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POLYMERIZATION INITIATED BY THE SYSTEM TRIETHANOLAMINE/HYDROGEN SULFITE WITH AND WITHOUT THE COOPERATION OF HYDROGEN PEROXIDE. 1. POLYMERIZATION OF ACRYLAMIDE

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ABSTRACT

Attempts to initiate the aqueous polymerization of acrylamide, AAm, by the hydrogen sulfite/oxygen system failed. This is contrary to acrylic acid, whose monomer indeed undergoes initiation by the above initiator. Efforts to start the AAm polyreaction by hydrogen sulfite without air also yielded no polymer. It was discovered, however, that sodium pyrosulfite, PS, coupled with triethanolamine, TEA, in equimolar ratios provides a system, TEA/PS, able to generate radicals even at relatively low temperatures. On the basis of ESR investigations, these proved to be $H\dot{S}O_3$ active centers. At three temperature (273, 278, 283 K) at an initiator (TEA/PS) molar concentration range of $c_{I(0)}$ = 0.0066–0.02 mol/dm^3, and for a monomer (AAm) concentration range of $c_{M(0)}$ = 0.43–1.374 mol/dm^3, high rates of polymerization lying between $r_p = 24.9 \times 10^{-6}$ and 727.5×10^{-6} mol/dm$^3\cdot$s were determined. Linear relationships between lg(r_p) vs lg($c_{I(0)}$) at constant $c_{M(0)}$, and lg(r_p) vs lg($c_{M(0)}$), at constant $c_{I(0)}$ display slopes of 1.0 and 2.5, respectively. Due to "cage effects," the reaction yields are not very high, amounting to 70% at best. By supplementing the TEA/PS system with equimolar amounts of H_2O_2, a significant change of the mechanism of radical generation takes place. According to the ESR spectrum, the unpaired electrons appear here to be centered on the *tert*-amine molecules. By employing either the TEA/

PS or the TEA/PS/H_2O_2 system at temperature levels of 35 or 60°C respectively, under proper conditions, the possibility exists to tailor the molecular masses of polyacrylamides in the $\overline{M}_w = 1 \times 10^5$ to 4×10^6 g/mol range. The presence of H_2O_2 improves the reaction yield.

INTRODUCTION

Komar and Palit [1] were the first to report the possibility of polymerizing water-soluble monomers using hydrogen sulfite ions as the initiator. The presence of air in the system was indispensable, and this requirement was new, since efforts are normally made to remove even traces of oxygen from the reactor. This removal is a cumbersome undertaking, especially in large-scale processes.

In connection with the above finding, the mechanism of radical generation from hydrogen sulfite ions remains questionable, and this stimulated the present investigations. The problem, however, proved to be difficult. Sulfite ions display a selective kind of action toward individual monomers. For instance, no polymerization takes place when acrylonitrile is subjected to sulfite initiation, whereas acrylic acid [2] polymerizes if air is present. Acrylamide, on the other hand, also polymerizes, but certain conditions must be fulfilled, as will be shown further on. Our aim was to investigate these conditions.

The HSO_3^-/O_2 initiator presents a redox system in which the oxidizing agent is practically free of charge. In that respect, air is very beneficial as regards cost-effectiveness. Sulfite also is relatively cheap and easily available in the form of pyrosulfite, PS. Pyrosulfite exists in the solid state, only decomposing to hydrogen sulfite ions when dissolved in water:

$$S_2O_5^{2-} + H_2O \longrightarrow 2HSO_3^- \tag{1}$$

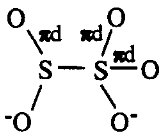
At pH 7, hydrogen sulfite ions are the products of dissociation of sulfurous acid, to which the following constants refer [3]:

$$H_2SO_3 \xleftrightarrow{K_1} H^+ + HSO_3^-, \qquad K_1 = 1.72 \times 10^{-2} \tag{2}$$

$$HSO_3^- \xleftrightarrow{K_2} H^+ + SO_3^{2-}, \qquad K_2 = 6.24 \times 10^{-8} \tag{3}$$

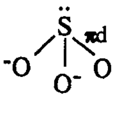
The oxidizing of sulfites with oxygen was investigated by Abel [4] who found that the rate of the process is proportional to the hydrogen sulfite anion concentration and reciprocal to $([H^+])^{1/2}$. Therefore, the maximal rate appears to be at pH $\cong 7$. This statement is important because the creation of radicals here can only be due to sulfite oxidation. The orbital structures of the individual sulfites can be described as follows [5].

X-ray analysis results show that in pyrosulfite ions two oxygen atoms are linked with one sulfur atom and the remaining three oxygen atoms with the other sulfur atom:



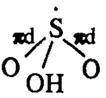
1

Due to its pyramidal structure, the hydrogen sulfite ion contains a free pair of electrons on the sulfur atom. There is easy access to these electrons.



2

Based on investigations carried out by Igarashi et al. [2], polymerization of acrylic acid started by the $HSO_3^-/O/_2$ initiator provides polymeric chains terminated at both ends with sulfonic groups, $-SO_3^-$. Since the structure of these groups is tetrahedral, the unpaired electron of the initiating radical must be localized at the sulfur atom:



3

Consequently in order to generate radicals, the sulfite ions must transfer from the fourth to a higher level of oxidation, which generally can be represented by

$$HSO_3^- + A \longrightarrow H\dot{S}O_3 + A^- \tag{4}$$

where A = electron acceptor.

That is, when one component of a system undergoes oxidation, another one must be reduced. Potential components which can suffer reduction when contacted with hydrogen sulfite ions are the following.

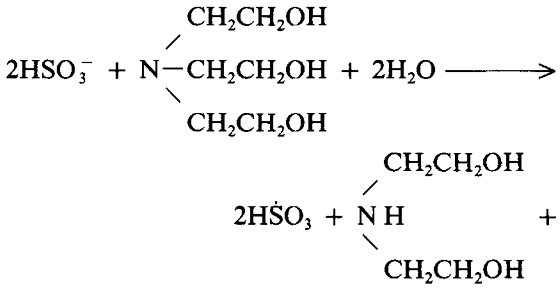
Oxygen from air:

$$HSO_3^- + \dot{O}{-}\dot{O} + H_2O \longrightarrow H\dot{S}O_3 + HO^- + HO\dot{O} \tag{5}$$

where $HO\dot{O}$ is less active since it decomposes quickly, releasing O_2.
Transition metal cation, e.g.:

$$HSO_3^- + Cu^{2+} \longrightarrow H\dot{S}O_3 + Cu^{\bullet} \tag{6}$$

tert-Amine:



$$2HSO_3^- + N(CH_2CH_2OH)_3 + 2H_2O \longrightarrow 2H\dot{S}O_3 + NH(CH_2CH_2OH)_2 + CH_3CH_2OH + 2OH^- \quad (7)$$

Peroxides:

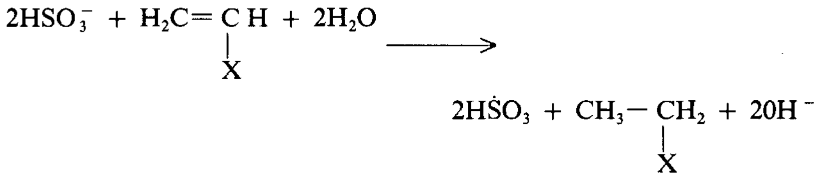
$$HSO_3^- + {}^-SO_3{-}O{-}O{-}SO_3^- \longrightarrow H\dot{S}O_3 + SO_4^{2-} + \dot{O}{-}SO_3^- \quad (8)$$

$$HSO_3^- + HO{-}OH \longrightarrow H\dot{S}O_3 + HO^- + \dot{O}H \quad (9)$$

and

$$\dot{O}{-}SO_3^- + H_2O \longrightarrow HO{-}SO_3^- + H\dot{O} \quad (10)$$

Vinyl monomers

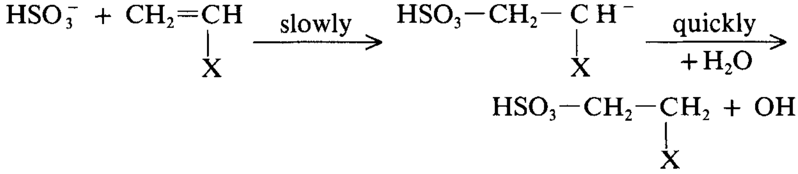


$$2HSO_3^- + H_2C{=}\underset{\substack{|\\X}}{C}H + 2H_2O \longrightarrow 2H\dot{S}O_3 + CH_3{-}\underset{\substack{|\\X}}{C}H_2 + 2OH^- \quad (11)$$

where X = functional group.

The progress of Eq. (11) will depend on the nature of X. It is assumed that ionogenic groups containing negative charges will tend to repel hydrogen sulfite anions, thus delaying the progress of the reaction. A similar effect can result from large substituents. Any probable resonance stabilization brought about by X may also be considered. Nevertheless, the nature of the monomer will certainly exert synergic effects on radicals formation according to Eqs. (5)-(11).

An addition reaction between vinyl monomers and hydrogen sulfite anions should also be taken into account [6]:



$$HSO_3^- + CH_2{=}\underset{\substack{|\\X}}{C}H \xrightarrow{\text{slowly}} HSO_3{-}CH_2{-}\underset{\substack{|\\X}}{C}H^- \xrightarrow[+H_2O]{\text{quickly}} HSO_3{-}CH_2{-}\underset{\substack{|\\X}}{C}H_2 + OH^- \quad (12)$$

The problem was studied in detail by Kudla [7]. When equimolar amounts of hydrogen sulfite and acrylic acid react under conditions normally employed in radical polymerizations, afford less than 5% yields of addition products. Since in the present investigation the molar ratios of the respective reagents amount to PS/AAm = 0.01/1, Eq. (12) can be regarded as negligible.

The aim of the investigation was to answer the following problems:

Does air influence the polymerization of AAm initiated by hydrogen sulfite as favorably as it does in the case of acrylic acid?

Do tertiary amines promote the polymerization of AAm initiated by hydrogen sulfite, and if they do, what will be the probable mechanism of the initiation?

How does the addition of peroxide in the form of H_2O_2 influence the *tert*-amine/hydrogen sulfite initiator employed in AAm polymerization?

How are the molar ratios *tert*-amine/sulfite/H_2O_2/AAm to be varied in order to tailor the molecular masses of the PAAm's in a broad range?

Some of the conclusions resulting from our investigation are based on ESR spectra of radicals trapped by 2-methyl-2-nitrosopropane, MNP.

The investigation was divided into two parts. In the first one the influence of the molar ratios triethanolamine/sulfite/AAm and triethanolamine/sulfite/H_2O_2/AAm, on AAm polymerization was tested. The second part was devoted to a more detailed study of the kinetic aspects of AAm polymerization initiated by the triethanolamine/sulfite system.

EXPERIMENTAL

Materials

Acrylamide (Fluka AG), AAm, reagent grade, was recrystallized from chloroform and dried in vacuum, and checked for purity by its melting point and ^{1}H-NMR spectrum. Sodium pyrosulfite (Merck), PS, analytically pure, was used as received. Triethanolamine (POCh Gliwice, Poland), TEA, was vacuum distilled, and checked for purity by its refractive index and ^{1}H-NMR spectrum. Hydrogen peroxide (POCh Gliwice, Poland), H_2O_2, used for analysis, was submitted to acid $KMnO_4$ tritration before each use in order to determine the H_2O_2 content, which oscillated around 30–33 wt%. Ethanol (POCh Gliwice, Poland) analytically pure, was dried over zeolite A4 and distilled. 2-Methyl-2-nitrosopropane (Aldrich Chemical Co.), MNP, reagent grade, was used as received for spin trapping. Water was redistilled.

Procedures

Preparation of Polymers Listed in Table 1

Prior to polymerization, stock solutions were made by dissolving 10 g AAm in 100 cm^3 aqueous solution and 3.34 g H_2O_2 in 100 cm^3 aqueous solution. Appropriate amounts of the stock solutions corresponding to the present molar ratios were placed in vials. These amounts were matched to reach a final volume of 20 cm^3. The contents of the vials were bubbled with pure nitrogen (or, if they were not, they are marked with an asterisk in Table 1), and thermostated at one of the two temperature levels. The PS stock solution was always introduced after the temperature stabilized. From that moment, the time of polymerization was measured. After 4 hours the vials were chilled, opened, and the contents precipitated into 7-fold volumes of ethanol. Each sediment was brought quantitatively onto a filter, washed, and then vacuum dried to constant weight for yield determination.

TABLE 1. Yields α and Weight-Average Molecular Weights $\overline{M}_w$ for Polyacrylamides PAAm-1–PAAm-16 Obtained in Series 1–4 at Two Temperature Levels T and Different Molar Ratios (TEA/PS/H_2O_2/AAm = triethanolamine/pyrosulfite/hydrogen perioxide/acrylamide) in the Presence of Air (designed by asterisks) and Under Exclusion of Air

Series	Polymer	Molar ratio TEA/PS/H_2O_2/AAm	T, °C	Yield α, %	$\overline{M}_w \times 10^{-6}$
1	PAAm-1*	0.006/0.006/0/1	35	<2	–
	PAAm-2*	0.006/0.006/0/1	60	15.7	0.23
	PAAm-3*	0.01/0.01/0/1	35	<2	–
	PAAm-4*	0.01/0.01/0/1	60	32.1	0.16
	PAAm-0*	0.00/0.01/0/1	35	0.0	–
2	PAAm-5	0.006/0.006/0/1	35	25.5	1.66
	PAAm-6	0.006/0.006/0/1	60	63.5	1.69
	PAAm-7	0.01/0.01/0/1	35	48.9	1.38
	PAAm-8	0.01/0.01/0/1	60	70.4	1.15
	PAAm-0	0.00/0.01/0/1	35	0.0	–
3	PAAm-9*	0.006/0.006/0.06/1	35	<2	–
	PAAm-10*	0.006/0.006/0.06/1	60	53.3	0.42
	PAAm-11*	0.01/0.01/0.01/1	35	<2	–
	PAAm-12*	0.01/0.01/0.01/1	60	60.8	0.28
4	PAAm-13	0.006/0.006/0.006/1	35	81.5	2.07
	PAAm-14	0.006/0.006/0.006/1	60	97.2	3.77
	PAAm-15	0.01/0.01/0.01/1	35	85.5	1.90
	PAAm-16	0.01/0.01/0.01/1	60	99.9	1.91

Polymerizations for Determining Kinetics

Appropriate volumes of water were introduced into vials (200 cm^3) so that the final volume of the solutions was 50 cm^3. The contents of the vials were continuously bubbled with nitrogen. AAm was first dissolved in amounts corresponding to the molar concentrations listed in Table 2. The vials were then placed in a thermostated bath, and after stabilization of the temperature at the desired level (see Table 2), TEA and PS were added in equimolar amounts that guaranteed the molar concentrations listed in Table 2. The time of polymerization was measured (τ = 392 seconds) from that moment when PS was introduced.

Then a measured volume was taken from the vials, weighted, and introduced into cool water for analysis. The degree of conversion was determined from the content of unreacted double bonds.

TABLE 2. Degrees of Conversion $\alpha = \left(1 - \frac{C_M}{C_{M(0)}}\right) \times 100 = (1 - c_{red}) \times 100$; Rates ($r_p$) of Acrylamide (AAm) Polymerization Performed under Nitrogen in Time $\tau = 392$ seconds at Three Temperature (T) Levels in the Presence of Equimolar Amounts of Triethanolamine (TEA) and Sodium Pyrosulfite (PS) as Initiator, Employing at $\tau = 0$) Molar Concentrations of Initiator ($c_{I(0)}$ and of Monomer ($c_{M(0)}$) (c_M molar concentration obtained at the end of the polyreaction)

T, °K											
273				278				283			
$C_{M(0)}$, mol/dm^3	$c_{I(0)}$, mol/dm^3	α, %	$r_p \times 10^6$ mol/dm$^3 \cdot$s	$C_{M(0)}$, mol/dm^3	$c_{I(0)}$, mol/dm^3	α, %	$r_p \times 10^6$ mol/dm$^3 \cdot$s	$C_{M(0)}$, mol/dm^3	$c_{I(0)}$, mol/dm^3	α, %	$r_p \times 10^6$ mol/dm$^3 \cdot$s
0.430	0.0066	2.27	24.9	0.430	0.0066	5.16	56.6	0.430	0.0066	3.98	43.7
0.887	0.0066	7.53	170.4	0.655	0.0066	7.57	126.5	0.655	0.0066	14.45	241.4
1.126	0.0066	9.89	284.1	0.887	0.0066	15.43	349.1	1.126	0.0066	20.50	588.9
1.374	0.0066	14.08	493.5	1.127	0.0066	17.00	488.8	1.225	0.0066	23.28	727.5
0.655	0.010	7.57	126.5	0.655	0.010	9.05	151.2	0.655	0.010	9.87	164.9
0.655	0.014	9.87	164.9	0.655	0.014	13.62	227.5	0.655	0.014	14.42	240.9
0.655	0.017	13.32	222.6	0.655	0.017	17.00	284.1	0.655	0.017	17.94	299.8
0.655	0.020	15.98	267.0	0.655	0.020	18.82	314.5	0.655	0.020	20.49	342.4

Measurements and Analyses

The degree of conversion was calculated from unsaturation. The latter was determined by bromination according to a procedure adapted from the method of Lucas and Pressman [10].

Molecular weight determinations of the polymers were carried out in a photogoniodiffusometer Sofica type 1200 at 25 ± 0.02°C on five solutions of each polymer covering the concentratin rate $c = 0.02\text{–}0.1$ g/100 cm^3 in aqueous 0.1 N NaCl solutions. The wavelength was 546.1 nm. The data were processed according to Zimm [11]. The refractive increment $dn/dc = 0.160$ cm^3/g was determined by the use of a differential refractometer Zeiss Jena type PR-2. From the intercepts at the ordinate of the extrapolated double reciprocal plots, the weight-average molecular weights $\overline{M}_w$ were estimated.

The ESR spectra were obtained with a Bruker ER 200D-SRC spectrometer at room temperature. To a small test tube were added a solution of MNP (about 20 mmol/dm^3 in ethanol), a solution of TEA (150 mmol/dm^3 in ethanol), and then PS (about 150 mmol/dm^3 in aqueous solution) or an equimolar mixture of PS (150 mmol/dm^3 in aqueous solution) and H_2O_2 (150 mmol/dm^3 in aqueous solution). After the respective mixture had been bubbled with argon for about 4–5 minutes to remove oxygen, it was transferred into a flat sample cell and the ESR spectra were recorded by using the DR cavity at the X band, a microwave power of 200 μW, and a modulation frequency of 100 kHz.

RESULTS AND DISCUSSIONS

The objective was to investigate new initiator systems made up of PS, H_2O_2, and TEA for the polymerization of AAm in water solution.

In the first step, four series of polymerizations were carried out, each at two temperature levels, and differing in the TEA/PS/H_2O_2/AAm ratios and in the admission or exclusion of air as listed in Table 1. α and $\overline{M}_w$ were determined.

No polymerization of AAm takes place when only PS is used as the initiator (see PAAm-0* in Series 1 and PAAm-0 in Series 2 in Table 1). The nonpolymerization in these systems results from the lack of radicals, as can be seen from the ESR spectrum shown in Fig. 1. The spectrum was taken in the presence of MNP as the spin label.

Under similar conditions as applied for AAm-0* in Series 1, acrylic acid undergoes polymerization, in agreement with the findings of Igarashi and coworkers [2]. The behaviors of these monomers are in contradiction. Actually, in some factories acrylic acid is polymerized commercially in the presence of air with the use of PS as the sole initiator [7]. Considering this fact, attempts were made to do the same with AAm, but without result. That problem required separate handling by means of ESR experiments.

Unexpectedly, it was discovered that hydrogen sulfite anions derived from PS in water display an ability to initiate AAm polymerization but only when a tertiary amine, preferably triethnolamine, is present in the system.

Investigations involving Series 1 and 2 focused on the TEA/PS system. This system is of interest for two reasons:

It contains no oxidizing agents like peroxides or molecular oxygen (when air is exluded.)

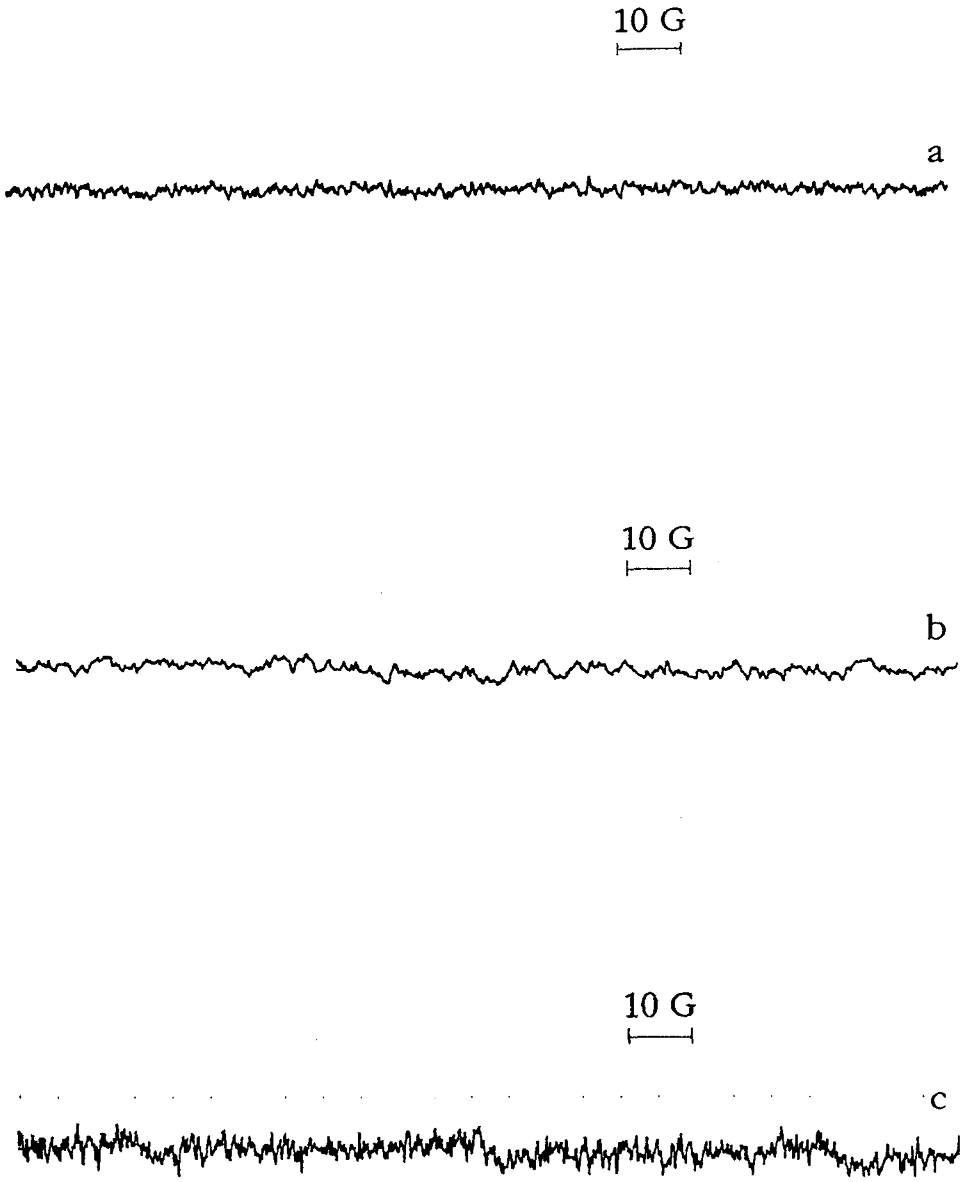


FIG. 1. ESR spectra assigned to (a) 2-methyl-2-nitrosopropane (MNP) in ethanol at room temperature for 1 hour and [MNP] = 20 mmol/dm^3; (b) sodium pyrosulfite (PS) in aqueous solution at room temperature for 1 hour and [PS] = 150 mmol/dm^3; (c) triethanolamine (TEA) in ethanol solution for 1 hour and [TEA] = 150 mmol/dm^3.

Radicals are generated even in the absence of peroxides, which leads to the question—What is their source?

As can be seen from the data for probes PAAm-1*-PAAm-4* and PAAM-5-PAAm-8, the presence of air (indicated by an asterisk) has a negative influence on α, and $\overline{M}_w$. When air was admitted, only a small amount of polymer was formed at 60°C and none formed at 35°C, whereas polymers were formed in an inert atmosphere at both of these temperatures.

Higher yields were generally found at the higher (0.01) mole ratios than at lower (0.006) ones. The molecular weights proved to be higher at the lower initiator concentration (cf. Series 1 and 2).

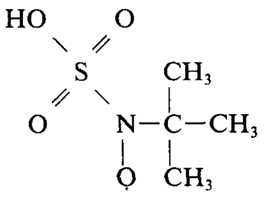
The TEA/PS initiator does not provide high enough yields to satisfy practical demands. Nevertheless, this system is interesting from a scientific point of view.

In the next step, investigations were carried out aimed at modifying the TEA/PS initiator in order to improve the yields. For that reason a third constituent was introduced into the system by way of H_2O_2. All constituents forming the initiator were taken in equimolar amounts. Other conditions (temperature levels and initiator/AAm mole ratios) were kept the same as in Series 1 and 2. Gravimetrically determined yields and weight-average molecular weights relating to the Series 3 and 4 are listed in Table 1. From the data it is evident that the addition of hydrogen peroxide to the TEA/PS system causes a substantial improvement of yields and an increase of average molecular weights. Here again, the negative influence of air can easily be seen by comparing Series 3 with Series 4. A higher temperature generally improves the yields whereas a higher initiator concentration diminishes the molecular weights. Optimal values are for PAAm-14.

The investigations described hitherto disclosed some problems requiring solution. The question is: What are the radicals which appear in the TEA/PS and TEA/PS/H_2O_2 systems?

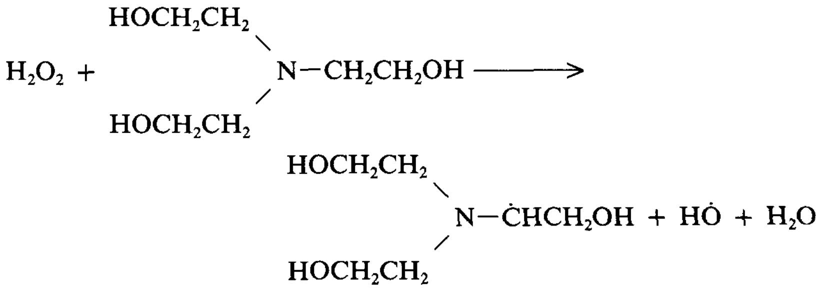
It should be noted in the TEA/PS system that this initiator, unlike others, is devoid of any peroxide or any other compound that easily generates radicals. According to the literature [2], acrylic acid initiated by PS/O_2 provides polymers with sulfonic end groups. It is therefore assumed that this polyreaction was initiated by $H\dot{S}O_3$ species.

In the present work the TEA/PS system, rather than PS/O_2 system, proved to be an efficient initiator for polymerization of AAm. The question as to why hydrogen sulfite initiates the polymerization of acrylic acid ion in the presence of O_2 but not the polymerization of acrylamide remains unanswered. Probably O_2 is a too powerful retarder for AAm polymerization but not for acrylic acid polymerization. In order to identify the active species initiating AAm polymerization, ESR measurements were carried out using MNP as the label. If $H\dot{S}O_3$ radicals are present, they should form the following species with MNP:



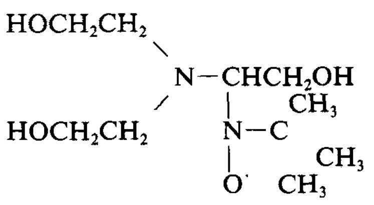
A

A should provide an ESR spectrum consisting of only three lines distinguished by a splitting constant in the range a_N^α = 14-16 G. The ESR spectrum of the TEA/PS system as shown in Fig. 2 reveals only three lines marked by a splitting constant a_N^α = 14-16 G. It is assumed that the $H\dot{S}O_3$ radicals are created in accordance with Eq. (7) in which TEA appears to be an acceptor of electrons resulting from reduction. The role of the tertiary amine is quite different here compared to its mode of action in typical redox systems, where the amine is being converted to a radical [9]. In fact, the TEA/PS/H_2O_2 initiator presents a redox system and therefore, in addition to Eq. (9), a further reaction must be considered which, in the case of TEA [9], should proceed as follows:



$$H_2O_2 + \begin{array}{l} HOCH_2CH_2 \diagdown \\ \qquad\qquad N{-}CH_2CH_2OH \\ HOCH_2CH_2 \diagup \end{array} \longrightarrow \begin{array}{l} HOCH_2CH_2 \diagdown \\ \qquad\qquad N{-}\dot{C}HCH_2OH + H\dot{O} + H_2O \\ HOCH_2CH_2 \diagup \end{array} \quad (13)$$

If the above radical is trapped by MNP, **B** is provided:



$$\begin{array}{l} HOCH_2CH_2 \diagdown \\ \qquad\qquad N{-}CHCH_2OH \\ HOCH_2CH_2 \diagup \quad \; | \\ \qquad\qquad\quad N{-}C(CH_3)_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O^{\cdot} \end{array}$$

B

FIG. 2. ESR spectrum of the TEA/PS system in the presence of MNP obtained at room temperature by mixing equal volumes of TEA ethanol solution, PS aqueous solution and MNP solution in ethanol; [TEA] = [PS] = 150 mmol/dm^3, [MNP] = 20 mmol/dm^3.

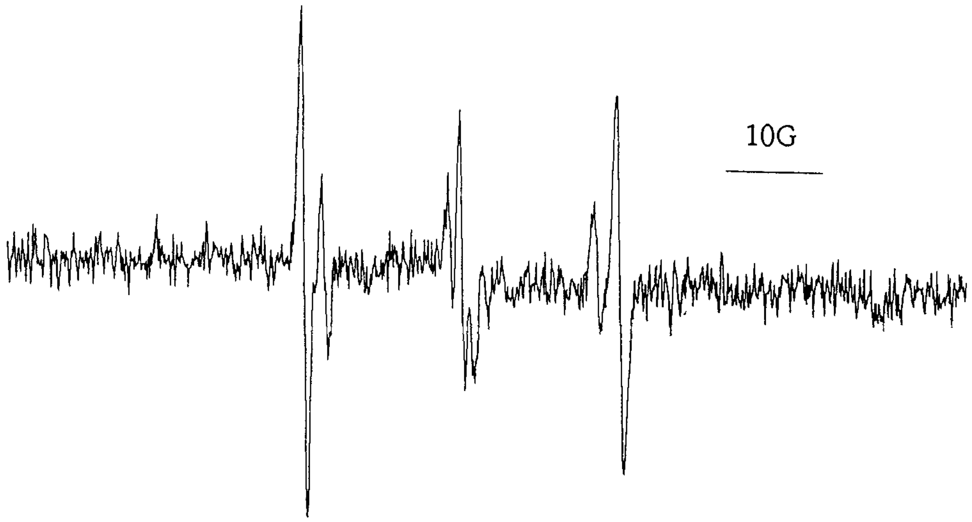


FIG. 3. ESR spectrum of TEA/PS/H_2O_2 system in the presence of MNP obtained at room temperature by mixing equal volumes of TEA in ethanol solution, PS in aqueous solution, H_2O_2 in aqueous solution, and MNP in ethanol solution; [TEA] = [PS] = [H_2O_2] = 150 mmol/dm^3, [MNP] = 20 mmol/dm^3.

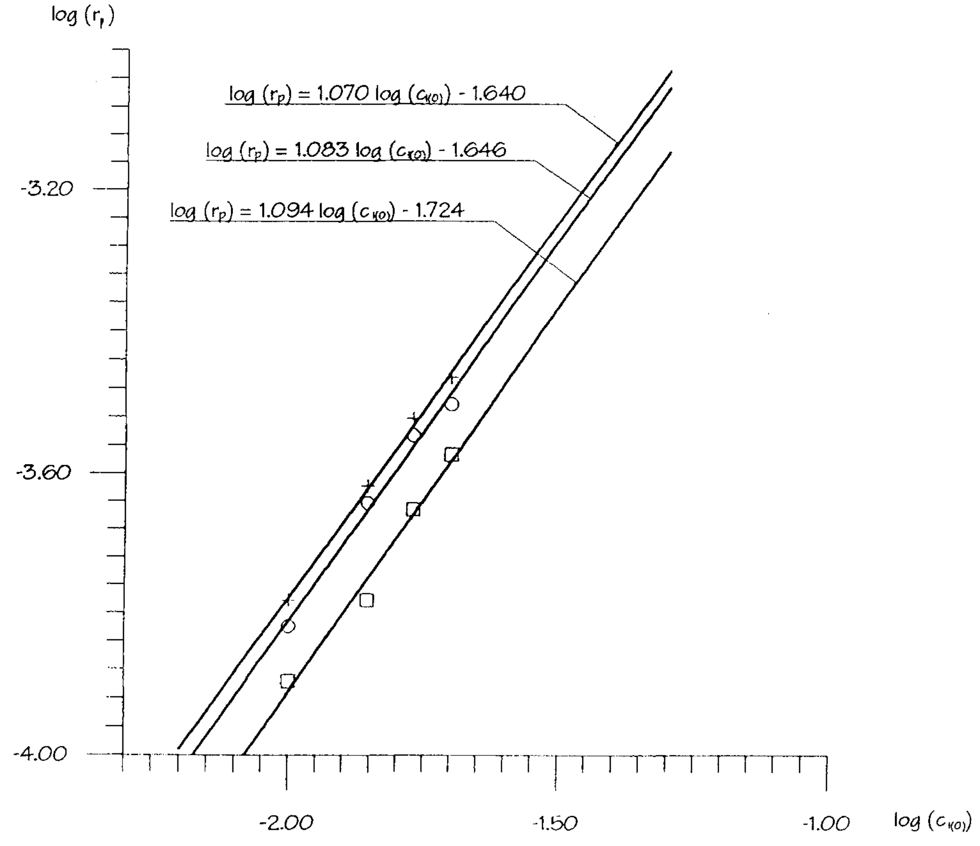


FIG. 4. Relationship between rate of polymerization, r_p, and initiator concentration, $c_{I(0)}$, for acrylamide (AAm).

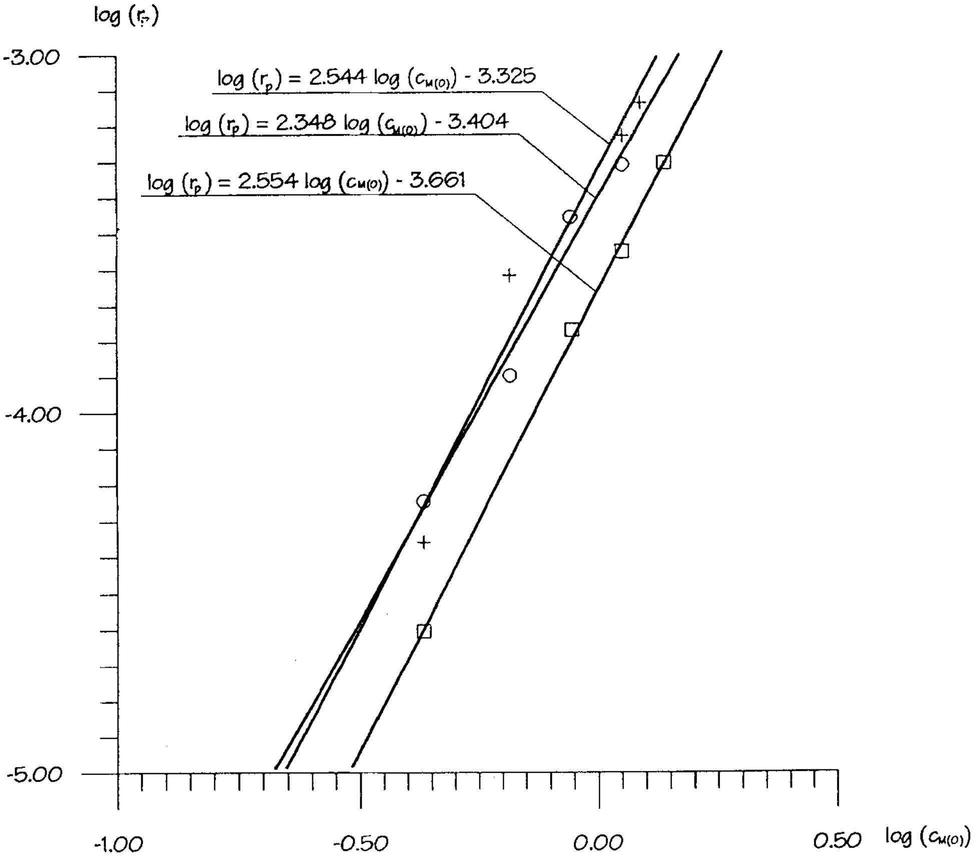


FIG. 5. Relationship between rate of polymerization, r_p, and monomer concentration, $c_{M(0)}$, for acrylamide (AAm).

Theoretically, the ESR spectrum of **B** should reveal six lines. Indeed, the ESR spectrum of the TEA/PS/H_2O_2 system shown in Fig. 3 displays six lines distinguished by two splitting constants: $a_N^\alpha = 16.3$ G and $a_N^\alpha = 14.2$ G.

Additional investigations focused on kinetic issues related to the original TEA/PS system which has never been described in the literature. Initial experiments revealed a rapid AAm polymerization, even at 273 K, started by the above initiator in an inert atmosphere. In order to keep the degree of conversion, α, below 10%, it was necessary to make the measurements at low temperatures, e.g., 273, 278 and 283 K, rather unusual for radical processes, and in the relatively short time of 310 seconds. Despite these measures, in most cases the degree of conversion appeared to be greater than the desired 10% (see Table 2), thus indicating a quick generation of radicals, which is not desired in practice.

From the data listed in Table 2, it is evident that there are increases in the initial molar concentrations of the monomer, $c_{M(0)}$; the initial molar concentrations of the initiator, $c_{I(0)}$; the temperature, T; and the acceleration rates of polymerization, r_P, calculated from $r_P = c_{M(0)} (\alpha/100\tau)$.

Functional relationships $r_p = f(c_{M(0)})$ as well as $r_p = f(c_{I(0)})$ are displayed in Figs. 4 and 5 by double logarithmic plots which show linearity, together with the corresponding numerical equations.

From the rates of polymerization of probes for which $\alpha < 10\%$ (cf. Table 2), reaction orders n_M vs monomer concentration and n_I vs initiator concentration were calculated according to the following relationships [12]:

$$n_I = \frac{\lg r_{p(1)} - \lg r_{p(2)}}{\lg c_{I(0)(1)} - \lg c_{I(0)(2)}}, \qquad \text{at } c_{M(0)} = \text{constant}$$

and

$$n_M = \frac{\lg r_{p(1)} - \lg r_{p(2)}}{\lg c_{M(0)(1)} - \lg c_{M(0)(2)}}, \qquad \text{at } c_{I(0)} = \text{constant}$$

It should be stressed that only a few data were available at low levels of conversion, and the values which resulted oscillate around $n_I \approx 1$ in initiator concentration and $n_M \approx 2.5$ in monomer concentration, which is somewhat unusual.

CONCLUSIONS

AAm, unlike acrylic acid, does not polymerize when PS is employed as an initiator in the presence of air. The reason for the different behaviors is unknown.

On the other hand, as a result of our investigations it was discovered that a system made up of equimolar amounts of TEA and PS displays good efficiency as an initiator for AAm polymerization in aqueous solution. Air, however, must be excluded. A higher temperature (60°C as compared to 35°C) favors greater yields, whereas a higher initiator/monomer mole ratio (0.01 as compared to 0.006) decreases $\overline{M}_w$. The highest yield amounted to 70% whereas the highest average molecular weight reached 1.7×10^6 g/mol.

Yields can be markedly improved by the addition of an equimolar amount of H_2O_2 to the TEA/PS system. By employing this TEA/PS/H_2O_2 redox initiator for AAm polymerization under exclusion of air, yields can be increased to about 99% and molecular weights to about 3.8×10^6 g/mol.

There was some question about the source of radicals in the TEA/PS system. ESR measurements performed with MNP as the label gave a spectrum consisting of three lines with the splitting constant $a_\alpha^N = 14.6$ G. This spectrum relates well to $H\dot{S}O_3$ radicals trapped by MNP (Compound **A**). Assumedly, these radicals are generated through reduction of TEA molecules as shown in Eq. (7).

In case of the TEA/PS/H_2O_2 initiator, TEA plays a different role than it does in the two-component system. According to the literature [9], tertiary amines in redox systems are transformed into radicals. Expectedly, ESR measurements on the TEA/PS/H_2O_2 system revealed a spectrum consisting of six lines with two splitting constants: $a_N^\alpha = 16.3$ G and $a_H^\alpha = 14.2$ G. This spectrum can reasonably be ascribed to the $(HOCH_2CH_2)_2N\dot{C}HCH_2OH$ radical trapped by MNP (Compound **B**).

Rates of AAm polymerization, r_p, started by the TEA/PS initiator are relatively high even at low temperatures (273-283 K). They depend on the initial monomer concentration $c_{M(0)}$, as well as on the initial initiator concentration, $c_{I(0)}$. Functional relationships $r_p = f(c_{M(0)})$ and $r_p = f(c_{I(0)})$ displayed as double logarithmic plots show linearity.

Reaction orders, n, determined at low levels of conversion ($\alpha < 10\%$) oscillate around somewhat unusual values, i.e., $n_I \approx 1$ in initiator concentration and $n_M \approx 2.5$ in monomer concentration.

By using either TEA/PS or TEA/PS/H_2O_2 as the initiator system, it is possible to tailor the molecular weights of polyacrylamide in the range between 1×10^5 and 4×10^6 g/mol.

It was shown that sulfites behave differently in various initiator systems. In redox systems they act as reducing agents, decreasing the activation energy of the peroxide decomposition, whereas under certain conditions in the absence of peroxides they can provide an abundant source radicals.

REFERENCES

[1] R. S. Komar and S. R. Palit, *J. Indian Chem. Soc.*, *63*, 815 (1961).
[2] T. Igarashi, A. Kondo, R. Tsushima, and S. Aoki, *Makromol. Chem.*, *190*, 2109 (1989).
[3] H. V. Tartar and H. H. Garretson, *J. Am. Chem. Soc.*, *63*, 808 (1941).
[4] E. Abel, *Monatsh. Chem.*, *82*, 815 (1951).
[5] P. J. Durrant and B. Durrant, *Introduction to Advanced Inorganic Chemistry*, Longmans, London, 1962, p. 839.
[6] C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, p. 327.
[7] S. Kudla, Doctor Thesis, Jagellonian University, Cracow, 1994.
[8] W. M. Thomas and D. Wang, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 1 (H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds.), Wiley, New York, 1985, p. 169.
[9] X. Q. Guo, K. Y. Qiu, and X. De Fang, *Makromol. Chem.*, *191*, 577 (1990).
[10] H. J. Lucas and D. Pressman, *Ind. Eng. Chem. Anal.*, *10*, 140 (1938).
[11] B. Zimm, *J. Chem. Phys.*, *16*, 1093 (1948).

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