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A Comparative Study of Aqueous Polymerization of Acrylonitrile in Presence of Oxygen and Nitrogen Atmosphere

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Heterogeneous polymerization of acrylonitrile (AN) initiated by potassium bromate-thiomalic acid (TMA) redox couple was studied in the atmosphere of oxygen and nitrogen in aqueous medium. The square root dependence of rate on initiator, activator and monomer concentration was observed. The activation energy and the number average molecular weight were higher in oxygen atmosphere.

INTRODUCTION

It is known that molecular oxygen exert inhibiting as well as catalytic effects on free radical initiated polymerization[1,2]. About 70% of the commerical output of acrylonitrile is polymerized to give polymers for textile fibres. It would be worthwhile to study the behaviour of oxygen in aqueous polymerization of acrylonitrile by potassium bromate-thiomalic acid redox couple.

EXPERIMENTAL

A calculated quantity of TMA solution, monomer (AN), and double-distilled water were taken in a reaction vessel, maintained at 35 ± 2°C. The reaction was initiated by adding initiator ($KBrO_3$) solution in the vessel. At desired intervals of time, the reaction was stopped by adding required volume of alkaline hydroquinone (1.5% w/v). At last, aqueous solution of $MgSO_4$ was added to break the colloidal phase. The polymer thus obtained was filtered through sintered crusible and washed with warm water. It was dried overnight at 40–50°C.

The polymerization under nitrogen atmosphere was carried out by bubbling dry nitrogen gas at the rate of 1–2 bubbles per second for 30 minutes, before adding a calculated quantity of initiator.

RESULTS AND DISCUSSION

We have already reported the mechanism of the polymer formation in oxygen atmosphere[5], where oxygen helped to produce larger number of the initiating species ($\dot{S}R$).

Initiator Dependence

The effect of initiator concentration ($KBrO_3$) on the rate of polymerization is summarized in Table 1. It was observed that the rate of polymerization was retarded in the presence of oxygen. The reason behind this activity of oxygen is the biradical character of oxygen. Oxygen reacts with most of the free radicals initially produced in the system to form peroxide radicals, resulting in slow reaction of these radicals with monomer molecules.

The order of reaction was determined from double logarithmic plot and observed as 0.604 and 0.5 at low range of initiator concentration under oxygen and nitrogen atmosphere respectively.

It was noteworthy that at higher initiator concentration, a transition in reaction order took place from 0.604 to 0.11 and from 0.5 to 0.078 under oxygen and nitrogen atmosphere respectively. This means that the rate of reaction became independent of higher initiator concentration and the rate of radical generation become almost independent of potassium bromate at higher initiator concentration.

Thus it may be concluded that the dependence of reaction rate on initiator concentration and the progress of polymerization were unaffected due to change in atmosphere from oxygen to nitrogen.

Activator Dependence

It was shown that oxygen retarded the rate of the polymerization (Table 2). It was found that the initial rate and maximum conversion both increases upto 10.0×10^{-3} of TMA and decreases with further rise in activator concentration[4]. The decrease in the rate at high activator concentration was due to the suppression in the rate of generation of initiating species because of increase in H^+ concentration.

The order of reaction was determined from double logarithmatic plot and obtained as 0.46 and 0.43 in the increasing region of TMA in oxygen and nitrogen atmosphere respectively. Thus the rate of polymerization remained the same in both the atmospheres.

Monomer Dependence

It was found that the initial rate of polymerization and maximum conversion increases with the monomer concentration. The monomer exponents as evaluated in oxygen and nitrogen atmosphere were found as 0.625 and 0.60 respectively, also monomer exponent depends largely upon the solubility of the monomer in water as compared to that of its polymer in it and also on the mode and rate of initiation.

Temperature Dependence

The effect of temperature is summarized in Table 4. It is found that the rate increases at 45°C. It appears that at higher temperature, not all

TABLE 1

VARIATION OF THE RATE OF POLYMERIZATION WITH INITIATOR ($KBrO_3$)CONCENTRATIONS UNDER OXYGEN AND NITROGEN ATMOSPHERE AT 35 ± 0.2°C.

Exp. no.	$[KBrO_3]\times10^3M$	Atmosphere of Expt.	Extent of polymerization with time (min.), %							Initiator exponent 'θ'
			2	4	6	8	10	15	20	
1.	3.0	O_2	5.24	8.98	12.52	15.22	17.45	21.25	26.57	in oxygen $\theta_1 = 0.604$ $\theta_2 = 0.11$
		N_2	6.02	11.90	15.52	18.23	21.0	25.81	27.77	
2.	4.5	O_2	6.68	12.62	16.72	19.77	25.04	31.58	33.25	
		N_2	7.22	13.52	17.52	20.29	24.04	27.56	33.40	
3.	6.0	O_2	7.88	15.52	20.35	25.75	30.63	35.62	33.72	in nitrogen $\theta_1 = 0.5$ $\theta_2 = 0.078$
		N_2	8.59	16.59	21.49	25.04	28.51	31.46	37.76	
4.	7.5	O_2	8.34	16.26	23.56	27.58	32.52	—	44.35	
		N_2	9.63	17.98	22.88	27.56	31.20	34.89	44.86	
5.	15.0	O_2	9.60	18.72	25.12	31.87	35.87	40.42	46.75	
		N_2	10.63	19.77	26.65	31.03	37.61	42.23	52.13	
6.	35.0	O_2	10.20	20.21	27.86	38.92	41.88	48.85	52.72	
	30.0	N_2	11.20	21.52	27.64	32.50	42.38	48.82	56.53	

Recipe : $[TMA] = 10.0\times10^{-3}M$; $[AN, O_2] = 75.39\times10^{-2}M$;

$[AN, N_2] = 75.65\times10^{-2}M$

TABLE 2

VARIATION OF RATE OF POLYMERIZATION WITH VARYING ACTIVATOR (TMA) CONCENTRATIONS UNDER OXYGEN AND NITROGEN ATMOSPHERE AT 35 ± 0.2°C

Exp. no.	Atmosphere of Expt.	[TMA]×10^3 M	Extent of polymerization with time (min.), %							Activator exponent 'θ'
			2	4	6	8	10	15	20	
1.	O_2	2.5	4.28	8.18	11.06	13.65	14.72	21.06	24.02	
	N_2		4.93	9.52	13.05	14.5	16.32	18.58	21.33	
2.	O_2	5.0	5.96	11.66	13.60	20.95	21.90	30.06	36.08	$\theta = 0.46$ in oxygen
	N_2		6.65	12.22	16.05	18.02	18.52	23.58	26.88	
3.	O_2	10.0	7.88	15.52	20.35	25.75	30.69	35.62	39.72	
	N_2		8.59	15.92	21.55	25.05	28.62	31.48	38.05	$\theta = 0.43$ in nitrogen
4.	O_2	20.0	5.70	10.33	13.50	18.58	20.62	28.06	29.92	
	N_2		6.79	13.28	16.72	18.52	21.88	26.78	31.05	
5.	O_2	30.0	4.76	6.78	8.74	10.12	11.70	12.05	12.25	
	N_2		4.95	8.62	9.50	10.85	11.33	12.02	12.25	
6.	O_2	40.0	2.60	4.22	5.65	6.05	7.02	7.06	7.09	
	N_2		4.83	5.72	7.20	7.13	7.56	7.65	7.85	

Recipe: $[KBrO_3] = 6.0\times10^{-3}M$; $[AN, O_2] = 75.39\times10^{-2}M$;

$[AN, N_2] = 75.65\times10^{-2}M$

TABLE 3

VARIATION OF THE RATE OF POLYMERIZATION WITH VARYING MONOMER (AN) CONCENTRATIONS UNDER OXYGEN AND NITROGEN ATMOSPHERE AT 35 ± 0.2°C

Exp. No.	Atmosphere	$[AN] \times 10^2$ M	Extent of polymerization with time (min.), %							monomer exponent 'θ'
			2	4	6	8	10	15	20	
1.	O_2	—	—	—	—	—	—	—	—	
	N_2	15.14	3.48	5.85	7.52	8.02	11.52	12.52	13.88	$\theta = 0.625$ (in oxygen)
2.	O_2	30.16	4.08	6.85	8.96	11.87	12.56	14.02	15.02	
	N_2	30.28	5.82	8.08	10.22	12.28	13.52	15.98	17.82	
3.	O_2	45.23	5.30	10.88	13.55	18.02	20.75	22.52	24.45	
	N_2	45.39	7.32	11.26	12.01	15.06	18.08	20.24	22.42	
4.	O_2	60.31	6.34	13.02	17.28	19.22	23.62	29.52	32.05	
	N_2	60.53	8.56	14.63	19.24	21.20	23.23	25.74	30.10	
5.	O_2	75.39	7.88	15.02	20.12	25.75	30.63	—	34.72	
	N_2	75.65	8.59	16.59	21.49	24.04	27.81	31.48	37.76	$\theta = 0.60$ (in nitrogen)
6.	O_2	90.46	8.28	16.61	23.28	27.58	31.55	—	44.91	
	N_2	90.78	10.65	20.98	25.48	28.52	31.53	35.53	40.39	

Recipe: $[KBrO_3] = 6.10^{-3}$ M; $[TMA] = 10.0 \times 10^{-3}$ M

TABLE 4

ROLE OF TEMPERATURE ON AQUEOUS POLYMERIZATION OF 'AN' UNDER OXYGEN AND NITROGEN ATMOSPHERE

Exp. no.	Temperature (°C)	Atmosphere	Extent of polymerization with time (min.), %							activation energy 'E_a'
			2	4	6	8	10	15	20	
1.	—	O_2	—	—	—	—	—	—	—	$E_a = 9.587$ Kcals deg^{-1} $mole^{-1}$ in oxygen
	25.7	N_2	6.71	9.72	14.81	17.45	23.63	29.03	34.32	
2.	30.0	O_2	5.44	10.62	16.05	20.12	23.22	25.52	27.32	
	30.2	N_2	7.52	12.95	18.43	22.04	26.79	32.53	36.25	
3.	35.0	O_2	7.88	15.58	20.28	25.75	30.63	35.62	39.72	$E_a = 4.57$ Kcals deg^{-1} $mole^{-5}$ in nitrogen
	35.1	N_2	8.59	16.59	21.49	25.04	28.52	33.52	37.50	
4.	40.0	O_2	9.48	17.32	21.86	29.90	33.17	42.86	48.07	
	40.4	N_2	10.34	19.60	23.52	26.89	27.72	31.75	33.95	
5.	45.0	O_2	11.90	20.26	26.38	25.97	30.62	38.08	41.45	
	45.5	N_2	10.84	17.28	21.44	23.50	25.75	26.68	31.90	

Recipe : $= [KBrO_3] = 6.0 \times 10^{-3}$ M : $[TMA] = 10.0 \times 10^{-3}$ M; $[AN, O_2] = 75.29 \times 10^{-2}$ M
and $[AN, N_2] = 75.65 \times 10^{-2}$ M

TABLE 5

CALCULATION OF NUMBER AVERAGE MOLECULAR WEIGHT '$\overline{M}$' OF POLYACRYLONITRILE AT 30°C UNDER OXYGEN AND NITROGEN ATMOSPHERE

Exp. no.	Atmosphere	'C' (gms/100 ml)	t_1	t_2	$\eta_r = t_1/t_2$	$\eta_{sp} = \eta_r - 1$	$\eta_{red} = \eta_{sp}/C$	$\eta_i = \underset{C-O}{\eta_{cPC}}$	'$\overline{M}_n$'
1.	O_2	1.1488	59	15	3.39	2.93	2.55		3.715×10^4 (in oxygen)
	N_2	1.2038	36	15	2.4	1.4	1.1629		
2.	O_2	0.5744	28.7	15	1.91	0.91	1.59	0.65	
	N_2	0.6019	22	15	1.466	0.466	0.7742		2.5×10^4 (in nitrogen)
3.	O_2	0.2872	20	15	1.33	0.33	1.149	0.49	
	N_2	0.3010	18	15	1.20	0.20	0.664		

Reactions conditions: $[KBrO_3] = 6.0\times10^{-3}$ M $[TMA] = 10.0\times10^{-3}$

$[AN, O_2] = 75.39\times10^{-2}$ M, $[AN, N_2] = 75.65\times10^{-2}$ M

Solvent used = dimethyl formamide

where 't_1' and 't_2' are afflux times for polymer solution and solvent, η_r, η_{sp}, η_{red} are respectively relative, specific and reduced viscosity and 'C' is the concentration of polymer solution in gms/100 ml.

radicals initially produced in the system reacted with oxygen and thus its retarding effect was overpowered by the chain initiation step.

The fall in the maximum conversion after a period of initiation was observed which was probably due to a good amount of initiating species being destroyed at higher temperature by side reactions, such as dimerization $(R\dot{S} + \dot{S}R \rightarrow RS-SR)$.

The activation energy (E_a) was obtained as 9.587 and 4.57 kcals deg^{-1} $mole^{-1}$ in oxygen and nitrogen atmosphere respectively These values are well near to those reported for other redox initiated polymerization in aqueous system[6].

Determination of number average molecular weight ($\overline{M}_n$)

The number average molecular weights were determined viscometrically at 30°C in N,N-dimethyl formamide (Table 5). The relationship used is as follows.

$$\eta_i = 3.335 \times 10^{-4} \overline{M}_n 0.72$$

where η_i = intrinsic viscosity.

It is observed that the number average molecular weight of polymers found in oxygen ($\overline{M}_n = 3.715 \times 10^4$) was higher than that obtained in nitrogen atmosphere ($\overline{M}_n = 2.5 \times 10^4$).

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