A Tracer Study of the Persulfate–Bisulfite-Catalyzed Polymerization of Acrylonitrile

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INTRODUCTION

The persulfate–bisulfite redox system has been used industrially to polymerize acrylonitrile, but little is known about the mechanism involved,[1] owing, perhaps, to the complexity of the reaction mechanisms in this redox system. The primary step in this redox system has been thought to be:[2]

$$S_2O_8^{--} + HSO_3^- \rightarrow SO_4^{--} + SO_4^{-}\cdot + HSO_3\cdot \quad (1)$$

Both the sulfate radical-ion and the bisulfite radical can initiate the polymerization, giving the polymer, sulfate and sulfonate endgroups, respectively. On the other hand, the following side reactions, in which the radicals are transferred and disappear have been postulated:[3]

$$SO_4^-\cdot + HSO_3^- \rightarrow SO_4^{--} + HSO_3\cdot \quad (2)$$
$$2HSO_3\cdot \rightarrow H_2S_2O_6 \quad (3)$$
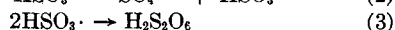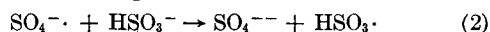
It has been difficult, however, to account for the kinetic data with this hypothetical reaction scheme.

The purpose of the work reported here was to determine the relative amounts and nature of the endgroups of polymer polymerized in this redox system, and to obtain some information about the polymerization initiation process.

The S^{35}-labeled initiators $K_2S_2O_8$ and $NaHSO_3$ were used to determine the small quantities of catalyst residues combined with the polymer. Similar radiochemical methods have been used satisfactorily in studies of other polymerization processes.[4,5] Owing to the insufficient reproducibility of acrylonitrile polymerization by this redox catalysis, the isotope dilution method was used to determine the relative amounts of the two end groups.

EXPERIMENTAL

Materials

The radioactive $NaHS^{35}O_3$ was obtained as an aqueous solution from the Radiochemical Centre of England; radioactive $K_2S^{35}{}_2O_8$ was synthesized from $H_2S^{35}O_4$ by electrolytic oxidation. These materials were diluted with inactive $NaHSO_3$ and $K_2S_2O_8$, respectively.

Monomeric acrylonitrile was purified by fractional distillation.

Polymerization Procedures

Polymerizations were performed at $25° \pm 0.1°C$. without agitation. The pH of every monomer-catalysts solution was maintained at 3 by adding small quantities of sulfuric acid. Either $NaHS^{35}O_3$–$K_2S_2O_8$ or $K_2S^{35}{}_2O_8$–$NaHSO_3$ was used as the redox catalysts system. Polymerization was stopped at small conversions ($<10\%$); polymers were purified by precipitation in water from solution in dimethylformamide. Radioactivity measurements showed that the polymer is completely purified by this treatment.

Acrylonitrile was also polymerized with $NaHS^{35}O_3$–Fe^{+3} at $25°C$. and with $K_2S^{35}{}_2O_8$ alone at $60°C$. These polymers were used for estimating the specific radioactivities of the sulfur of the labeled initiators in the isotope dilution analyses.

Radioactivity Measurements

The radioactivity of polymer in powder form was measured in infinite thickness.

The radioactive sulfur standards were prepared as follows. Known amounts of $K_2S^{35}{}_2O_8$ or $NaHS^{35}O_3$ were dissolved in water and the solution was absorbed into inactive polymer powder. The polymer powder was then mixed in several different proportions with another inactive polymer powder. The mixtures were dried and their radioactivities were measured in infinite thickness. The radioactivities of the standards were observed to vary in a fairly linear way with the calculated amounts of sulfur of the labeled initiator contained in the polymer. A comparison of the

radioactivity of a polymer with the radioactivities of the standards gives the amount of sulfur of the labeled initiators incorporated in the polymer.

Isotope Dilution Method

In this polymerization system, reproducibility was not always sufficient. Therefore, both types of end groups had to be determined on the same batch of polymer in order to obtain accurate data. The isotope dilution method was applied in order to determine the ratio of the amount of labeled-initiator sulfur residue to the amount of unlabeled sulfur residue.

Sulfur incorporated into the polymer was isolated by the use of tin(II)–strong phosphoric acid.[6] This reagent is a powerful reducing agent at high temperatures (200–300°C.), so that sulfate and sulfonate endgroups in the polymer are easily reduced to hydrogen sulfide when the polymer is heated with this reagent. In addition, the reagent becomes sulfur-free during the course of its preparation, as is essential for a reagent which is to be used in isotope dilution analysis. The hydrogen sulfide evolved was absorbed into a zinc acetate–acetic acid solution and then converted to methylene blue by addition of p-aminodimethylaniline and ferric chloride. The optical density D_i of the methylene blue was measured at 655 mμ. A

known quantity of the methylene blue was then allowed to adsorb onto a constant amount of active carbon, the radioactivity of which was measured (A_i). The specific radioactivity of the sulfur incorporated into the polymer is proportional to A_i/D_i. A similar experiment was performed with the polymer polymerized with NaHS^{35}O$_3$–Fe^{+3} or with K$_2$S$^{35}_2$O$_8$ alone, A_0 and D_0 being estimated. An estimate of the ratio P_i of the amount of labeled-initiator sulfur residue to the total amount of sulfur incorporated into the polymer is given by the following relationship:

$$P_i = (A_iD_0)/(A_0D_i)$$

The residual content of unlabeled initiator was calculated from the residual content of labeled initiator and its molar ratio P_i to the total initiator residues.

RESULTS

In one series of experiments (nos. 1–9) with NaHS^{35}O$_3$ at a concentration of 0.0040 mole/l., K$_2$S$_2$O$_8$ or monomer was used at various concentrations. The optical density D_0 of the methylene blue derived from the polymer polymerized with NaHS^{35}O$_3$–Fe^{+3} was 0.94 and its radioactivity A_0 was 1200 counts/min., A_0/D_0 being 1280. The results are shown in Table I. In the other

TABLE I
Polymerization with NaHS^{35}O$_3$–K$_2$S$_2$O$_8$

Expt. no.	AN, concn., mole/l.	NaHS^{35}O$_3$, concn., mole/l.	K$_2$S$_2$O$_8$, concn., mole/l.	[η], dl./g.	Radioactivity of polymer, counts/min.	Optical density D_i	Radioactivity A_i, counts/min.
1	0.50	0.00438	0.0115	1.59	3770	0.73	496
2	0.50	0.00438	0.00764	1.80	1156	0.17	119
3	0.50	0.00438	0.00382	2.26	1172	0.71	600
4	0.50	0.00438	0.00191	2.54	703	0.28	288
5	0.50	0.00438	0.00115	2.77	711	0.21	233
6	0.80	0.00438	0.00382	3.39	830	0.23	173
7	0.65	0.00438	0.00382	3.25	899	0.79	639
8	0.35	0.00438	0.00382	1.67	1974	1.15	1081
9	0.20	0.00438	0.00382	0.98	5820	0.41	420

TABLE II
Polymerization with K$_2$S$^{35}_2$O$_8$–NaHSO$_3$

Expt. no.	AN concn., mole/l.	K$_2$S$^{35}_2$O$_8$ concn., mole/l.	NaHSO$_3$ concn., mole/l.	[η], dl./g.	Radioactivity of polymer, counts/min.	Optical density D_i	Radioactivity A_i, counts/min.
10	0.50	0.00377	0.0158	1.11	237	0.87	33
11	0.50	0.00377	0.0079	1.79	225	0.79	46
12	0.50	0.00377	0.00395	2.40	194	0.40	38
13	0.50	0.00377	0.00158	2.79	164	0.40	42

series of experiments (nos. 10–13) with $K_2S^{35}_2O_8$ at a concentration of 0.0040 mole/l., $NaHSO_3$ was used at various concentrations and the concentration of monomer was maintained constant at 0.50 mole/l. In this case D_0 was 0.50 and A_0 was 125 counts/min., so that the calculated value of A_0/D_0 was 250. The results are shown in Table II. From Tables I and II the contents of sulfonate and sulfate endgroups were calculated, as shown in Table III.

TABLE III
Contents of Sulfate and Sulfonate Endgroups

Expt. no.	Sulfate endgroups		Sulfonate endgroups	
	Relative content	Content, mmole/g.	Relative content	Content, mmole/g.
1	0.47	0.048	0.53	0.055
2	0.44	0.0092	0.56	0.017
3	0.34	0.0060	0.66	0.017
4	0.22	0.0029	0.78	0.010
5	0.13	0.0015	0.87	0.010
6	0.42	0.0088	0.58	0.012
7	0.37	0.0077	0.63	0.013
8	0.27	0.0106	0.73	0.029
9	0.19	0.0198	0.81	0.084
10	0.15	0.016	0.85	0.089
11	0.23	0.015	0.77	0.050
12	0.38	0.013	0.62	0.022
13	0.42	0.011	0.58	0.015

Table III indicates that under every experimental condition sulfonate is the major endgroup, even if the concentration of $NaHSO_3$ is much less than that of $K_2S_2O_8$. It is also observed that the higher the concentration of $K_2S_2O_8$ the higher the proportion of sulfate endgroups, and the higher the concentration of $NaHSO_3$ the higher the proportion of sulfonate endgroups. Moreover, it is apparent that the proportion of sulfate endgroups increases with increase in the monomer concentration.

The relationship among proportional contents of the endgroups and the concentrations of initiators and monomer was examined in the experimental results, and the following empirical relationship was derived:

$$\frac{[\text{Sulfonate endgroups}]}{[\text{Sulfate endgroups}]} = 1 + 0.27\left\{\frac{[NaHSO_3]}{[AN][K_2S_2O_8]}\right\}^{1.5}$$

All the experimental data conform to this relationship, as is seen in Figure 1.
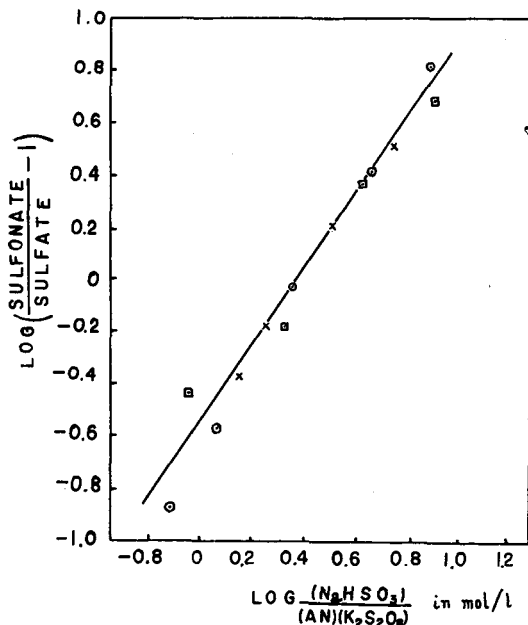

Fig. 1. Relationship between the ratio of sulfonate to sulfate end groups and the concentrations of initiators and monomer: (⊙) Expts. 1–5; (×) Expts. 6–9; (□) Expts. 10–13.

DISCUSSION

Radiochemical studies of redox polymerization have been performed for the polymerization of vinyl chloride[5] with $KClO_3$–$NaHSO_3$ and the polymerization of tetrafluoroethylene[2] with $K_2S_2O_8$–$NaHSO_3$. In the polymerization of vinyl chloride, sulfur and chlorine incorporated in the polymer were determined, and it was shown that increasing the catalyst concentration causes an increase in the amount of catalyst residue combined with PVC. In the polymerization of tetrafluoroethylene, sulfonate was the only endgroup observed; no sulfate endgroup was detected, owing to the rapid hydrolysis of the sulfate endgroup in this polymer.

In the present experiment both sulfate and sulfonate endgroups were observed; moreover, it was shown that the formation of each type of endgroup depends on the polymerization conditions.

If there were no reactions beside the primary reaction (1) in this redox system, half of the endgroups would be sulfate and half sulfonate. The observed relationship between the ratio of the two types of endgroups and the concentrations of catalysts and monomer indicates that some concurrent side reactions, such as reaction (2), do, in fact, compete with the polymerization initiation reaction. With increasing monomer concentration

the polymerization initiation reaction becomes prevalent over concurrent side reactions, so that the ratio of sulfonate to sulfate endgroups approaches one.

According to the side reaction (2) it is expected that the proportion of sulfonate endgroups increases with increasing concentration of bisulfite.

In order to account for the increase in the number of sulfate endgroups with increasing concentration of persulfate, the formation of an intermediate $(S_2O_8 \cdot HSO_3^{-3})$ in the primary reaction (1) is postulated:

$$S_2O_8^{--} + HSO_3^- \rightleftharpoons (S_2O_8 \cdot HSO_3^{-3})$$
$$\rightarrow SO_4^-\cdot + SO_4^{--} + HSO_3\cdot \quad (1')$$
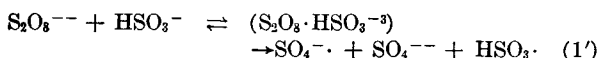
Owing to the equilibrium between the intermediate and the catalysts, the increase in the concentration of persulfate reduces the concentration of free bisulfite and accordingly reduces the formation of bisulfite radical by the side reaction (2).

In addition to the side reactions mentioned above, the following chain-transfer reaction should be considered:

$$M_n\cdot + HSO_3^- \rightarrow M_nH + SO_3^-\cdot \quad (4)$$

where $M_n\cdot$ represents a polymer radical. When the concentration of bisulfite is high, this side reaction becomes important and consequently causes the increase in the number of sulfonate endgroups and the reduction in the degree of polymerization.

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Synopsis

A tracer study has been made of the polymerization of acrylonitrile in an aqueous solution at 25°C with the use of radioactive $K_2S^{35}_2O_8$ and $NaHS^{35}O_3$ in a redox catalyst system. Persulfate and bisulfite give sulfate and sulfonate endgroups, respectively. The contents of these endgroups in the polymer were determined and the following empirical equation was derived:

$$\frac{[\text{Sulfonate endgroups}]}{[\text{Sulfate endgroups}]} = 1 + 0.27 \left\{ \frac{[\text{NaHSO}_3]}{[\text{AN}][\text{K}_2\text{S}_2\text{O}_8]} \right\}^{1.5}$$

Sulfonate is the major endgroup under every condition of polymerization. A tentative discussion of the polymerization initiation reaction in this redox system is given in order to account for the above experimental results.

Résumé

En utilisant des atomes marqués, on a étudié la polymérisation de l'acrylonitrile en solution aqueuse à 25°C, utilisant $K_2S^{35}_2O_8$ et $NaHS^{35}O_3$ radioactifs comme système catalytique rédox. Les persulfates et bisulfites donnent respectivement des groupes terminaux sulfates et sulfonates. La présence de ces groupes terminaux dans le polymère a été déterminée et l'équation empirique suivante en découle:

$$\frac{(\text{groupes terminaux sulfonate})}{(\text{groupes terminaux sulfate})} = 1 + 0{,}27 \left\{ \frac{[\text{NaHSO}_3]}{[\text{AN}][\text{K}_2\text{S}_2\text{O}_8]} \right\}^{1.5}$$

Les groupes sulfonates sont les groupes terminaux les plus importants dans n'importe quelle condition de polymérisation. Un essai d'interprétation est donné pour une réaction de polymérisation initiée par un système rédox, en accord avec les résultats expérimentaux obtenus ci-dessus.

Zusammenfassung

Eine Traceruntersuchung der Polymerisation von Acrylnitril in wässriger Lösung bei 25°C unter Verwendung von radioaktivem $K_2S^{35}_2O_8$ und $NaHS^{35}O_3$ in einem Redoxsystem wurde durchgeführt. Persulfat und Bisulfit liefern Sulfat- bzw. Sulfonatendgruppen. Der Gehalt des Polymeren an diesen Endgruppen wurde bestimmt und die folgende empirische Gleichung abgeleitet:

$$\frac{(\text{Sulfonatendgruppe})}{(\text{Sulfatendgruppe})} = 1 + 0{,}27 \left\{ \frac{[\text{NaHSO}_3]}{[\text{AN}][\text{K}_2\text{S}_2\text{O}_8]} \right\}^{1.5}$$

Sulfonat ist unter allen Polymerisationsbedingungen die vorwiegende Endgruppe. Eine vorläufige Diskussion der Startreaktion der Polymerisation in diesem Redoxsystem wurde durchgeführt, die die angeführten Versuchsergebnisse erklären kann.