The Redox Aqueous Polymerization of Acrylonitrile under Pressure

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Synopsis

Effect of pressure (atmospheric to 20×10^6 Pa) on the $K_2S_2O_8$–$Na_2S_2O_4$ initiated aqueous polymerization of acrylonitrile has been studied at 25°C. The conversion and rate of the polymerization tend to rise initially with increase of pressure and fall subsequently to a limiting value. The initial rise in the rate is consistent with an increase of k_p or a decrease in k_t due to high pressure. The ultimate tendency of the rate to fall is possibly due to a decrease in the diffusion rate of the monomer from the aqueous phase to the growing polymer radical site. The molecular weight shows a more or less similar trend except that the fall in the molecular weight begins at a lower pressure range than the same in the rate or conversion. This is explained on the basis of enhanced monomer transfer reaction. These observed kinetic characteristics are not sensitive to the appearance of heterogeneity in the system due to insoluble polymer phase in as much as homogeneous reaction systems in DMF or DMSO essentially exhibit the same features. The rate is proportional to the square root of the product of $[K_2S_2O_8]$ and $[Na_2S_2O_4]$ and varies linerarly as the first power of the monomer concentration.

INTRODUCTION

The aqueous polymerization of water soluble vinyl monomers by redox systems is a much investigated topic. It has already been established by Palit et al.[1-5] that the rate and molecular weight characteristics of these systems are sensitive to the physical characteristics (sol, gel, coagulum, etc.) of the growing polymer phase, which control the number of primary radicals generated in the system and maintain the propagation.

However, it may be interesting to examine to what extent such processes are, if at all, influenced by working under high pressure conditions. Literature reveals that a significant amount of research has already been done to study the effect of high pressure on free radical polymerization systems, and that propagation, termination, and transfer reactions are influenced by working under high pressure conditions. Ogo[6] has recently reviewed the present status of polymerization reactions under high pressure. Sasuga and Takehisha[7] studied the effect of pressure on the radiation induced bulk polymerization of MMA and reported autocatalytic polymerization. Yokawa et al.[8] also studied the photosensitized polymerization of MMA under high pressure and reported k_p to increase with pressure as in styrene polymerization. The earlier literature is already reviewed.[6,9] In one report[10] Baikova et al. studied the polymerization of acrylonitrile in homogeneous system (DMF, AIBN) under high pressure. To our knowledge, sufficient information

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is not available as to how high pressure affects the relevant parameters in redox-initiated aqueous polymerization systems, which are usually of considerable technological relevance.

The aqueous polymerization of AN, methyl methacrylate, and vinylacetate under atmospheric pressure has been studied in detail by Biswas et al.[2,3–5] We have now examined one of these systems under high pressure conditions. From preliminary experimentations we were impressed to find that under an elevated pressure of 12×10^6 Pa, the conversion of polyacrylonitrile nearly doubled (74%) compared to that at atmospheric pressure (38%) under all other identical conditions (monomer and initiator concentration temperature of polymerization maintained constant). Detailed experimentations were subsequently performed to assess the effect of pressure on the various kinetic parameters of the system, and the salient results are highlighted in the present article.

EXPERIMENTAL

Materials

Monomer acrylonitrile (B.D.H) was purified by adopting the method of Biswas and Palit.[3] Potassium persulfate and sodium dithionite (both of E. Merck) were used without further purification. Double distilled water was prepared by distilling ordinary distilled water with alkaline permanganate.

Polymerization

The polymerizations were carried out by transferring calculated aliquots of deaerated water, monomer, initiator ($K_2S_2O_8$) and activator ($Na_2S_2O_4$) under nitrogen in a dry, cleaned glass liner. The glass liner containing the reaction mixture was placed inside the autoclave just after the induction period as apparent from the appearance of a slight turbidity in the system.

The autoclave was sealed and flushed adequately with nitrogen. The pressure inside the reaction was raised to the desired level by introducing purified and dried nitrogen gas under pressure. The reactor temperature was raised to 40°C through an electrical heater attached to the autoclave. After a specified residence period, e.g., 2 h, the autoclave was cooled to room temperature with release of the pressure. The glass liner containing the reaction mixture was taken out, and the entire liquid mixture was poured into methanol quantitatively. The precipitated polymer was isolated by filtration and dried at 60°C and subsequently characterized.

Characterization

Intrinsic viscosity of the polymers were determined in DMF at 35 ± 0.1°C with an Oswald viscometer. The $\overline{M}_v$ values were calculated by using the relations $[\eta] = K M^{\alpha}$,[11] were $K = 3.17 \times 10^{-3}$, solvent DMF (distilled), and $\alpha = 0.746$.

The IR spectra of the polymers were recorded in a Perkin-Elmer 237B spectrophotometer in KBr pellet.

X-ray diffraction patterns were obtained with a Dorn 1 (USSR) x-ray diffractometer with molybdenum target ($\lambda = 0.711$ Å) at 46 kV operating voltage and 19 mA current using a ZrK_α filter.

Thermal analyses (DTA, TGA, TG, DTG) of the polymer samples were performed on a Mom-Derivatograph using Al_2O_3 as a reference sample.

RESULTS AND DISCUSSION

General Features

The polymerizations are accompanied by phase separation owing to the insolubility of PAN in water. At the concentration range of $K_2S_2O_8$ or $Na_2S_2O_4$ used in these experiments, a coarse coagulum[2,3] is obtained. The polymer is white in color and is recovered as a powdery mass after usual processing.

X-ray data suggest 60% crystallinity in PAN (12×10^6 Pa). Thermogram reveals weightlosses at 350°C (25%) and at 550°C (50%) and thereafter exhibits no loss till 1000°C.

Kinetic Characteristics

Figure 1 shows a typical conversion–time plot obtained with a particular polymerization recipe, $[AN] = 0.61M$, $[K_2S_2O_8] = 3.32 \times 10^{-3}M$, $[Na_2S_2O_4] = 1.14 \times 10^{-3}M$ at pressure $= 12.4 \times 10^6$ Pa, and temperature $= 40°C$. The conversions linearly increase with time till 3 h and level off thereafter around 90% conversion. In all subsequent experiments, the polymerization time was maintained at 2 h unless otherwise stated. Notably, conversions are never complete suggesting termination to be dominant.
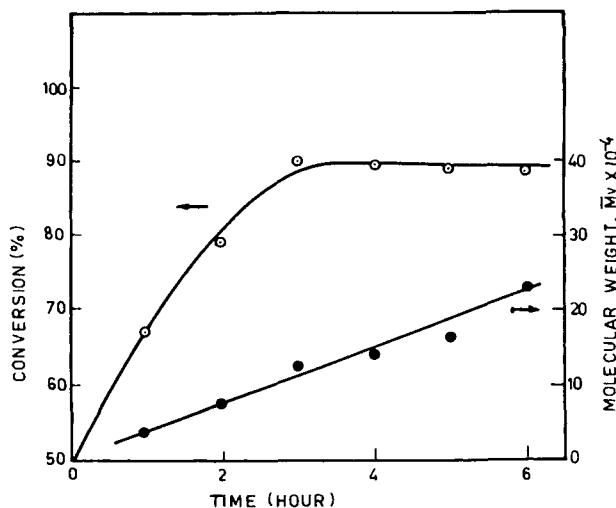

Fig. 1. Variation of percentage conversion and viscosity average molecular weight with time. Polymerization conditions: $[AN] = 0.61M$; $[K_2S_2O_8] = 4.7 \times 10^{-3}M$; $[Na_2S_2O_4] = 1.4 \times 10^{-3}M$; temp 40°C; pressure $= 12.4 \times 10^6$ Pa.

Effect of Pressure on Polymerization

This was studied by carrying out the polymerization at different pressures with a fixed concentration of AN, $K_2S_2O_8$, and $Na_2S_2O_4$, respectively. Figure 2 presents the variation of percent conversion and rate with applied pressure. Figure 3 represents the variation of $\overline{M}_v$ with applied pressure. It is observed that initially, as the pressure is raised from atmospheric to 12×10^6 Pa, conversion as well as rate increase consistently, but start falling thereafter with further increase of pressure, to a limiting value.

The initial increase in conversion and rate with pressure has also been reported in several instances.[9] This behavior may be explained in terms of an increase in chain propagation rate[9] and/or a decrease in the rate of termination of chain ends.[9] However, it is likely that, as the pressure is raised, some of the primary radicals generated from the redox systems are also lost by increased collision. This would imply a decrease in conversion. Apparently, this effect is outweighed by the increase in k_p or in the decrease in the k_t factors, and hence the enhancement in conversion and rate.

Beyond the optimum pressure limit, the conversion, as well as rate, fall with pressure. It is suggested that under these conditions diffusion of monomer from the aqueous medium to the growing polymer radical site is being gradually impaired[9] as the system becomes more dense on exposure to higher pressures.

In fact, Sasuga et al.[7,10,12] has confirmed from pressure–volume relation studies with methacrylic/acrylic esters and acrylonitrile that monomer molecules indeed undergo short-range alignment under pressure even in the liquid state. Further, acrylonitrile with a planar $CH_2 =CHR$ and rodlike
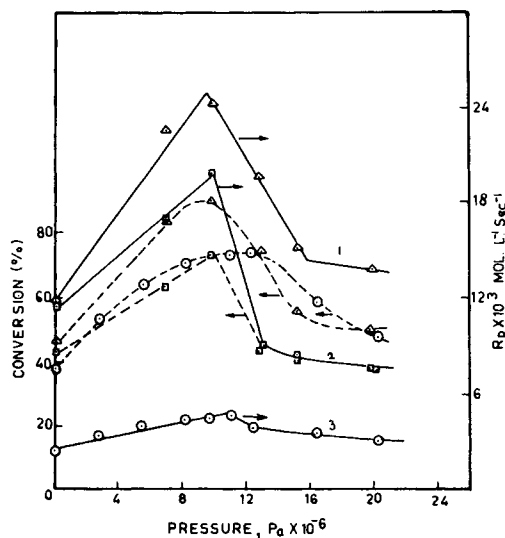

Fig. 2. Dependence of percentage conversion (⋯) and rate (—) of polymerization on pressure. Polymerization conditions: (1) and (2) [AN] = 1.9M; [$K_2S_2O_8$] = 7.7 × 10^{-3}M; [$Na_2S_2O_4$] = 2.8 × 10^{-3}M; total reaction volume = 24 mL; solvent: (1) DMF, (2) DMSO. (3) [AN] = 0.46M; [$K_2S_2O_8$] = 1.8 × 10^{-3}M; [$Na_2S_2O_4$] = 0.57 × 10^{-3}M. Total reaction volume = 100 mL (water). For all runs Time = 2 h, temp = 25°C.
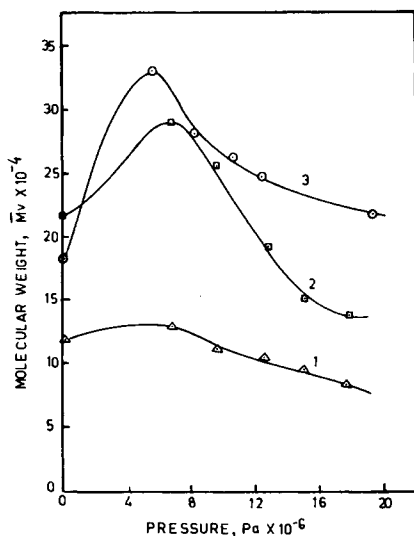
Fig. 3. Variation of molecular weight with pressure. Polymerization conditions for 1, 2, and 3 are same as in Figure 2.

(—C≡N) arrangement[11] is particularly favored for such high pressure alignment. The possibility of such high pressure alignment of acrylonitrile molecules may therefore not be excluded in the present systems. In any event, such alignments will evidently create a situation, where diffusion of the monomer molecules—thus aligned—to the propagation site will be less than if they are randomly distributed in the solution as in the absence of any pressure. This would imply a fall in conversion or rate if this process can kinetically outweigh the chance of an increase in conversion or rate due to decreased chain-termination possible under these conditions. Several instances are known[9] where such a rate decrease with increasing pressure has been reported.

The molecular weights of the polymers tend to rise initially with increasing pressure and fall thereafter. In fact, as evident from Figure 3 the fall in molecular weight begins at somewhat lower pressure than the same in conversion or rate. We suggest that bimolecular transfer[9] reaction between polymer radicals and monomer molecules become important in the increasing pressure range. However, had there been exclusive chain transfer only, the conversions would not have been affected. Since the conversions are seen to fall somewhat, termination seems to be important also.

The aqueous polymerization of AN is a heterophase reaction. To examine whether or not, the observed pressure effect on the conversion is influenced by such phase separation of the polymer in the aqueous medium, the polymerization of AN under high pressures was studied in homogeneous reaction systems using DMF and DMSO as the solvent. The percent conversion, rate and molecular weight data (Fig. 2 and 3) clearly demonstrate the strikingly similar trends in the results to those reported for the aqueous system.

The overall activation volume, $\Delta V^{\neq}_{pol}$ has been calculated in the three cases corresponding to solvents, water, DMF, and DMSO, from the usual

log ($- d[M]/dt$) vs. pressure plots over the initial pressure range (atmospheric—19.3 $\times$ 10^6 Pa) where the conversions rise with pressure. $\Delta V_{pol}^{\neq}$ values for polymerizations in water, DMF, and DMSO media are -15.7, -14.8, and -17.3 cm^3/mol, respectively, which are not widely different from each other.

Table I compares the $\Delta V_{pol}^{\neq}$ observed for this system with the same reported for the free radical polymerizations of a few other vinyl monomers.[10,13,14] An exhaustive compilation of activation volumes for the high pressure polymerization of a wide variety of monomer moieties has been done by Ogo.[6]

Dependence of Rate on the Concentration of the Redox Initiator

The polymerization was conducted at a fixed concentration of AN but with different concentrations of the redox initiators. In fact, in one set of experiments, the [$K_2S_2O_8$] was varied, keeping the [$Na_2S_2O_4$] fixed, while, in another series of experiments, the [$Na_2S_2O_4$] was varied at a fixed [$K_2S_2O_8$]. The pressure was throughout kept constant at 12.4 $\times$ 10^6 Pa. Figure 4 represents the plot of rate (averaged over 1 h of total polymerization) against [($K_2S_2O_8$)($Na_2S_2O_4$)]$^{1/2}$. Apparently, as evident, from the data, the rate is proportional to the square root of the product of the concentration of the redox pair up to a certain concentration of the latter, beyond which the rate seems to level off. An exactly similar trend was reported by Biswas and Palit[3] for the aqueous polymerization of this monomer by the same redox system at atmospheric pressure. This suggests that, in the range studied, the applied pressure does not influence the initiation mechanism.

Dependence of Rate on [Acrylonitrile]

This feature was examined by carrying out the polymerization at a fixed pressure = 12.4 $\times$ 10^6 Pa, fixed concentrations of [$K_2S_2O_8$] and [$Na_2S_2O_4$] with varying [AN]. The average rate computed from the total conversion over 2 h of polymerization has been plotted against [AN] in Figure 5, which clearly indicates a direct first-order dependence. This behavior is fully consistent with the reported by Biswas and Palit[3] for the polymerization of this monomer (at atmospheric pressure) by the same redox pair at moderate concentrations of the latter.[3]

Evaluation of k_m/k_p

Earlier in the text the suggestion has been made that the fall in the molecular weight beyond the maximum (Fig. 3), beginning at a particular pressure of 5.5 $\times$ 10^6 Pa is partly due to enhanced transfer of growing chains with monomer. To lend credence to this contention, k_m/k_p has been evaluated in the present system conducted at high pressure (12.40 $\times$ 10^6 Pa) and at atmospheric pressure following the procedure due to Onyon.[15] The usual relationship

$$\frac{1}{\overline{DP}} = \frac{d[P]/dt}{-d[M]/dt} = \frac{k_m[M][X] + 2k_{td}[X]^2 + k_{tc}[X]^2}{k_p[M][X]}$$

TABLE I
Comparison of Activation Volumes for the Free Radical Polymerization of Some Vinyl Monomers under High Pressure[a]

Monomer	Maximum pressure (MPa)	Temp (°C)	Solvent	Initiator	$\Delta V^{\ddagger}_{pol}$ (cm^3/mol)	Reference
Acrylonitrile	200	50	DNF	AIBN	−22	10
Methyl methacrylate	200	40	—	DPO	−19	13
Styrene	100	50	—	AIBN	−20.2	14
Acrylonitrile	19	40	Deserated water	$K_2S_2O_8$–$Na_2S_2O_4$	−15.7	This study
Acrylonitrile	18	40	DMF	$K_2S_2O_8$–$Na_2S_2O_4$	−14.8	This study
Acrylonitrile	18	40	DMSO	$K_2S_2O_8$–$Na_2S_2O_4$	−17.3	

[a] Abbreviations: AIBN = 2,2′-azobisisobutyronitrile, BPO = benzoyl peroxide, DMF = dimethyl formamide, DMSO = dimethyl sulfoxide.
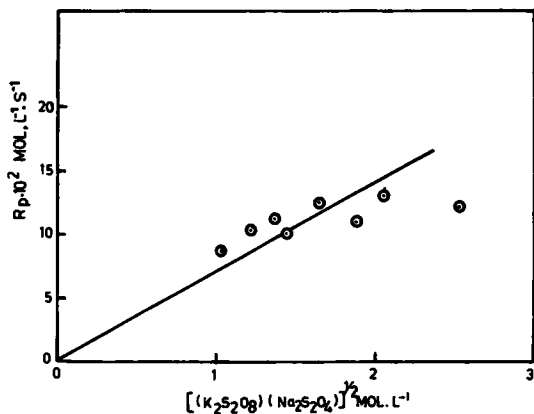
Fig. 4. Dependence of rate on the initiator and activator concentration. [AN] = 0.61M; time = 1 h, temp = 40°C; pressure = 12.4 × 10⁶ Pa.
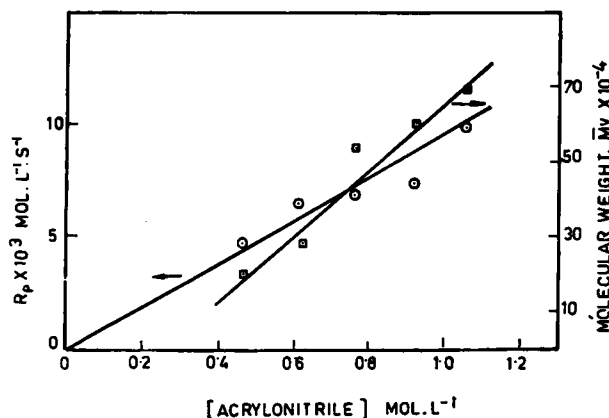

Fig. 5. Dependence of rate and molecular weight on monomer concentration. Polymerization conditions [K₂S₂O₈] = 1.8 × 10⁻³M; [Na₂SₛO₂] = 0.57 × 10⁻³M; pressure = 12.4 × 10⁶ Pa; time = 2 h; temp = 40°C.

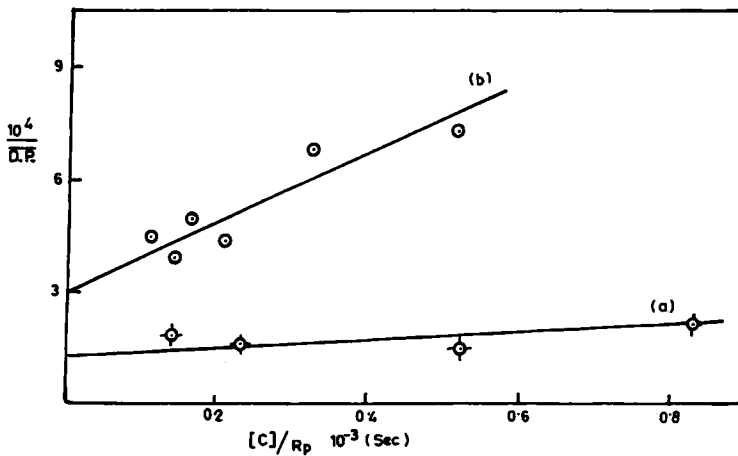Fig. 6. Evaluation of km/kp from a plot of $\dfrac{1}{DP}$ vs [c]/RP.

TABLE II
Rate and $\overline{DP}$ of Aqueous Polymerization of Acrylonitrile[a] at Atmospheric Pressure and at High Pressure (12.40 × 10⁶ Pa)

[K₂S₂O₈] [Na₂S₂O₄] × 10⁶ (mol² L⁻²)	R_p × 10³ (mol lit⁻¹ s⁻¹)	[C]/R_p × 10⁻³ (s)	10⁴/$\overline{DP}$	k_m/k_p
	1.06	7.54	0.140	1.78
1a 1.3 × 10⁻⁴	4.23	8.09	0.522	1.25
	6.36	7.65	0.831	2.24
	1.90	8.21	0.231	1.59
	1.06	8.62	0.112	4.43
	2.12	10.12	0.209	4.31
1b 3 × 10⁻⁴	4.23	12.99	0.325	6.81
	6.36	12.34	0.515	7.31
	1.48	10.16	0.145	3.93
	1.90	11.20	0.166	4.97

[a] Polymerization conducted at 40°C with [AN] = 0.61M; (1a) runs conducted at atmospheric pressure; (1b) at high pressure (12.4 × 10⁶Pa).

has been used where [M] and [X] are the concentrations of acrylonitrile and radicals and k_m, k_p, k_{td}, and k_{tc} are the usual rate constants. It has been tacitly assumed that transfer to solvent (H_2O) and to the redox catalyst moiety is absent. Denoting [C] as the product $[K_2S_2O_8][Na_2S_2O_4]$, the steady state condition gives

$$2fk_d[C] = 2(k_{td} + k_{tc})[X]^2$$

and putting[15] $x = k_{td}/k_{tc} + k_{td}$

$$\frac{1}{\overline{DP}} = \frac{fk_d[C](1+x)}{k_p} + \frac{k_m}{k_p}$$

Figure 6 shows te plots of $1/\overline{DP}$ against $[C]/R_p$ under high pressure $= 12 \times 16^6$ Pa and normal pressure conditions. k_m/k_p value (Table II) is evidently higher under high pressure conditions which fully endorses our contention.

CONCLUSION

The aqueous polymerization of acrylonitrile monomer by the redox system $K_2S_2O_8-Na_2S_2O_4$ shows an initial enhancement in conversion, rate, and molecular weights with increasing pressure to a certain value of the latter, beyond which these parameters decrease with a still further increase of pressure.

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