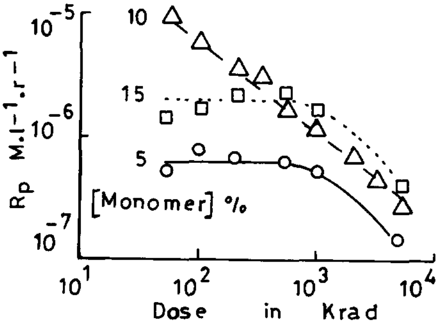

Fig.3

Fig.3 shows that for 5 and 15 %, R_p is independent of the absorbed dose up to D = 550 K.r. This is in consistent with the free radical theory of polymerization (CHAPIRO 1962). At D > 550 K.r., however, R_p decreases with increasing dose. This may be due to increasing radical population and thus termination.

On the other hand, the onset of polymerization at 10 % acrylamide shows higher R_p values than both other concentrations. This is characteristic of the gel effect, being attributed to decreasing termination(ODIAN 1970 & KOPEČEK 1974) though the latter rises with increasing doses. Thus, R_p would decrease with increasing dose, as seen from the figure.

It is worthy to note that the obtained data imply that gelation requires a definite monomer concentration. This mostly allows formation of a spatial structure (KABANOV 1975) via some bonds. For instance, hydrogen bridging between amino and carbonyl groups of neighboring molecules (MIYAGAWA 1961) and/or enhanced molecular aggregation due to reinforced hydrogen bonds (CHAPIRO 1971 & 1973). These would hinder the solubility of the product gel.

On this basis, the monomer concentration has been kept constant at 2 M/l, i.e. 14.22 % to avoid gelation. The dose is chosen 500 K.r. This is the highest dose sustaining free radical mechanism of polymerization (AZZAM).

The influence of hydroxides, bicarbonates and carbonates of Li, NH_4, Na, K & Rb on acrylamide polymerization has been studied. The ingredients were added to hydrolyze monomer to 30 % degree. The results are given in Table 1 .

Table 1 shows that hydroxides produce lowest q & $\bar{M}_w$. Considering reactions (2) & (3) :

$$CH_2{=}CHCONH_2 + MOH \longrightarrow CH_2{=}CHCOOM + NH_3 \quad (2)$$

$$3CH_2{=}CHCONH_2 + NH_3 \longrightarrow N(CH_2CH_2CONH_2)_3 \quad (3)$$

The decrease in polymer yield could be attributed to the monomer depletion via (3). The reduction in $\bar{M}_w$ may imply that nitrile tripropionamide, NPA, is an efficient chain transfer agent (GROMOV 1974). Thus the decrease in q & $\bar{M}_w$ is evidently due to ammonia.

Although carbonates are biacidic, they yet produce an overall amount of NH_3 equivalent to that of hydroxides. Thus, the higher q & $\bar{M}_w$ values found with carbonates can be related to their incomplete dissociation. The pK_a value of carbonic acid is 6.46 . On this

TABLE 1
Influence of the hydrolyzing agents

Hydrolyzing agents	Hydroxides q %	Hydroxides $\bar{M}_w \cdot 10^{-5}$	Carbonates q %	Carbonates $\bar{M}_w \cdot 10^{-5}$	Bicarbonates q %	Bicarbonates $\bar{M}_w \cdot 10^{-5}$
Li	9.65	1.06	13.73	3.18		
NH_4-	7.55	0.86	16.57	6.32	20.01	15.37
Na	9.20	0.69	18.24	2.38	24.84	18.80
K	9.03	0.66	14.97	3.56	26.12	17.26
Rb	10.08	0.53	15.06	2.68		

account both the hydrolyzed acrylamide and NH_3 would decrease. Qualitative tests have proved the existence of carbonates even after refluxing for 48 hr. Only Li_2CO_3 has initiated polymerization under these conditions.

Bicarbonates are even weaker electrolytes. The pK_a of bicarbonic acid is 10.25[a]. They have thus produced higher q & $\bar{M}_w$ values.

It is worthy to note that whenever constant dose rates and doses are employed, the following relation (AZZAM) holds:

$$\overline{DP}_n = \frac{100\ N}{D\ G_i}\ q \qquad (4)$$

where N is the Avogadro number and G_i is the yield of initiating species. This explains well the proportionality between $\bar{M}_w$ and q seen from Table 1 .

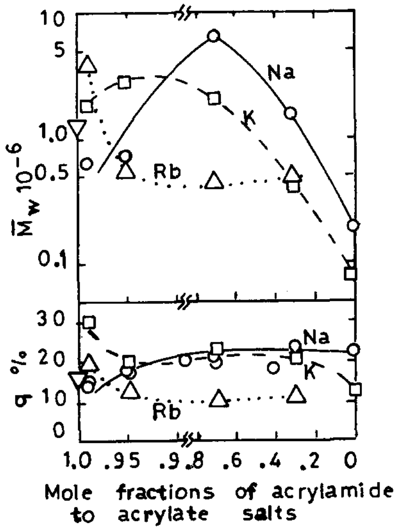

Fig.4
Effect of acrylate salts of varying cation.

Acrylate salts of Na, K & Rb were prepared by adding stoichiometric amounts of the corresponding hydroxides dropwise to ice-cooled acrylic acid stirred magnetically. These were mixed with acrylamide to total 2 M/l then deaerated and irradiated. The results are shown in Fig. 4 .

Fig. 4 shows that within a 0.9 to 0.2 molar ratio of acrylamide:acrylate, conversion and molecular weight decrease in the order Na > K > Rb . This is in good agreement with the reactivity of acrylate towards acrylamide (PŁOCHOCKA 1971). Further, the order of the elements is the same for increasing cationic radii and decreasing degree of hydration. Thus, Płochocka and Wojnarowski have attributed this order to the strength of cationic binding , although sodium in the product was found by flame photometry to be much less than theoretically expected. This casts some doubt on the role of cations for polymer segments. On the other hand, cation hydration would reduce the unbound free water (HALLABA 1968) in the system. This virtually increases the monomer concentration. On this basis, the conversion would increase (CHAPIRO 1962 & WILLIAMS 1968) and thus $\bar{M}_w$ (Eq. 4).

Consequently, highly hydrated cations are favourable for producing HMW polymer. On this account lithium would be the best, though its acrylate salt spontaneously polymerizes on removal of water. Sodium is the next element. Its salt is seemingly stable. q & $\bar{M}_w$ are highest at 7:3 acrylamide : acrylate of sodium.

At [acrylamide:acrylate] > 0.9 the behaviour is complicated by the predominance of acrylamide. The same can be said about comonomer ratios < 0.2 .

The influence of comonomer concentrations at this composition (7:3) has been studied. Raychem's accelerator was employed in the irradiation of samples at 500 K.r. The results are shown in Fig. 5 .

Fig. 5 shows that q increases continuously with increasing concentration. However, $\bar{M}_w$ increases with increasing concentration of the comonomers up to 5.63 M/1

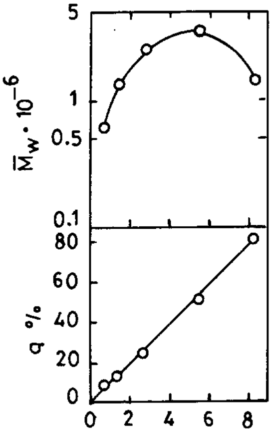

Fig.5
Influence of total concentration of comonomers at const. 7:3 acrylamide:acrylate

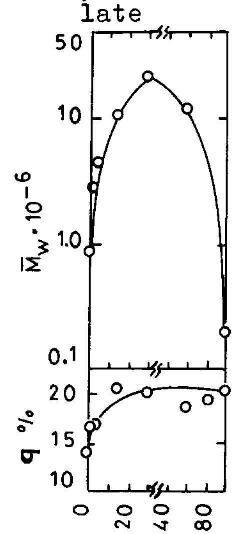

Fig.6
Effect of pre-prepared Na-acrylate at total 2M/1.

then decreases. The former increase is expected from Eq. 4 . However, the latter decrease lies at 8.4 M/l, i.e. 59.7 % comonomers. This is very near if no exceeding saturation occurs (GROMOV 1974). Thus the reasons are mostly related to a two-phase formation.

Once again, sodium acrylate was prepared, separated by a rotary vacuum evaporator at 30°C then dried in a vacuum oven at room temperature over sicapent to constant weight. This was employed to re-investigate the influence of the sodium acrylate to acrylamide ratio at constant comonomer conc. of 2M/l. Risø's accelerator was used for irradiating samples at 500 K.r. The results are shown in Fig. 6 .

The relations in Fig. 6 are similar to the corresponding of Fig. 4, irrespective of changing dose-rates. It shows once again the validity of the comonomer ratio of 7:3 , acrylamide:acrylate of sodium.

The influence of Cl^-, NO_3^- & SO_4^{2-} as sodium salts on acrylamide polymerization has been studied. Acrylamide, hydrolyzed by NaOH or Na_2CO_3 to 30 %,, was heated to near boiling to expel ammonia, then left overnight prior to mixing with salt solutions and irradiation. The results are shown in Fig. 7 .

Fig. 7 shows once more that q is higher with carbonates than with hydroxides. This further consolidates results of item (2) irrespective of changing ambient conditions, i.e. the presence of solutes. Moreover, the variation of q with increasing concentration of a given anion has more or less the same pattern irrespective of the hydrolyzing agent. This can be attributed

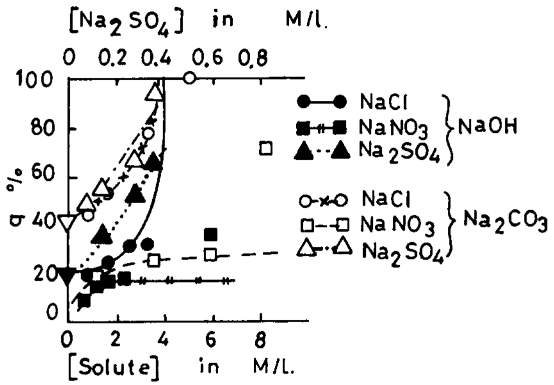

Fig.7
Influence of neutral salts of sodium on acrylamide polymerization.

to the effect of solutes on precursors of the molecular products H_2 or H_2O_2 (ANBAR 1968 & VERESHCHINSKII 1964). This can be expressed by:

$$\frac{1}{G_M} = \frac{1}{G_M^o} + \frac{k_2}{k_1}\cdot\frac{1}{G_M^o}[S]^n \quad (5)$$

where G_M refers to G_{H_2} or $G_{H_2O_2}$ while G_M^o is the same at the solute activity $[S] = 0$; k_1 & k_2 are rate constants of the reactions of the precursors with water and solute, respectively.

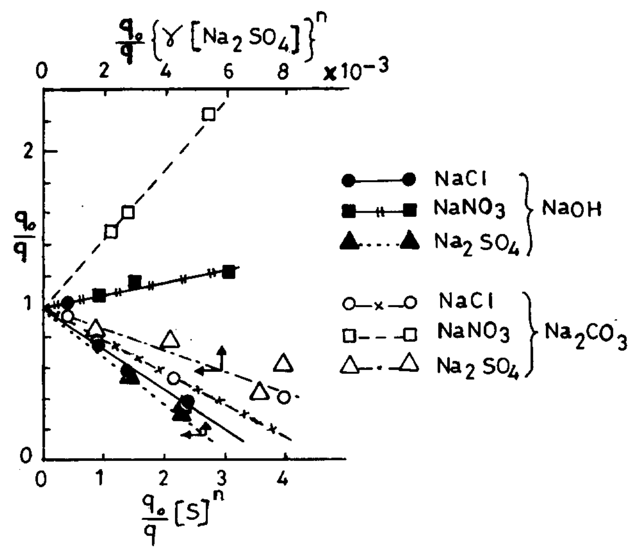

Fig.8
Graphical determination of k_2/k_1

Eq.5 in terms of conversion becomes:

$$\frac{q_o}{q} = 1 - \frac{k_2}{k_1}\frac{q_o}{q}[S]^n \quad (6)$$

Rearranging Eq.6

$$\frac{q}{q_o} - 1 = \frac{k_2}{k_1}[S]^n \quad (7)$$

and taking the logarithms, n was calculated. Inserting the value of n into Eq.(6), k_2/k_1 were found graphically from Fig. 8. Knowing the constants, the

TABLE 2
The constants of Eqs. 5-9

Solute	Concentration range M/l	Hydrolyzing agent@	Solute activity power n	Rate constants solute : water k_2/k_1
NaCl	0.86-3.42	NaOH	1.52±0.34	0.26± 0.06
NaCl	0.86-5.13	Na_2CO_3		0.21± 0.04
$NaNO_3$	0.59-2.35	NaOH	-1.89±0.22	- 0.08± 0.01
$NaNO_3$	1.18-5.88	Na_2CO_3	-0.40±0.04	- 0.45± 0.005
Na_2SO_4	0.14-0.35	NaOH	1.84±0.57	154.00±12
Na_2SO_4	0.07-0.35	Na_2CO_3		70.00±21

@ Calculated amounts for 30 % hydrolysis of acrylamide, the concentration of which is 2 M/l .

influence of neutral solutes, S, on the conversion, q, relative to q_o ,at[S]=0 could be foreseen from:

$$q = q_o(1 + \frac{k_2}{k_1}[S]^n) \qquad (8)$$

All the lines drawn among the experimental data presented in Fig.(7) are based on Eq.(8). Thus, the validity of the equation is evident.

From Fig.7 it is clear that the polymer yield decreases in the order $SO_4^{2-} > Cl^- > NO_3^-$.

Moreover, from Eqs.(4) and (8) one gets:

$$\overline{DP}_n = \frac{100N}{DG_i} q_o(1 + \frac{k_2}{k_1}[S]^n) \qquad (9)$$

Knowing a single value of $\bar{M}_n$ at a given solute activity, the constant of Eq.(9) can be evaluated, although the average of two values has been employed. Fig.9 is an illustrative example.

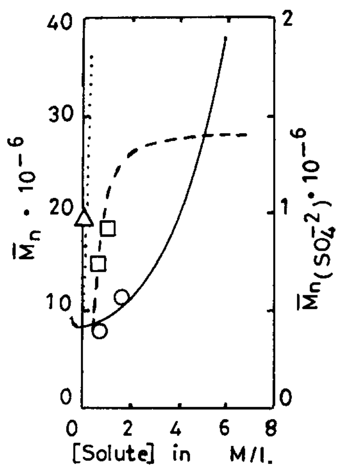

Fig.9
Effect of solute on $\bar{M}_n$

Fig. 9 shows that the number average molecular weight is decreasing in the order $NO_3^- > Cl^- > SO_4^{2-}$. For Cl^- & SO_4^{2-} the limiting values are governed by the solubility of the salts in water. However, NO_3^- has shown that k_2/k_1 ratios change sign at [sodium nitrate] > 7 and < 0.5 M/l. This mostly implies a change in mechanism of the radiolytic transformation beyond these concentrations. It may be related to the particular behaviour of NO_3^- involving disproportionation of the NO_2-intermediate product. For instance:

$$NO_3^- + H \longrightarrow NO_2 + OH^- \qquad (10)$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \qquad (11)$$

Eqs.(10) & (11) show that two H-atoms are consumed in the reduction of one NO_3-anion. The higher reactivity of NO_3^- has seemingly increased $\bar{M}_n$,as compared to Cl^- or SO_4^{2-}(Fig. 9). This may be attributed to decreasing termination. Practically, 10 % $NaNO_3$ has increased $\bar{M}_n$ from 8.64 to 18.13 mil. under the present experimental conditions. Thus, it is concluded that anions reactive towards precursors of the molecular products are favourable for preparing HMW polyacrylamide. However, at [solute]>5 M/1, the $\bar{M}_n$ value in the presence of Cl^- exceeds that of NO_3^-, possibly because of changing mode of radiolytic transformation.

It is concluded beyond much doubt that ammonia effectively terminates acrylamide polymerization in solutions possibly via formation of NPA . Table 3 summarizes some of the relevant data.

TABLE 3

Change of q & $\bar{M}_w$ with removal of ammonia

Run No.	Experimental Conditions	RESULTS q %	$\bar{M}_w.10^{-6}$
1.	Direct addition of NaOH(0.3) to acrylamide(1.0) in solutions prior to irradiation.	9.20	0.07
2.	Heating acrylamide(1.0) with NaOH (0.3) near to boiling	18.40	1.87
3.	Heating acrylamide(0.3) with NaOH (0.3) then leaving overnight before adding acrylamide(0.7).	18.00	8.64
4.	Neutralizing acrylic acid(0.3)with NaOH(0.3)then adding acrylamide(0.7)	20.47	6.74
5.	Mixing pre-prepared sodium acrylate (0.3) with acrylamide(0.7)	21.50	21.62

The numbers in brackets are the fractional molar concentrations of the ingredients.

Table 3 shows that q & $\bar{M}_w$ have increased from run 1 to 2 by heating the hydrolyzing media to expel NH_3 . Further increase in $\bar{M}_w$ by 4.6 fold has been achieved in run 3 by separating the hydrolyzing media from remaining monomer to avoid contact of the latter with ammonia. In run 4, evolution of ammonia has been avoided though $\bar{M}_w$ has decreased while q has increased. In run 5, the salt is dried before application. This has increased both q & $\bar{M}_w$. Thus, the reasons for the low $\bar{M}_w$ value of run 4 are not clear. They may be related to some NaOH contamination or macromolecular structure if not being fortuitous.

Keeping the monomer concentration beyond gelation results in sustained solubility of polyacrylamide in water. Practically, irradiation of 14.22 % acrylamide having 30 % pre-prepared sodium acrylate produces polyacrylamide with $\bar{M}_w = 21.62$ mil. at $q = 21.5$ % . Increasing the comonomers to 40 % increases both q & $\bar{M}_w$ to 58.27 % and 39.78 mil. respectively. Replacing water by 10 % $NaNO_3$ solution results in a further increase of $\bar{M}_w$ to 83.47 mil. whereas q is reduced to 50%.

One of the authors (R.A.) thanks DANIDA deeply for having supported financially this work in Chemistry Dept., Risø National Lab., Denmark.

Mr. H. Abou Helal of Reactor Phys. Dept., Inshas, is also thanked for his help in the theoretical part of this work.

ABKIN, A. D., et al., Ger. Offen. 1795705 (1975)
ANBAR, M.: Water and Aqueous Solutions, in Fundamental Processes in Radiation Chemistry, AUSLOOS, P., ed., Intersci. Publ., New York (1968) pp. 651-85
ANDO, S., et al., Japan Kokai. 7544255 (1975)
AZZAM, R. and SINGER, K., The Role of Oxygen in Radiation Induced Polymerization of Acrylamide in Solutions, under publication
BARBER, W. A., in Acrylamide, Am. Cyanamid Co., N. J. (1957) Wayne
CHAPIRO, A., Radiation Chemistry of Polymeric Systems, Intersci. Publ., New York (1962)
CHAPIRO, A. and PEREC, L., Europ. Polymer J., 7, 1335 (1971)
CHAPIRO, A., Europ. Polymer J., 9, 417 (1973)
COLLINSON, E., et al., Trans. Faraday Soc., 53, 489 (1957)
GROMOV, V. F., et al., Polymer Sci., USSR, 16 (2) 423 (1974)
HALLABA, E. and AZZAM, R., Z. phys. Chem., 237, 177(1968)
KABANOV, V. A., J. Polymer Sci., Symp. No. 50, 71 (1975)
KOLODNY, E. R., US Pat. 3215680 (1965)
KOPEČEK, J. and BAŽILOVÁ, H., Europ. Polymer J., 10, 465 (1974)
KORNEEVA, G. P., et al., Soviet Plastics (5) 12 (1973)
MIYAGAWA, I. and GORDY, W., J. Am. Chem. Soc., 83, 1036 (1961)
NORTH, A., et al., J. Polymer Sci., A1, 1311(1963) and Trans. Faraday Soc., 57, 859(1961) & 60, 960 (1964)
ODIAN, G., Principles of Polymerization, McGraw-Hill Book Co., New York (1970) pp. 255-60
PŁOCHOCKA, K. and WOJNAROWSKI, T. J., Europ. Polymer J., 7, 797 (1971)
PROFFITT, A. C., US Pat. 3022279 (1962)
SCANLEY, C. S., US Pat. 3414552 (1968)
VERESHCHINSKII, I. and PIKAEV, A., Introduction to Radiation Chemistry, Jerusalem (1964) pp. 61-140
WILLIAMS, F., Principles of Radiation-induced Polymerization, in Fundamental Processes in Radiation Chemistry, AUSLOOS, P., ed., Intersci. Publ., N. Y. (1968)

Received September 23/ December 1o, 1979