Effect of Oxygen on Intensity Exponents of Radiation-Induced Polymerization Rates

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Synopsis

Gamma radiation-induced graft polymerization to natural rubber in benzene solution (solution grafting), graft polymerization to natural rubber latex (emulsion grafting), and emulsion polymerization of three vinyl monomers—styrene (St), methyl methacrylate (MMA) and acrylonitrile (AN), were carried out under air atmosphere to compare the radiation intensity exponent of each polymerization rate under air atmosphere with that under nitrogen atmosphere or under vacuum. The intensity exponents of the solution grafting both under air atmosphere and under exclusion of air were found to be numerals near one half. This indicates prevailing normal radical mechanism. However, the intensity exponents of the emulsion grafting under air atmosphere were found to be 0.94, 1.00, and 0.82 for St, MMA, and AN, respectively, and those of the emulsion polymerization under air atmosphere, 0.16 and 0.15 for St and MMA, respectively, although those of both emulsion grafting and emulsion polymerization under exclusion of air were found to be numerals near to one half except for that of emulsion polymerization of AN. For emulsion grafting, the initiating species is considered to be trunk polymer radical but the terminating species is assumed to be the radical(s) produced in the water phase in the presence of oxygen. For emulsion polymerization, both initiating and terminating species are assumed to be the radical(s) produced in the water phase in the presence of oxygen.

INTRODUCTION

In the course of our study on gamma radiation-induced graft polymerization of acrylonitrile to natural rubber latex, we found an anomaly that under an atmosphere of air the polymerization rate is nearly proportional to the first power of the radiation intensity. (Hereafter, throughout this paper, the term "polymerization" means gamma radiation-induced polymerization and "intensity" means radiation intensity, unless otherwise stated.) To elucidate this anomaly which must result from the presence of oxygen in the specific polymerization system, dependence of polymerization rate on radiation intensity was studied both in the presence and absence of air by using the following three polymerizing systems: (1) graft polymerization to natural rubber in benzene solution, (2) graft polymerization to polymer emulsion (natural rubber latex), and (3) emulsion polymerization of vinyl monomers—styrene (St), methyl methacrylate (MMA), and acrylonitrile

(AN). Another anomaly, that the intensity exponent in emulsion polymerization approaches zero, was observed when the polymerization was carried out under an atmosphere of air. Although inhibiting and retarding effects of oxygen have been well known, the above anomalies suggest that oxygen in air may exert an influence not only on the initiation and propagation but also on the termination steps. These anomalies were satisfactorily explained by assuming various initiating and terminating species in each system.

EXPERIMENTAL

Irradiation was carried out at various constant dose rates with a ^{60}Co source of 8,000 curies at room temperature, unless otherwise described. Dosimetry measurements were made by a Fricke dosimeter ($G_{Fe^{3+}}$ = 15.6). The vinyl monomers, St, MMA, and AN, were purified by the usual method and then distilled.

Procedure for Solution Grafting

Masticated natural rubber (pale crepe) was dissolved in benzene, precipitated with methanol, dried, and again dissolved in benzene and precipitated with acetone. The sample solution was prepared from the purified rubber, a monomer, and benzene to contain 0.147 isoprene unit/l. and 1.5 moles/l. of the monomer. For the irradiation under air atmosphere, 25 ml of the prepared sample solution was placed in each test tube, which was tightly sealed after the charge. The volume of the air above each charge was 2 ml. For irradiation under exclusion of air, 25 ml of the sample was degassed by three freezing-thawing cycles in each test tube, which was then fused by using a vacuum line. Several reaction tubes were placed at the points of the same dose rate. After the given irradiation time periods, the mixture in each tube was thrown into excess methanol.

The precipitates were dried and weighed. Within a range of the conversions obtained in the present study (See Figures 3, 4, and 5), we confirmed by the procedures mentioned below that little or no homopolymerization occurred. Polymers obtained were stirred in an excess of a good solvent for a homopolymer (dimethyl formamide at 60°C for 7 hr for poly-AN and acetone at room temperature for 7 hr for poly-MMA). The solvent gave no polymer after mixing with excess methanol, and the weights of the raw polymer before and after extraction coincided, except for the following case. When MMA was converted to 5.0×10^{-1} mole/kg (see Figure 4), 34.2% of the starting monomer and 6.5% of the homopolymer (poly-MMA) was observed. Another procedure was applied to St-grafted raw polymer, which was dissolved in a 1:2 mixture of benzene and methyl ethyl ketone. After precipitation of polymer from this solution with a minimum amount of methanol, the filtrate did not give any polymer with excess methanol.

Procedure for Grafting to Latex

Commercial, concentrated (60%) natural rubber latex stabilized with ammonia was diluted with water to contain 20% solid substances. Commercial nonionic-type surface-active agent (block copolymer of ethylene oxide and propylene oxide from Sanyo Kasei Co.) was used as emulsifier. The sample was prepared to contain 200 g/l. (2.94 isoprene units/l.) of rubber substances, 43 g/l. of the emulsifier, and 4.3 moles/l. of a monomer. For irradiation under air atmosphere, 25 ml of the sample was placed in each tube and treated quite similarly as for the solution grafting. For the irradiation under nitrogen atmosphere, a mixture of the emulsifier and the monomer was degassed by the usual method in a vessel connected with a side arm to the main reaction tube indicated in Figure 1. After the latex was bubbled sufficiently with nitrogen, the mixture of emulsifier and monomer was added to the latex. Irradiation and treatment of the reaction mixture were quite similar to those for solution grafting.

Procedure for Emulsion Polymerization

The sample was prepared to contain 2.4 moles/l. of a monomer and 1.3 g/l. of chemical-grade sodium laurate in water. To obtain reproducible
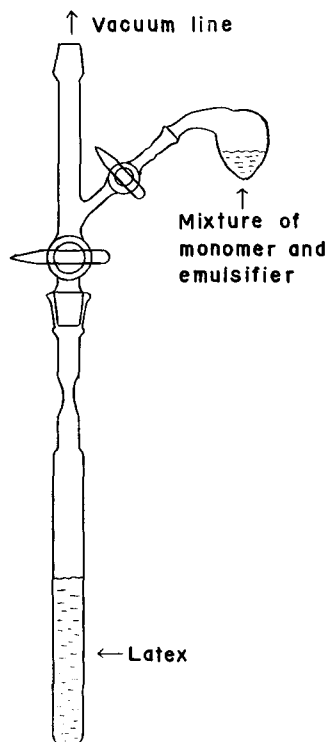

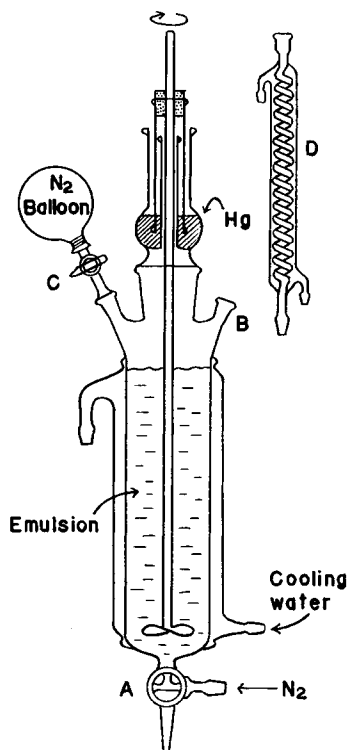Fig. 1. Sample tube for emulsion grafting under exclusion of air.

Fig. 2. Apparatus for emulsion polymerization under air atmosphere.

results, the following procedure was found convenient for irradiation in the presence of air. The atmosphere of the reaction vessel, the volume of which was 170 ml (Figure 2), was replaced with nitrogen by streaming it into the vessel through cock A and letting it escape through the mercury seal of a stirrer. During the replacing, cock C was closed and neck B was sealed with a rubber stopper. Afterwards, 150 ml of the sample which dissolved atmospheric air was injected through the rubber stoper of neck B, by closing A. Irradiation was carried out at constant temperature (18° ± 1°C) while water cooling and under stirring. If the atmosphere of the vessel above the charge was filled with air, stirring made the diffusion of air into the water phase rapid. The resulted long induction period made the determination of the conversion rate time consuming. Therefore, the irradiation was carried out in the presence of only oxygen dissolved in the water phase. For irradiation under nitrogen atmosphere, condenser D, which had a stopcock and was chilled with Dry Ice, was attached to B. After the atmosphere of the vessel was replaced with nitrogen similarly as for the previous case but by letting it escape through D, 150 ml of the sample was poured into the vessel through D. Thereafter, nitrogen was bubbled into the sample through A and let to flow out of the vessel through D. The completion of the replacement was checked by an oxygen analyzer,

Beckman-Toshiba 777. After the given irradiation time period, about 10 ml of the irradiated sample was taken through A. A thick rubber balloon of about 900 ml, filled with nitrogen, equilibrated the decline in the pressure that resulted from the sampling by keeping the stopcock C open during the irradiation. Accurately weighed sample was treated similarly as for the emulsion grafting. In the present case, however, molecular weights of the polymers precipitated and reprecipitated twice from benzene solution with methanol were determined viscometrically at 25° ± 0.01°C using the following equation:

$$[\eta] = KM^a.$$

For polystyrene[1] in benzene, $K = 2.7 \times 10^{-4}$, $a = 0.66$; for poly(methylmethacrylate)[2] in benzene, $K = 0.94 \times 10^{-4}$, $a = 0.76$; and for polyacrylonitrile[3] in dimethylformamide, $K = 3.92 \times 10^{-4}$, $a = 0.75$.

RESULTS AND DISCUSSION

Solution Grafting

Figures 3, 4, and 5 indicate radiation-induced polymerizations of St, MMA, and AN in the presence of natural rubber in benzene and under air atmosphere. As seen in the figures, each conversion was determined at each given irradiation time. As mentioned in the experimental section, the term conversion may be synonymous with grafting for further discussion. Figures 3, 4, and 5 indicate that at an earlier stage of polymerization oxygen acted as an inhibitor[4-6] and was consumed as the irradiation proceeded, and that the lower the dose rate the longer the induction period. It seems rather peculiar that some extent of retardation may be observed only in the
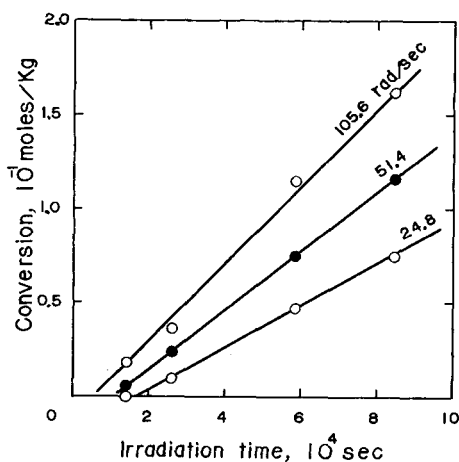

Fig. 3. Conversion rates of St at various dose rates in the presence of rubber in benzene under air atmosphere.
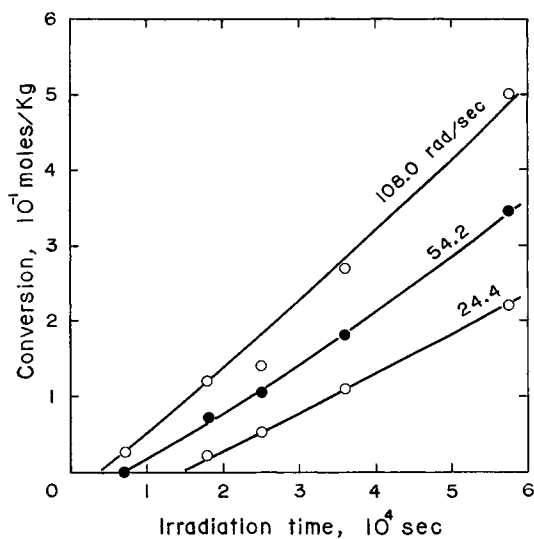
Fig. 4. Conversion rates of MMA at various dose rates in the presence of rubber in benzene under air atmosphere.
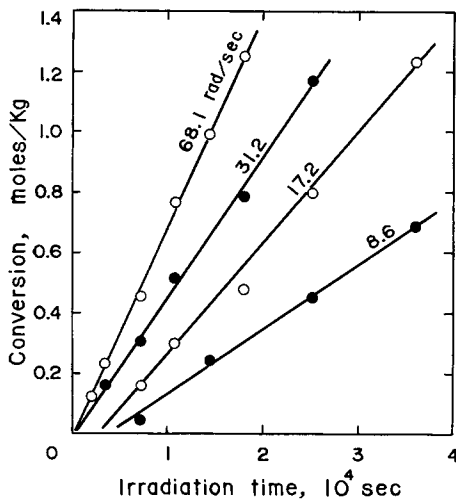

Fig. 5. Conversion rates of AN at various dose rates in the presence of rubber in benzene under air atmosphere.

case of MMA polymerization, shown in Figure 4.   It is not the object of the present paper to interpret this peculiarity.   The conversion rates of St, MMA, and AN under air atmosphere in Figures 3, 4, and 5 were calculated and plotted in Figure 6, together with the corresponding rates under vacuum, which were determined similarly to those under air atmosphere.   The conversion-versus-time curves under vacuum indicated little or no induc-
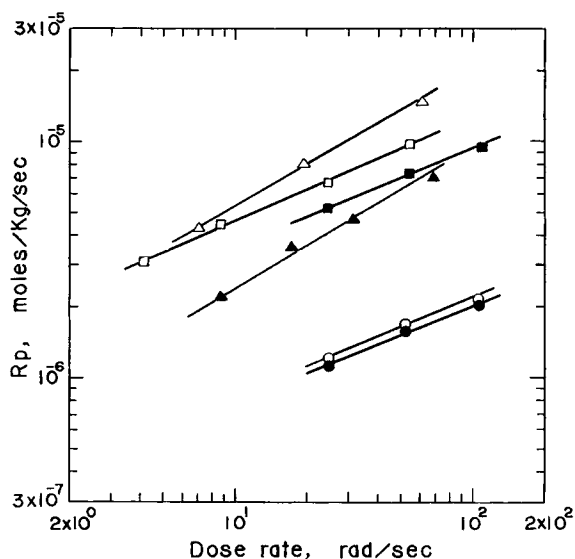
Fig. 6. Dose rate dependence of conversion rates of vinyl monomers in the presence of rubber in benzene both under vacuum (open symbols) and air atmosphere (closed symbols): (O, ●) St; (□, ■) MMA; (△, ▲) AN.

tion period and no retardation at all. The values of intensity exponent under these conditions are tabulated in Table I together with the values of other polymerizing systems.

Figure 6 indicates that each monomer has two lines parallel to each other, depending on whether polymerization is run under air atmosphere or under vacuum. These results suggest that termination by two growing polymer radicals, which is prevalent in normal radical mechanisms, is applicable to both cases. The small deviation from a half-power law (0.56 for AN, 0.44 for MMA, and 0.42 for St) was reported also in other papers[7] which stated intensity exponents in radiation-induced bulk and solution polymerizations.

TABLE I

Intensity Exponents[a] of Conversion Rates for Monomers St, MMA, and AN in Different Polymerizing Systems

	Solution grating			Emulsion grafting			Emulsion polymerization		
	St	MMA	AN	St	MMA	AN	St	MMA	AN
Under air atmosphere	0.42	0.44	0.56	0.94	1.00	0.82	0.16	0.15	0.87
Under vacuum or nitrogen atmosphere	0.42	0.44	0.56	0.50	0.50	0.60	0.35	0.43	0.87

[a] The value of a in $R_p \propto I^a$, where R_p is conversion rate and I is radiation intensity or dose rate.

Figure 6, however, indicates that the conversion rate of each monomer under air atmosphere is smaller than the corresponding rate under vacuum. This result must arise from the presence of oxygen during irradiation. Oxygen dissolved in the solution is consumed as the polymerization proceeds. The consumed amount of oxygen is supplied to some extent by the air in the space above the charge. However, the consumption rate is considered far greater than the diffusion rate. Therefore, the concentration of oxygen in the solution becomes low to such an extent that the consumption rate equilibrates the diffusion rate. Then the polymerization proceeds under a constant oxygen concentration, the value of which depends on the dose rate. This leads to a constant polymerization rate, each of which is indicated in Figures 3, 4, and 5, respectively, and is lower than the corresponding rate under vacuum, as indicated in Figure 6.

Emulsion Grafting

Radiation-induced polymerizations of St, MMA, and AN emulsified together with natural rubber latex under air atmosphere were carried out. Conversions at various dose rates were plotted versus irradiation times in Figures 7, 8, and 9. In each figure, the lower the dose rate the longer the induction period.

Figure 8, as compared with Figures 7 and 9, shows the comparatively long induction period and subsequent higher conversion rate characteristic for MMA polymerization. The corresponding polymerizations under nitrogen atmosphere were also carried out. In these cases little or no induction was observed, and conversion-versus-irradiation time plots fall on a straight line passing through the origin. Conversion rates calculated for each monomer both under air and nitrogen atmospheres were plotted against dose rates in Figure 10, from which intensity exponents for each polymeri-
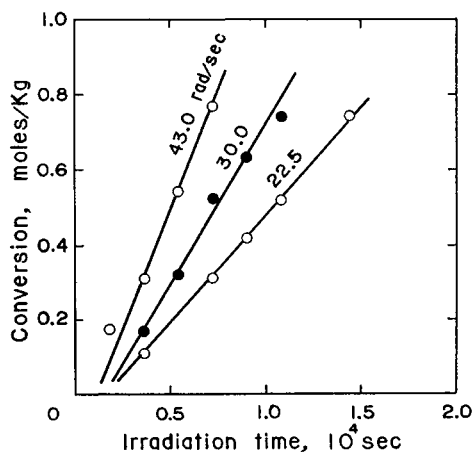

Fig. 7 Conversion rates of St at various dose rates in the presence of rubber latex under air atmosphere.
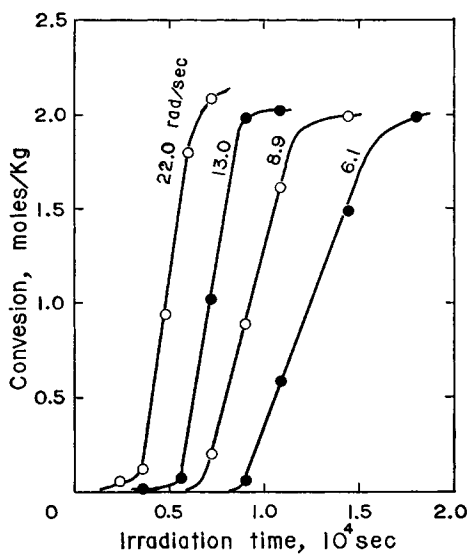
Fig. 8. Conversion rates of MMA at various dose rates in the presence of rubber latex under air atmosphere.
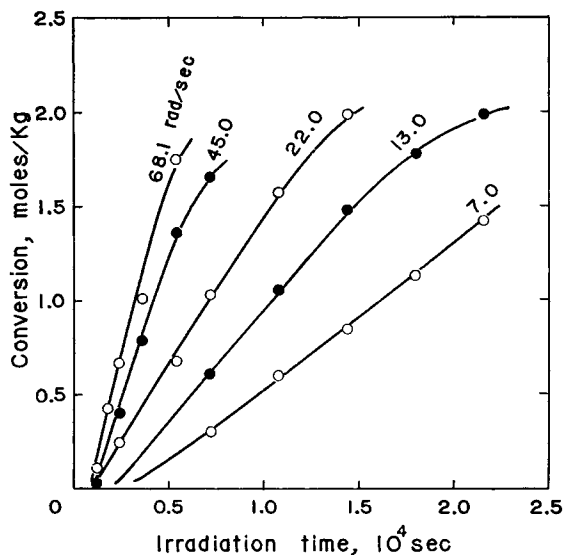

Fig. 9. Conversion rates of AN at various dose rates in the presence of rubber latex under air atmosphere.

zation were obtained and tabulated in Table I. The prominent distinction between these results and those of solution grafting is that the intensity exponent under air atmosphere is unity or a numeral smaller than but very near to unity, and that the exponent under nitrogen[8] is just one half or a numeral very near to one half.
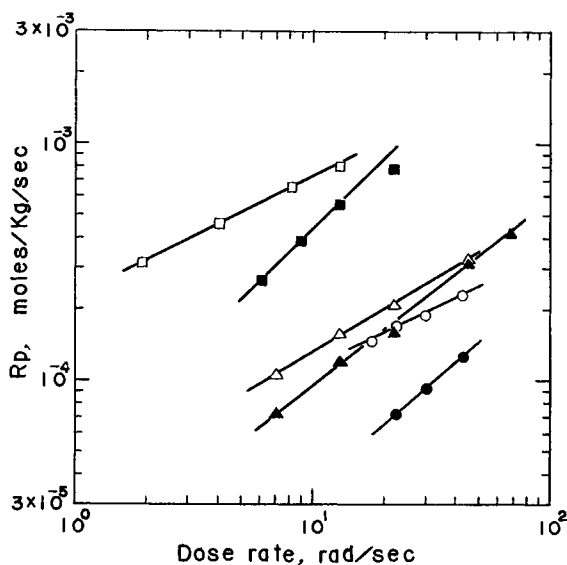
Fig. 10. Dose rate dependence of conversion rates of vinyl monomers in the presence of rubber latex both under exclusion of air (open symbols) and under air atmosphere (closed symbols): (○, ●) St; (□, ■) MMA; (△, ▲) AN.

The result that intensity exponent of the emulsion graft polymerization under air atmosphere is unity can be interpreted as follows. Monomer is distributed in the water phase as micelle and particles. In the particles the monomer may envelop rubber latex, and some monomers swell rubber according to its solubilizing power. During irradiation, the initiation species is considered to be trunk polymer radicals induced by direct action of gamma-irradiation or produced by dehydrogenation with the radicals that are formed. To explain the high value of the grafted/ungrafted ratio in gamma-induced emulsion grafting of MMA to natural rubber latex, Cooper et al.[8] presumed that any monomer radicals formed possess extra energy and can attack adjacent rubber molecules because of the high reactivity of the α-methylenic hydrogen of polyisoprene. The high grafted/-ungrafted ratio was observed also in the following experiments. AN emulsified together with rubber latexes under air atmosphere were polymerized by gamma irradiation at a dose rate of 8×10^4 rad/hr and the concentrations of rubber and monomer were quite the same as those in Figures 7, 8, and 9. At 20%, 30%, and 40% conversions (0.44, 0.63, and 0.84 mole/l. conversions, respectively), amounts of free polyacrylonitrile extracted from gross grafted polymers with dimethylformamide were found to be 1%, 5%, and 8.5%, respectively. Therefore, it can be said that at lower conversions even acrylonitrile, which is not compatible with rubber, can be graft-polymerized to rubber, and that graft polymerization is initiated by the trunk polymer radicals.

In the case of polymerization under air atmosphere, oxygen is consumed

predominantly in the particles where graft polymerization occurs. On the other hand, oxygen in the water phase, for example, reacts with hydrogen atoms produced by radiolysis of water.

$$H\cdot + O_2 \rightarrow HOO\cdot \tag{1}$$

This hydroperoxy radical, for example, as compared with hydrogen atom is far too stable to intrude into the polymer particle, and is satisfactorily active to abstract hydrogen from rubber molecule either directly or indirectly.[8] In Figure 10, conversion (or grafting)-versus-dose rate lines under air atmosphere make steeper slopes than those under nitrogen for all monomers. From this viewpoint, Figure 10 is in clear contrast to Figure 6, where both lines are parallel. The results in Figure 10 suggest that as dose rate increases, conversion (or grafting) rate under air may become greater than that under nitrogen, and that trunk polymer radicals capable of initiating graft polymerization are more abundant under air than under nitrogen.

Coming back to the problem of the effect of oxygen on the intensity exponent, we conclude that under nitrogen the normal radical process, i.e., initiation by trunk polymer radicals and termination by growing polymer radicals, leads to a half-power law. However, under air atmosphere the termination step should be different. Under air, the more abundant radicals may be formed. Since the diameter of natural rubber latex is well known in μ units, every intruded radical can initiate grafting in a single particle at an earlier stage. However, when several growing polymer radicals exist in the particle, intruded radicals can terminate or in some occasions initiate grafting. Thus initiation by a radical (trunk polymer radical) and termination by another radical (intruded radical) may lead to an intensity exponent of unity as indicated by kinetics.

Emulsion Polymerization

Figures 11, 12, and 13 show the conversions at various dose rates versus irradiation time for St, MMA, and AN, respectively. Here also, distinct induction period, fast conversion rate, and rapid decrease of the rate are peculiar to MMA (Fig. 12), similarly to MMA emulsion grafting (Fig. 8). Conversion rate-versus-dose rate lines both under air and nitrogen atmospheres are indicated in Figure 14 for each monomer. The values of intensity exponent under these conditions were tabulated also in Table I. In Figure 14, AN indicates an anomaly that both lines are parallel and show the same intensity exponent. Therefore, polymerization of only St and MMA will be discussed.

Similarly to ordinary catalyzed emulsion polymerization, the initiation can be considered to occur in micelles by the radicals produced in the water phase.[9] At an earlier stage of the polymerization, oxygen in the micelles or oxygen intruded into the micelles inhibits or retards the polymerization. However, when the micelles grow to particles, a similar situation to that for emulsion grafting holds in this case, although the diameter of the particle
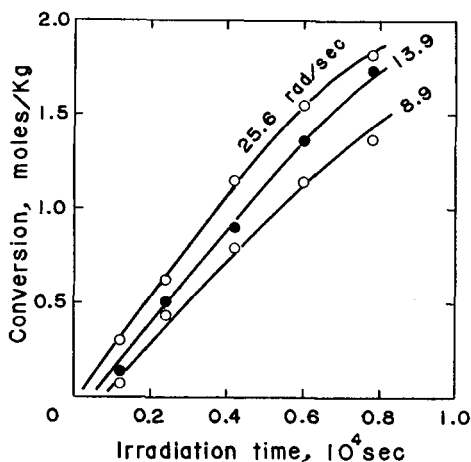
Fig. 11. Emulsion polymerization rates of St at various dose rates under air atmosphere.
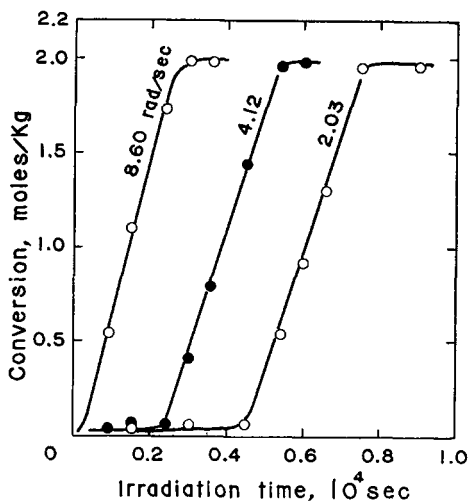

Fig. 12. Emulsion polymerization rates of MMA at various dose rates under air atmosphere.

is far smaller than that in emulsion grafting.   More radicals are produced in the water phase under air atmosphere than under nitrogen also in this case.   These radicals can intrude into the particles and terminate the polymerization.   Therefore, under air atmosphere, both initiating and terminating species are the same radicals produced in the water phase.   This leads to zero power in an ideal case.   However, deviations from ideality (0.16 for St, 0.15 for MMA) were observed in Table I, and may be attributed to some occurrence of termination by mutual collision of growing polymer radicals.   Under vacuum, initiation occurs by the radicals produced in the water phase, but termination may occur by mutual collision of growing
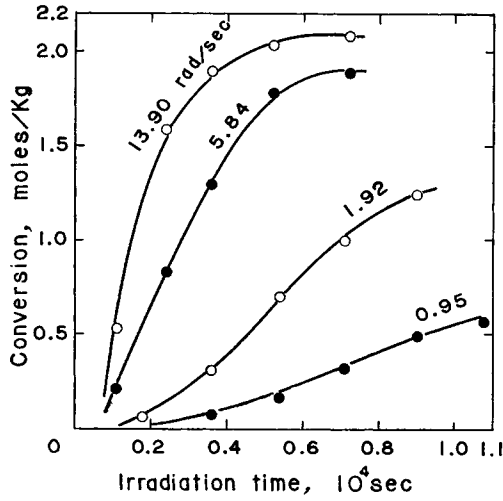
Fig. 13. Emulsion polymerization rates of AN at various dose rates under air atmosphere.
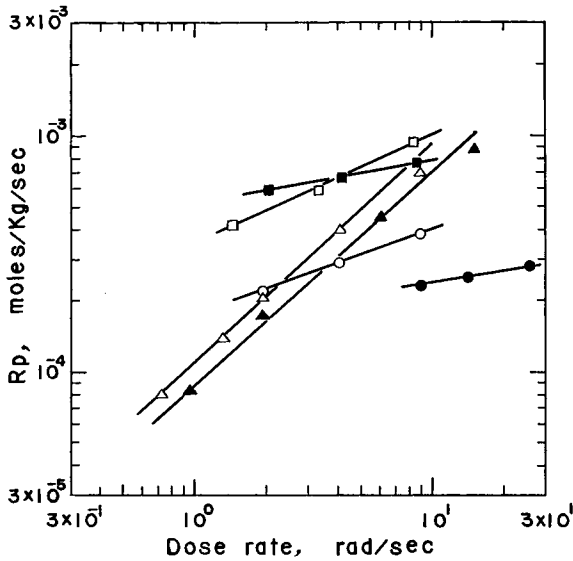

Fig. 14. Dose rate dependence of emulsion polymerization rates of vinyl monomers both under nitrogen (open symbols) and under air atmosphere (closed symbols). (O, ●) St; (□, ■) MMA; (△, ▲) AN.

polymer radicals. This leads to a half-power law but deviation from ideality (0.35 for St, 0.43 for MMA) may result from some occurrence of termination by the radicals produced in the water phase.[10,11]

If the above assumption that emulsion polymerization under air atmosphere is terminated by radicals produced in the water phase were true,

TABLE II

Viscosity-Average Molecular Weights ($\bar{M}_v$) of Polymers by Radiation-Induced Emulsion
Polymerization Under Air and Nitrogen Atmospheres

	Dose rate, rad/sec	Irradiation time, 10^3 sec	Conversion, %	$\bar{M}_v \times 10^{-6}$
PST				
air atm.	25.6	1.2	16.0	2.3
	13.9	1.2	7.1	2.5
	8.9	2.4	22.8	2.9
nitrogen atm.	8.9	1.8	29.1	3.4
	4.0	1.8	11.2	4.5
	1.9	1.8	23.8	13.0
PMMA				
air atm.	26.4	2.4	11.3	0.47
	14.7	4.8	52.3	0.52
	9.2	6.0	34.0	0.48
nitrogen atm.	26.4	1.2	39.0	0.72
	14.7	1.8	35.7	0.99
	3.3	2.4	24.0	1.12
PAN				
air atm.	37.0	1.2	58.3	0.45
	13.9	1.2	25.4	0.49
	5.8	1.2	10.7	0.45
nitrogen atm.	8.9	1.8	45.5	0.50
	4.0	1.8	29.6	0.63
	1.9	1.8	15.5	0.72

molecular weights of each polymer polymerized under air atmosphere would
be smaller than those of the corresponding polymers polymerized under
nitrogen atmosphere.   Table II indicates that this is true and that molecu-
lar weights of each polymer polymerized under air atmosphere are not so
different from each other, in spite of the different dose rates.   The latter

TABLE III

Initiating and Terminating Species Ideally Assumed for The Various
Radiation-Induced Polymerizing Systems[a]

	Emulsion grafting		Solution grafting		Emulsion polymerization	
	i.s.	t.s.	i.s.	t.s.	i.s.	t.s.
Under air	TPR	RPWP	TPR	GPR	RPWP	RPWP
	$R_p \propto I^1$		$R_p \propto I^{1/2}$		$R_p \propto I^0$	
Under nitrogen (or vacuum)	TPR	GPR	TPR	GPR	RPWP	GPR
	$R_p \propto I^{1/2}$		$R_p \propto I^{1/2}$		$R_p \propto I^{1/2}$	

[a] i.s. = Initiating species; t.s. = terminating species; TPR = trunk polymer radical;
GPR = growing polymer radical; RPWP = radicals produced in the water phase;
R_p = conversion rate as in Table I.

result corresponds to an intensity exponent of value very near to zero under these conditions.

In contrast, molecular weights of each polymer (except AN) polymerized under nitrogen atmosphere increase as the dose rate decreases. A short summary of this paper is tabulated in Table III, where the ideally assumed initiating and terminating species in each polymerizing system under air and nitrogen atmospheres (or vacuum) are indicated. It seems interesting to compare each value of the intensity exponent cited in Table I with the mechanisms for the ideal cases indicated in Table III. However, attention should be called to the fact that Table III cites only intensity exponents of polymerization rates and not the absolute values of the rates.

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