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γ-Radiation-Initiated Polymerization of Acrylonitrile in Aqueous Solution and in Emulsion

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ABSTRACT

The γ-radiation-initiated polymerization of acrylonitrile (AN) at 25°C has been studied, both in aqueous solution and in emulsion, at dose rates between 70 and 175 krad/hr. The effect of added emulsifier, sodium lauryl sulfate (SLS), on reaction rates, R_p, and on polymer molecular weight, M_n, has been investigated. G (monomer polymerized) values ranged from 7,500 in aqueous solution to 20,000 in bulk to 45,000 in emulsion, all based on the total energy absorbed. In the aqueous solution polymerization, where R_p is approximately first order in initial monomer concentration over the range $0.15 \leq [AN]_0 \leq 1.06$ moles/liter, addition of SLS increases R_p but does not influence the order of the reaction with respect to $[AN]_0$. In the emulsion system at 70 krad/hr

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and at a phase volume ratio AN/H_2O of 1/2, (PR = 1/2), R_p varies as $[SLS]^{0.1}$ over the concentration range $0.01 \leq [SLS] \leq 2.5\%$ wt/vol of aqueous phase. At the same PR value, and at 80 krad/hr, M_n of the polymer (measured by viscometry in dimethylformamide solution) is effectively independent of [SLS] in the range of $0.01 \leq [SLS] \leq 10\%$ wt/vol of aqueous phase. Initial R_p values are either independent of PR in the range $1/3 \leq PR \leq 1/1$ or exhibit an insensitive and unsystematic dependence thereon. Based on measurements at 70 and at 175 krad/hr, the intensity exponent of R_p at PR = 1/2 is approximately 0.4.

INTRODUCTION

When acrylonitrile (AN) is polymerized by a free radical mechanism in a nonsolvent for the polymer, such as the monomer itself or water, the polymer (PAN) precipitates out at very low percent conversions. This phase separation results both in the trapping or occlusion of free radicals within the essentially unswollen polymer, and in the formation of a polymer-liquid interface. The radical occlusion phenomenon was elucidated in the course of well-known investigations by Bamford and Jenkins and co-workers [1-9], who have estimated that in the typical case between 1 and 10% of the total number of radicals generated become occluded in the polymer matrix [9]. The real importance of this occlusion effect in the observed polymerization kinetics, however, is still under debate. Thus in a recent publication [10], Marquardt and Mehnert provide evidence that the initial stages of AN polymerization can be accounted for by steady-state kinetics as shown by the square-root dependence of initial reaction rate on initiator concentration. On the other hand, the later reaction rate does show strong deviations from a square-root dependence. This has recently been confirmed in the case of the γ-radiation-initiated bulk polymerization of AN, where Wada [11] and co-workers have found a 0.9 value for the dose-rate exponent of the polymerization rate. Certain workers [12], moreover, consider that the trapped radicals are insignificant, and postulate a steady-state process in solution and on the PAN particle surface. The fact that the particle surface does play an important role has been conclusively demonstrated by several workers who have reported that, in the case of the heterogeneous polymerization of AN in aqueous media, the reaction rate is diminished (in some cases to zero) when agglomeration of the particles is induced by stirring or centrifugation [9, 13]. No such fall in rate is found in systems containing a surface-active agent capable of stabilizing the particles against agglomeration [13].

The object of the present work was to investigate the emulsion polymerization of AN under γ-irradiation at high dose rates. Although the aqueous phase polymerization of AN in the presence of surfactants has been studied, little published work on the radiation-initiated reaction exists. In addition, very few published data are available on real emulsion systems involving AN as a separate monomer phase. The conversion curve published by Ley and co-workers [14] on the γ-radiation-initiated polymerization of acrylonitrile at a monomer phase ratio of 1:5 (AN:H_2O) exhibits strong deviations from typical emulsion polymerization behavior.

EXPERIMENTAL

Irradiation Facilities

Most of the polymerizations were carried out at dose rates of 70 and 175 krad/hr in a "swimming-pool" source consisting of an array of encapsulated ^{60}Co rods submerged in 3 m of shielding water. Dose rates could be varied by changing the number of radioactive rods in the array. The molecular weight determinations were done on polymer prepared in a γ-cell source at a dose rate of 80 krad/hr. Polymerization temperature was 25°C in all cases. The polymerization test ampules were irradiated in the enclosed Ferris wheel set-up described previously [15]. Agitation of the emulsion and good temperature control were ensured by pumping thermostatted water through the nozzle on the inside of the cannister lid and on to the vanes of the wheel. This gave end-over-end sample agitation at a rate of about 20 rpm, and guaranteed uniformity of radiation dose to all samples in a given run, despite any local variation in dose rate caused by the discrete nature of the array-type source. Fricke dosimetry (assuming $G_{Fe^{3+}} = 15.6$) with oxygenated solutions was used to determine the dose rates.

Materials

Acrylonitrile (AN), supplied by Eastman Kodak, was prepared for use by drying over calcium chloride, fractionating at atmospheric pressure and, as the final stage, by trap to trap distillation and degassing on the vacuum line. The monomer was stored under vacuum in a reservoir at -196°C.

Sodium lauryl sulfate (SLS) of U.S.P. grade was in general used as supplied by the Fisher Scientific Company without further purification. In some cases, however, a simple recrystallization from hot ethanol was carried out. No change in rates was observed after this treatment.

The water used for the preparation of the emulsions and the solutions of monomer was once distilled in a Barnstead distillation unit.

Procedure

Polymerization Kinetics

The polymerizations were carried out under vacuum in medium-wall Pyrex glass ampules, 3/4 in. o.d. and 6 in. long from the base to the constriction provided for flame sealing. This constriction was surmounted by a standard ground-glass conical joint (24/40) for connection to the vacuum system. A leak-proof seal was ensured by using Apiezon grease (H or N).

For the emulsion runs, the ampules were filled with the required volume of freshly prepared SLS solution and then very carefully degassed by the freeze-pump-thaw technique to a residual air pressure of approximately 10^{-5} Torr. Particular caution had to be exercised during the freezing operation, experience having shown that rapid freezing caused the ampules to shatter. The monomers were distilled into the cooled, degassed ampules (at liquid nitrogen temperature) from a graduated vessel at 20°C incorporated in the vacuum line. After a final pumping cycle the ampules were removed from the line by flame-sealing and were then stored in an ice-box.

Those ampules for the "solution" polymerization study were prepared by filling with freshly made up solutions of monomer in water or in dilute SLS solution with subsequent degassing and sealing as described above. In this case, care was taken to shield the ampules from sunlight during the thawing process.

The runs done with bulk acrylonitrile and with monomer containing 2% H_2O were carried out in similar fashion.

In all cases, conversions were determined gravimetrically either by pumping off excess monomer or, in those runs where a stable latex was formed, the polymer was isolated by coagulation in methanol followed by filtration, washing, and drying in vacuo to constant weight. Some conversions were measured using a total solids technique with addition of hydroquinone as short-stop.

Molecular Weight Determinations

For the molecular weight measurements on PAN prepared in the emulsion system, emulsions were made up at $AN/H_2O = 1/2$ vol/vol and irradiated under pure nitrogen at 0.08 Mrad/hr at an initial temperature of 25°C. As the reaction vessels could not be thermostatted in this case, the temperature increased by about 5°C before the polymerization was interrupted. The percent conversion was approximately 10% in each case. The PAN was filtered, washed thoroughly with distilled water and acetone, and dried overnight at 50°C in vacuo.

Solutions for viscometry were made up in distilled dimethylformamide, and measurements were carried out in an Ubbelohde dilution viscometer at 25°C equipped with calcium chloride tubes to prevent the DMF from absorbing atmospheric moisture. Solvent flow time was 111 sec. No kinetic energy correction was applied, and the viscosities were assumed to be independent of shear rate. The Cleland-Stockmayer relationship [16], as verified by Onyon [17], was used to compute M_n: $[\eta] = 3.92 \times 10^{-4} M_n^{0.75}$.

RESULTS AND DISCUSSION

Aqueous Solution Polymerization

The effect of SLS at a concentration below the critical micelle concentration (0.065 mole/liter) on the polymerization of AN in aqueous solution was studied over an initial concentration range of $0.15 \leq [M]_0 \leq 1.06$ moles/liter.

In the absence of soap the polymer precipitated from solution to form a flocculent deposit which at higher conversions agglomerated and gave an unswollen powder-like layer on the surface of the ampule. The results of these emulsifier-free runs are given graphically in Fig. 1. It can be seen that all of the curves present an acceleration period followed by a region of constant rate which, in those runs that were taken to a high conversion, continues up to about 40% removal of monomer. This apparent lack of dependence of rate on monomer concentration has been noted elsewhere [18, 19] and may be due to the activity of the polymer precipitated vis-à-vis the surface component of the reaction.

The reaction rate for the linear part of the conversion curve has been plotted as a function of initial monomer concentration in Fig. 2, lower line. There is some scatter on the log-log plot, but it would appear that an approximately first-order dependence is involved.

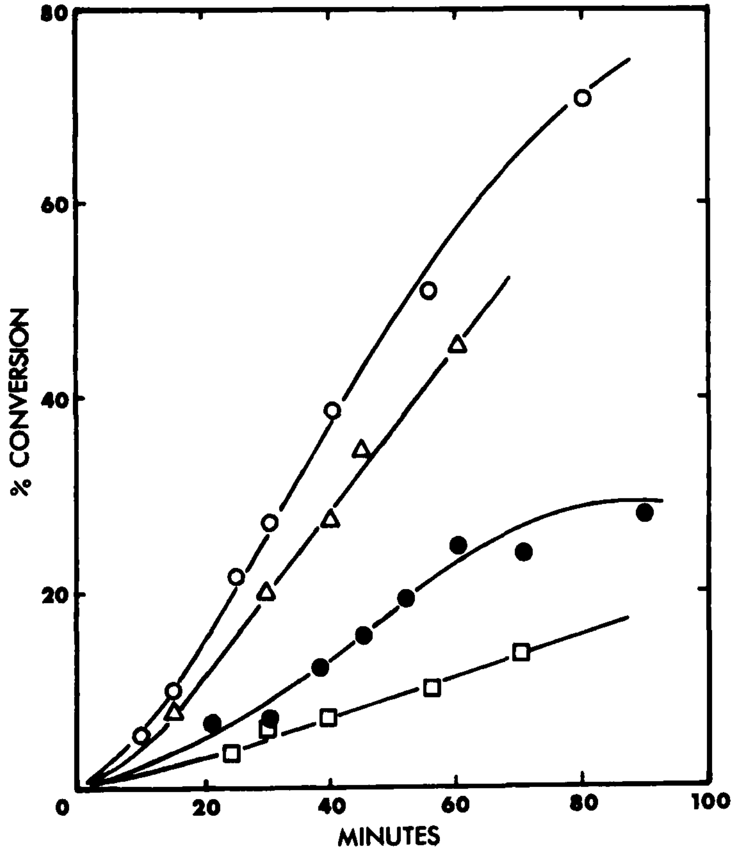

FIG. 1. Polymerization of acrylonitrile in aqueous solution in the absence of sodium lauryl sulfate. Dose rate, 0.07 Mrad/hr. $[M]_0$ = 0.15 (□), 0.30 (●), (△), and 1.06 (○) moles/liter.

This is in agreement with the results of Thomas and co-workers [20] and of Bero [21], both of whom used persulfate catalyst initiation.

The effect on the reaction rate of the addition of 0.21% wt/vol SLS is seen in Fig. 3. The general aspect of the conversion curves remain the same whereas the reaction rates have increased by a factor of approximately 4 in all cases. The SLS stabilizes the polymer particles formed and, as a result, the reaction mixture at low conversions

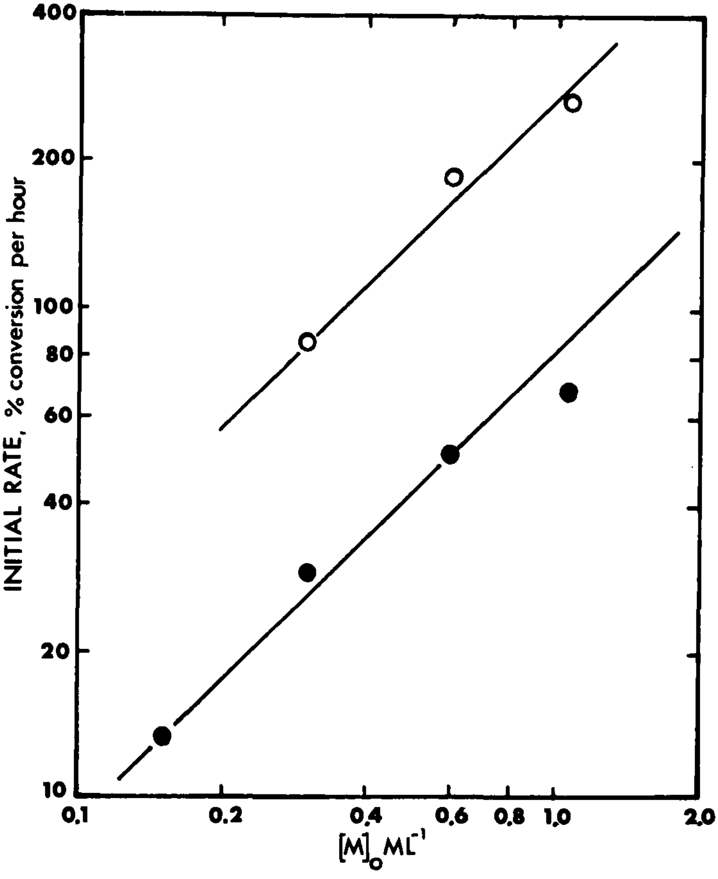

FIG. 2. Dependence of linear rate on the intial monomer concentration in the absence of SLS (•) and in the presence of 0.21% SLS (○).

appears as an opalescent latex which becomes progressively more milky as the reaction proceeds. It should be noted, however, that at the lowest [AN] studied, viz., 0.302 mole/liter, there was an apparent solubilization of the polymer by the soap. In this case the reaction mixture after irradiation remained without opalescence up to about 50% conversion, corresponding to [PAN] aqueous of around

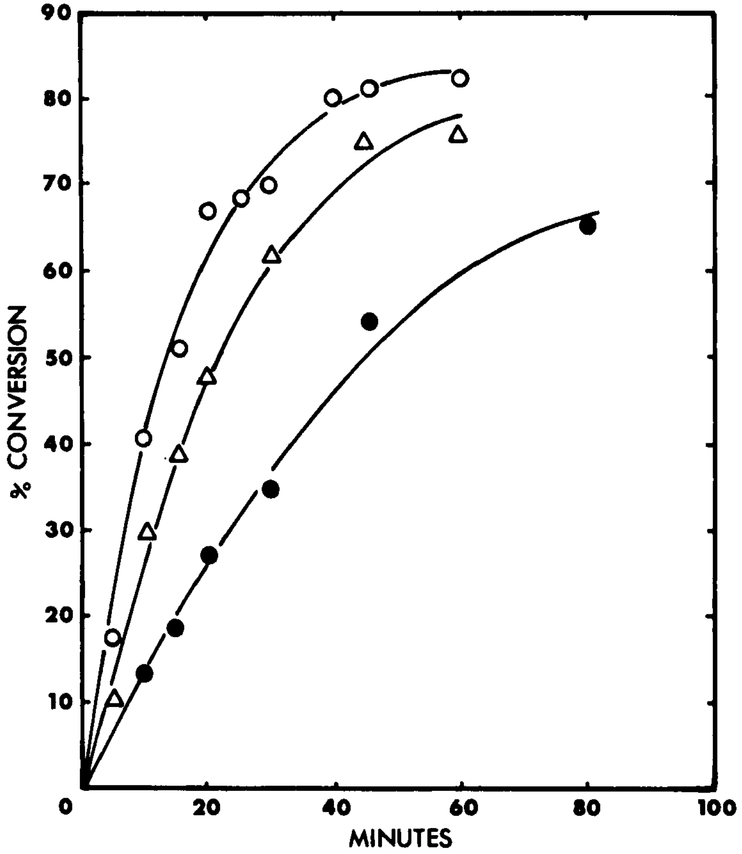

FIG. 3. Polymerization of acrylonitrile in aqueous solution in the presence of 0.21% wt/vol sodium lauryl sulfate. Dose rate, 0.07 Mrad/hr. $[M]_0 = 0.3$ (●), 0.60 (△), and 1.06 (○) moles/liter.

8 g/liter. This is a very interesting observation reminiscent of the vinyl acetate emulsion system [22].

The slopes of the linear parts of the curves have been plotted against initial monomer concentration in Fig. 2, upper line. It would once again appear that the reaction rate is approximately first order in monomer concentration. The absence of any significant change in reaction order with respect to monomer when SLS is added to the system is surprising, for, according to the mechanism proposed by Dainton [23], the adsorption of monomer on the polymer particles is a critical factor. The adsorption behavior should in principle be influenced by the emulsifier. The G (monomer) values ranged from 11,500 in solution to 20,000 in bulk, both calculated on the total energy absorbed.

Emulsion Polymerization

The foregoing results and discussion have dealt with the polymerization of AN in dilute solutions and not with what may be called the emulsion polymerization of this monomer. By emulsion polymerization we mean the polymerization of a system consisting of emulsified monomer droplets, monomer solubilized in swollen soap micelles, and a monomer saturated aqueous phase containing molecularly dissolved soap. The preceding section has been concerned with this last component of the system.

Kinetics

The emulsion polymerization of AN was studied at 25°C. Most of the systematic work was done using a dose rate of 0.07 Mrad/hr and an AN/H_2O phase ratio of 1/2. The reaction was studied also at one higher intensity (0.175 Mrad/hr) and at phase ratios of 1/1 and 1/3. Particular attention was paid to the effect of varying soap concentration on the reaction rate.

Some typical conversion curves are presented in Fig. 4, where it may be noted that the general shape of the curves is the same as found in the aqueous solution polymerization of this monomer as discussed earlier. The slopes of the linear part of the conversion curves obtained at the higher dose rate have been plotted vs soap concentration in Fig. 5.

The following comments may be made concerning Fig. 5. The data show good linearity in the range $0.01 \leq [\mathrm{SLS}] \leq 2.0\%$ – the reaction rate varies only as the 0.1 power of the soap concentration. No discontinuity is apparent in the region of the critical micelle concentration; this may be interpreted as implying that initiation within the micelles is negligible, and that "bulk" or aqueous phase initiation is dominant. It should be noted that in this system the term "emulsion polymerization" may be misleading. Even at low conversions apparently no latex is formed; the polymer is obtained as a milky slurry which is 100% filterable. This observation is difficult to explain as stable latices are seen to be formed during the aqueous solution polymerization of the monomer in the presence of low soap concentration. A possible explanation of this discrepancy may be that, in this

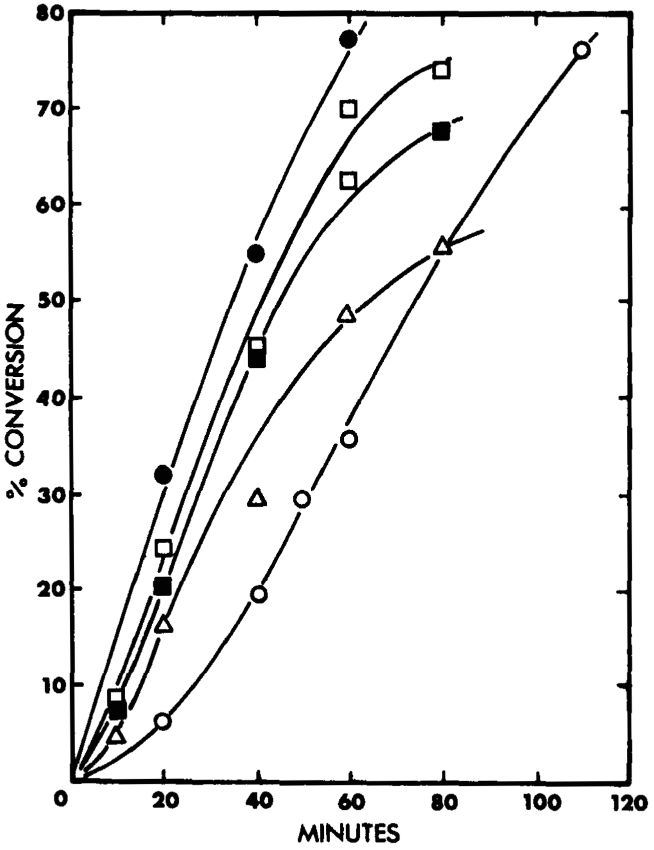

FIG. 4. Emulsion polymerization of acrylonitrile. Effect of varying soap concentration. T = 25°C, I = 0.07 Mrad/hr, monomer/water ratio = 1/2. SLS = 0.05% (○), 0.10% (△), 0.50% (■), 1.98% (●), and 11.34% (□).

system, we are in fact observing the bulk polymerization of the water-saturated monomer droplets. This reaction could easily be imagined to predominate in view of the sensitization of the monomer by traces of water shown in Fig. 6, and the higher monomer concentration involved (~14.7 as opposed to 1.4 moles/liter for the saturated aqueous phase). The bulk polymer formed could rapidly deplete the system of micellar soap and effectively sweep up any colloidal polymer latex particles.

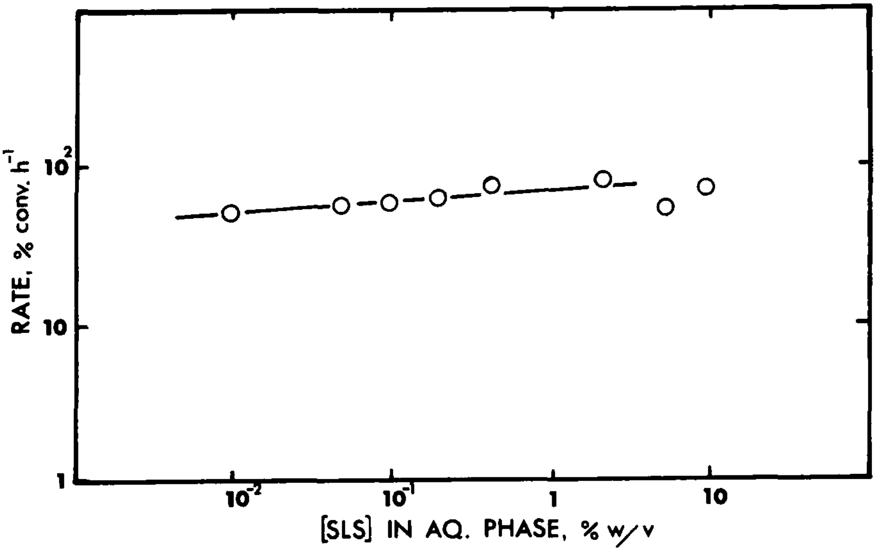

FIG. 5. Dependence of linear rate of polymerization of acrylonitrile in emulsion on sodium lauryl sulfate concentration.

In order to elucidate further the behavior of the bulk monomer in the emulsion system, some polymerization runs were carried out on AN solutions in dimethylformamide both in the presence and in the absence of SLS. The object here was to see whether molecularly dissolved SLS in the AN phase had any influence on polymerization rates of the monomer. From the experimental results which are given in Table 1, however, it is clear that SLS has only a negligible effect on AN polymerization rates.

It will be noted in Fig. 5 that some discontinuity occurs at [SLS] ~ 2%; the reaction rate falls somewhat between 2 and 11.3% soap. There is no immediately obvious explanation for this behavior, but in any case, the dependence of the rate on the emulsifier concentration is very low and the rates vary by a factor of only 1.6 over a range corresponding to more than a one-thousandfold change in the emulsifier concentration.

The occurrence of bulk polymerization within the monomer droplets was checked for by varying the AN/H_2O phase ratio in a series of runs carried out at 175 krad/hr. If no bulk polymerization occurs, the rate of polymerization expressed as weight of polymer formed

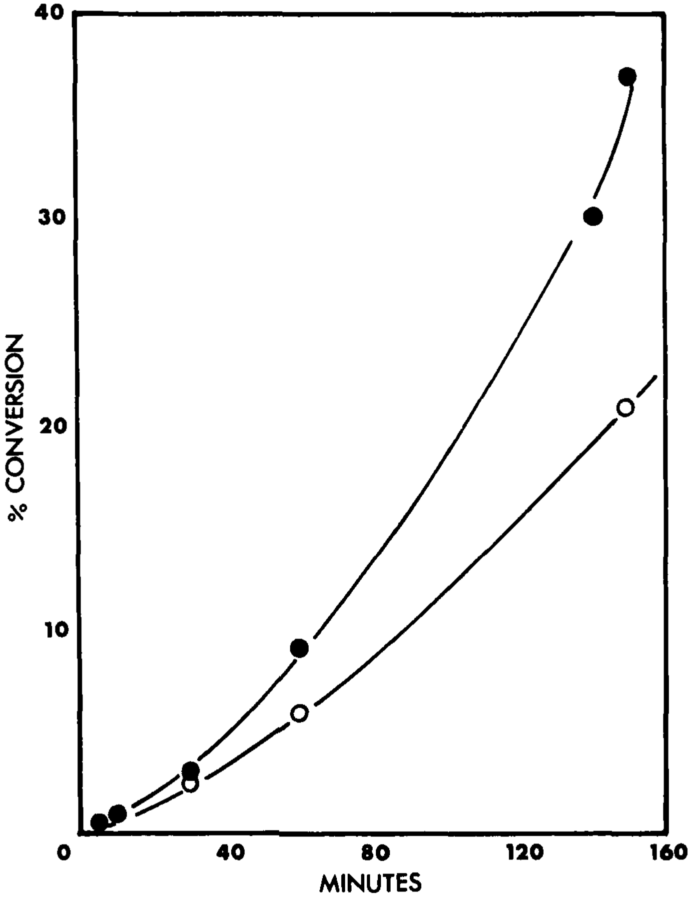

FIG. 6. Bulk polymerization of acrylonitrile. Influence of low water content. T = 25°C, I = 0.07 Mrad/hr. Dry (○) and 2% water (●).

per unit volume of aqueous phase per unit time should be independent of the phase ratio. Some results of this work are presented in Fig. 7, where the initial reaction time is seen to be independent of phase ratio. We should thus conclude that the bulk reaction within the droplets is negligible in this case. For the runs represented in Fig. 7, a constant SLS charge of 0.05 g/cc of monomer was used. This led to

TABLE 1. Effect of Dissolved SLS on Polymerization of AN in DMF Solution[a]

Dose (krad)	% Conversion	
	With SLS	Without SLS
210	15.4	13.7
670	39.3	38.3
820	45.0	43.9

[a] T = 25°C; dose rate = 175 krad/hr; AN/DMF = 1/4 vol/vol; SLS = 0.8% wt/vol.

some variation in the aqueous phase concentration of SLS which we neglect in view of the very low dependence of rate on this quantity (see Fig. 5). In other experiments carried out using SLS charges of 0.02 and 0.10 g/cc of AN, however, the results were less conclusive. No significant differences in rate per unit volume of water were found between runs at phase ratios of 1/2 and 1/3, but those runs involving emulsions of phase ratio 1/1 showed consistently higher rates of polymer formation per unit volume of water.

It is interesting to note that if we compare reaction rates at the two intensities studied for the system of phase ratio $AN/H_2O = 1/2$, we arrive at intensity exponent values of 0.38 and 0.41 for SLS = 1.0 and 2.5%, respectively (Table 2). These approximate values are close to those found by Thomas and co-workers [20] with a chemical redox system and not far from the value of 0.25 found by Collinson and Dainton [19] and by Izumi and co-workers [24, 25] for γ-rays and potassium persulfate, respectively.

Molecular Weights

Our investigation of the molecular weight dependence of PAN as formed in the emulsion system was limited to the elucidation of M_n variation with [SLS] over the range $0.01 \leq [SLS] \leq 10\%$ wt/vol of aqueous phase. The reaction conditions are described in the procedure section above.

The results of this series of runs are shown in Table 3. It can be seen that M_n is essentially independent of the emulsifier concentration. Over a one thousandfold range of concentration M_n remains effectively constant at about 6×10^5.

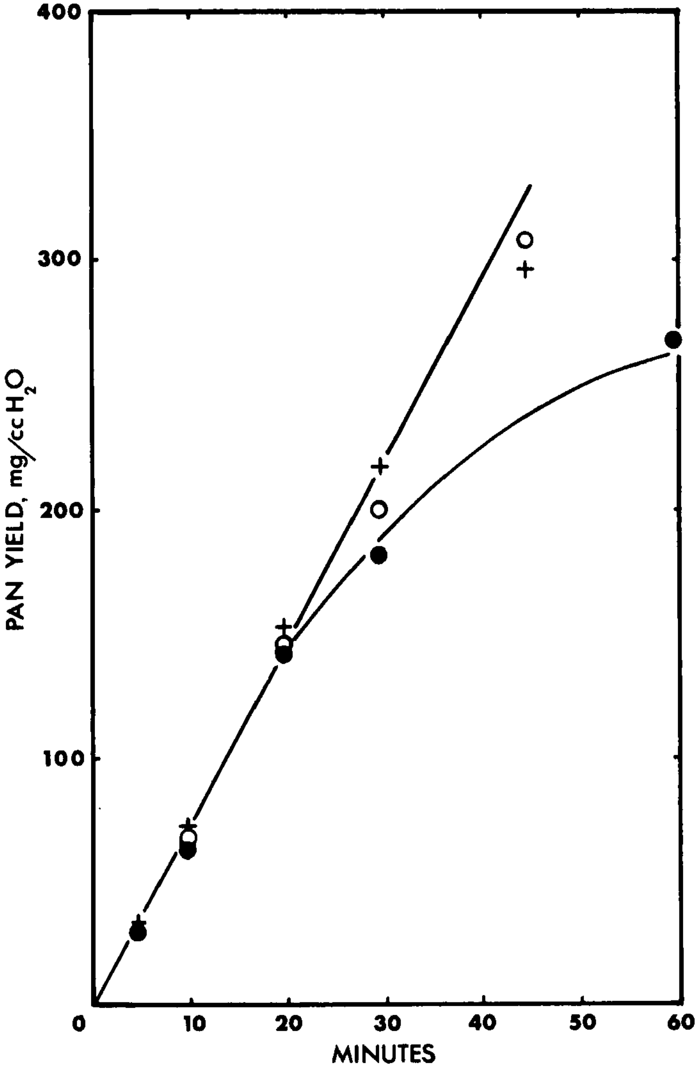

FIG. 7. Emulsion polymerization of acrylonitrile. Effect of varying phase ratio. T = 25°C, I = 0.175 Mrad/hr.

	$[SLS]_{aq}$	PR (AN/H_2O)
○	5%	1/1
+	2.5%	1/2
●	1.7%	1/3

TABLE 2. Intensity Exponent of the Reaction Rate

[SLS] (% wt/vol)	I (Mrad/hr)	Rate (% Conv/hr)	Exponent
1	0.175	106.5	0.38
	0.070	76.0	
2.5	0.175	121.8	0.41
	0.070	84.0	

TABLE 3. Variation of PAN M_n with $[SLS]_{aq}$

$[SLS]_{aq}$ (% wt/vol)	$[\eta]$ (ml/g $\times 10^{-2}$)	$M_n \times 10^{-5}$
0.01	10.7	8.3
0.05	7.0	4.8
0.10	8.6	6.3
0.50	6.8	4.5
1.0	10.7	8.3
5.0	9.5	7.1
10.0	8.9	6.8

Izumi, Kiuchi, and Watanabe [24] also have reported an almost complete independence of MW on [SLS] in their work on the ammonium persulfate-initiated polymerization of AN in 0.5 molar aq solution in the [SLS] range 0.005 to 0.1% wt/vol aqueous phase.

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