

# The Effects of MEHQ on the Polymerization of Acrylic Acid in the Preparation of Superabsorbent Gels

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**ABSTRACT:** The effect of the monomethyl ether of hydroquinone (MEHQ) on the polymerization of acrylic acid was studied. The rate of polymerization was quantified at various levels of MEHQ by use of an *in situ* NMR technique. While oxygen functions as an inhibitor in acrylic acid polymerizations, MEHQ was shown to function as a retarder. The decrease in the rate of polymerization allowed the calculation of an inhibition constant for this system. MEHQ was found to remain in the polymerizing mixture throughout the course of the reaction, significantly reducing the rate of polymerization, but not reducing the molecular weight of the polymer. The data are consistent with direct reaction of MEHQ with initiator fragments, but not termination of growing chains. Superabsorbent polyacrylic acid gels were prepared and the properties measured. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 577–589, 1997

**Key words:** superabsorbent; monomethyl ether of hydroquinone (MEHQ); NMR; kinetics; acrylic acid

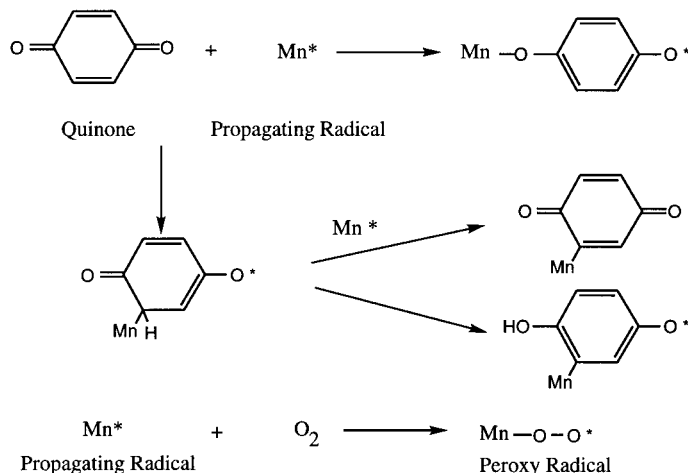
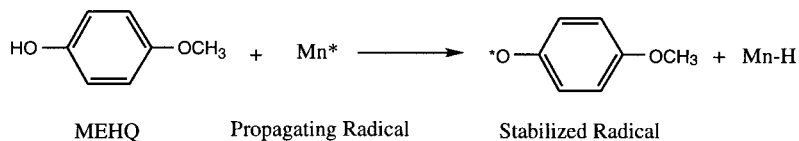
## INTRODUCTION

The polymerization of vinyl monomers can be affected by many different components or impurities. Retarders decrease the rate of polymerization from that which would be obtained with highly purified monomers. Inhibitors prevent the polymerization from occurring for some period of time (induction time) until they are consumed, after which the reaction proceeds at its normal rate. Both retarders and inhibitors react with initiator fragments or growing chains to terminate radicals that would otherwise lead to polymer formation. Retarders are just less efficient and do not terminate all of the radicals. Reactions can also be both inhibited and retarded.

Inhibitors and retarders are characterized by having the ability to form a stabilized free radical, generally by delocalization of the unpaired electron throughout a conjugated system. An effective inhibitor can be of the addition type, such as oxygen or quinone, where the radical adds to the component, or of the chain transfer type, such as the monomethyl ether of hydroquinone (MEHQ), where the active radical is terminated by transfer of a hydrogen (or halogen, etc.) atom with the generation of a less reactive, stabilized radical (Fig. 1). This less reactive radical does not participate in the polymerization process and, thus, the overall rate of polymerization is reduced or prevented depending upon the amount of inhibitor present, the rate of the termination step, and the reactivity of the newly formed, stable radical. Many stabilizers or antioxidant systems consist of two or more components that interact in a syn-

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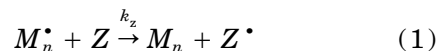
Addition MechanismChain Transfer Mechanism

**Figure 1** Mechanisms of inhibition in free radical polymerization reactions.

ergistic way to give significantly greater effect than either component individually. MEHQ and oxygen function together in a synergistic way.

About 200 ppm of MEHQ is added to glacial acrylic acid as an inhibitor to prevent polymerization during shipping and storage. The effectiveness of MEHQ is significantly increased in the presence of oxygen and many studies have focused on the role of these two components and their synergistic interaction. Even trace amounts of oxygen in otherwise very pure systems can depress the conversion of acids such as acrylic or methacrylic to polymer. Blauer<sup>1</sup> reported that even the trace amounts of oxygen remaining in purified nitrogen would retard the polymerization of methacrylic acid if continuously bubbled through the solution during the reaction.

The kinetics of inhibited and retarded polymerizations have been reviewed by Odian.<sup>2</sup> In addition to the normal initiation, propagation, and termination reactions, an inhibition reaction [eq. (1)] is introduced where  $Z$  is the inhibitor or retarder.



Making the assumption that the inhibitor radicals,  $Z^*$ , neither reinitiate polymerization nor reform the inhibitor  $Z$ , then the rate of change of concentration of growing radicals,  $d[M^*]/dt$ , is represented at steady state by eq. (2), where  $R_i$  is the rate of initiation (typically  $2k_d[I]$ ),  $k_t$  is the termination rate constant, and  $k_z$  is the rate constant for the reaction of the inhibitor and active radicals [eq. (1)].

$$d[M^*]/dt = R_i - 2k_t[M^*]^2 - k_z[Z][M^*] = 0 \quad (2)$$

The rate of propagation,  $R_p$ , is given by eq. (3).

$$R_p = -d[M]/dt = k_p[M^*][M] \quad (3)$$

Solving eq. (2) for  $[M^*]$ , combining with eq. (3), and rearranging gives

$$\frac{2R_p^2 k_t}{k_p^2 M^2} + \frac{R_p [Z] k_z}{k_p [M]} - R_i = 0 \quad (4)$$

In eq. (4), the rate of polymerization is inversely proportional to the ratio of the rate constants for inhibition,  $k_z$ , and propagation,  $k_p$ . That ratio is called the inhibition constant,  $z$ ,

$$z = k_z/k_p \quad (5)$$

Oxygen is a very active inhibitor for most vinyl polymerizations and has an inhibition constant ( $z$ ) of 33,000 for methyl methacrylate and 14,600 for styrene at 50°C.<sup>3,4</sup> Phenolic compounds such as the MEHQ have much lower inhibition constants. Phenol itself has an inhibition constant of 0.0002 for the polymerization of methyl acrylate at 50°C.<sup>3,4</sup> The polarity of the growing radical site influences the effectiveness of an inhibitor. Electron-poor inhibitors (e.g., *p*-benzoquinone) are effective at inhibiting the polymerization of electron rich propagating radicals such as the polystyryl radical but are only weak retarders toward electron-poor growing radicals such as that from methyl methacrylate.<sup>5-7</sup>

Although MEHQ is used as an inhibitor in acrylic acid, Levy<sup>8</sup> has shown that in the absence of oxygen, there is no induction time at 100°C, and no detectable amount of MEHQ is consumed or reacts with the polymer radicals. The inhibiting effect of phenolic compounds may be the result of their oxidation to quinones.<sup>9</sup> Persulfate will react directly with phenols, both substituted and unsubstituted, leading to quinones as the oxidation products.<sup>10</sup> This direct oxidation of phenols by persulfate is known as the Elbs reaction.<sup>11</sup>

Oxygen plays a very critical role in the stability of vinyl monomers, and many of the inhibiting systems require oxygen as an integral part of the mechanism. Whereas most purified vinyl monomers will not polymerize upon heating in the absence of oxygen, all vinyl monomers will readily form peroxides upon exposure to air. These peroxides have been found to be polymerization catalysts.<sup>12</sup> Oxygen functions as an efficient polymerization inhibitor when the peroxides are formed at lower temperatures, where they are relatively stable. There is a delicate balance between polymerization, inhibition, and reinitiation that is influenced by the temperature, oxygen content of the system, and thermal stability of the peroxide formed from the monomer. In a closed system, oxygen is depleted and polymerization eventually occurs. When there is an unlimited supply of oxygen, such as in an open vessel, vinyl monomers will "absorb" a large quantity of oxygen in forming

polyperoxides without polymerizing. When connected to an oxygen reservoir, methyl methacrylate absorbed twice its volume of oxygen upon heating at 65°C in the dark over a 26-h period without polymerizing.<sup>9</sup> Polymerization occurred only when the oxygen was subsequently replaced with nitrogen.

Kurland<sup>13</sup> determined the oxygen consumption during AIBN-initiated polymerization of neat acrylic acid at 50°C containing high levels (106 ppm) and low levels (1.7 ppm) of MEHQ by continuously monitoring the oxygen level in the reaction vessel. When only 1.7 ppm of MEHQ was present, a rapid increase in the rate of oxygen consumption was observed once the MEHQ was depleted. Initially about 6 molecules of oxygen were consumed per initiator radical generated, but when the MEHQ was gone, about 32 molecules per radical were consumed. Regardless of the MEHQ content, polymerization occurred when the oxygen content was reduced to about 0.5 ppm. Lower molecular weight, oxygen-containing oligomers, as well as adducts with quinone, will be produced, depending on the efficiency of deoxygenation. Several molecules of oxygen per initial radical will be consumed by these reactions, consistent with the findings of Kurland.<sup>13</sup>

Most of the prior work on the effects of MEHQ in acrylic acid have either been in the presence of oxygen, a powerful inhibitor, neat, or without added radical sources, and not under the normal conditions of polymerization as used, for example, to prepare polyacrylic acid or superabsorbent resins. Because the aqueous acrylic acid mixtures used to make polyacrylic acid superabsorbent resins are deoxygenated before polymerization, the MEHQ present from the monomer could potentially survive the reaction and remain in the product. The amount of MEHQ that survives the polymerization process may be the result of the efficiency of deoxygenation, the reaction temperature, and most importantly, the nature of the polymerization catalyst. Persulfates are commonly used to polymerize acrylic acid and are more powerful oxidants than azo compounds as well as more efficient at hydrogen abstraction, and thus, may convert more of the MEHQ to quinone and higher oxidation products. Nothing is known about the effects of MEHQ on the rate of polymerization of acrylic acid or the resulting molecular weight of the polyacrylic acid, both important issues for commercial production of polyacrylic acid and superabsorbent resins. The need to better un-

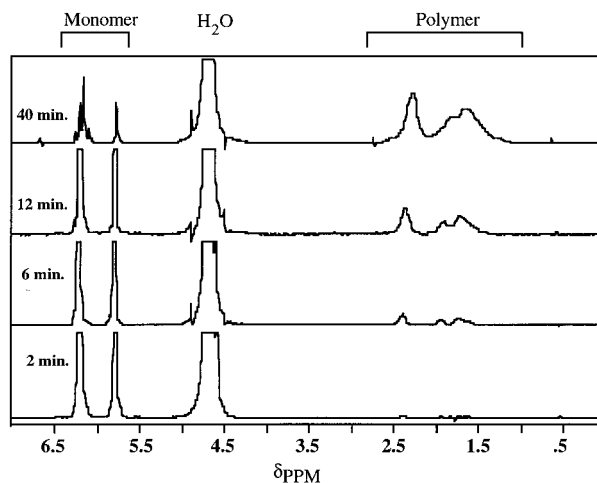
derstand the effect of MEHQ on the aqueous phase polymerization of acrylic acid in the absence of oxygen and initiated by persulfate led to this study.

## EXPERIMENTAL

### Typical Feed Batch Preparation Procedure

Because of the desire to minimize the number of samples to prepare and analyze, an experimental technique was developed, based on NMR spectroscopy, to follow the kinetics of the polymerization of acrylic acid *in situ*. This technique also made it possible to obtain isothermal data during exothermic conditions of up to 10% conversion/minute. Small feed batches of 50–100 g were prepared in glass bottles with the appropriate initiator level, monomer content, percent neutralization, and additives. A typical monomer mixture containing 33% solids, 65% neutralization, and 1600 ppm sodium persulfate (based on acrylic acid) was prepared by combining 28.18 g of glacial acrylic acid and 69.925 g of a 0.0644% persulfate stock solution (98+%, Aldrich). This mixture was neutralized by the slow addition, with stirring, of 13.456 g of granular sodium carbonate (Fisher Certified A.C.S., anhydrous).

Monomer mixtures containing from low to high levels of sodium persulfate were prepared by starting with a mixture with the lowest level of initiator and then spiking the solution with increasing levels of a solution of sodium persulfate. Small samples were withdrawn from the glass sample jar after each addition of the 10% persulfate solution and loaded into NMR tubes to polymerize. The amount of persulfate added and the quantity of material removed for each NMR experiment were determined using an analytical balance so that the persulfate concentration could be calculated. Approximately 1.0 g of material was loaded into 5 mm NMR tubes, or alternatively, 0.1 g of material was loaded into 2 mm (i.d.) NMR tubes via glass pipette and deoxygenated with nitrogen. Metal syringe needles were found to cause premature reactions. The initial feed batches were spiked with various levels of MEHQ that had been recrystallized from monochlorobenzene. The initial level of MEHQ in the acrylic acid was 177 ppm, which was reduced to < 1 ppm by distillation for the polymerization without MEHQ. Runs containing higher levels



**Figure 2**  $^1\text{H}$ -NMR spectra of the polymerization of acrylic acid as a function of time and conversion to polymer.

were prepared by addition of the recrystallized MEHQ to the acid containing 177 ppm inhibitor. Polymerizations were conducted on feed batches containing from 0 to 4667 ppm of MEHQ.

Changes in the concentration of the samples were minimized by the deoxygenation process. The nitrogen bubbler was connected to the NMR tube using a capillary tube that was inserted through a capped NMR tube, the cap possessing a small hole just large enough for the capillary to be inserted. After the deoxygenation, the cap was sealed and the sample was sonicated (20–30 s) to remove the nitrogen gas from the saturated liquid so that bubbles did not form in the sample as it polymerized. The sample was then placed into the temperature-equilibrated, nitrogen-filled probe of the NMR and data acquisition was initiated. The time of data accumulation for each spectrum was determined by the number of scans and the delay time between scans. A typical series of  $^1\text{H}$ -NMR spectra, from low to high conversion are given in Figure 2. Of the different NMR techniques,  $^1\text{H}$  was preferred over  $^{13}\text{C}$  because of the greater sensitivity, faster acquisition rates, and the ability to use smaller diameter tubes, which helped maintain isothermal conditions.

For very exothermic reactions, an apparatus was designed that allowed for good heat transfer and control. It consisted of a 2 mm i.d. NMR tube coaxially inserted into a 5 mm o.d. NMR tube. The sample was placed into the 2 mm tube and filled up to the point where the diameter increased. The space between the 2 mm and 5 mm tubes was

filled with D<sub>2</sub>O. The D<sub>2</sub>O acted both as a heat transfer fluid and as an internal lock for the NMR. This apparatus provided better heat transfer (liquid–liquid vs. gas–liquid) and minimized the sample size so that less heat was generated, and resulted in more nearly isothermal reactions.

The ampoule polymerizations used for preparing samples for molecular weight used the same solutions and techniques, but were performed in a thermostatically controlled water bath. The 2 mm tubes were not inserted into the 5 mm tubes for the ampoule polymerization experiments.

The <sup>1</sup>H-NMR spectra were obtained at 299.9 MHz using a Bruker AC-300 NMR spectrometer, model number HO2129-ECL-24, S/N 0898. The data acquisition parameters utilized were as follows: pulse width = 0.5 μs (~ 5°), delay time = 8.6 s, size = 16 K, accumulation time = 1.36 s, sweep width = 6 KHz, apodisation = exponential, 0.5 Hz broadening.

### MEHQ Analysis

MEHQ and quinone were selectively measured by oxidative and reductive electrochemical detection at 700 mV and –300 mV, respectively, vs. Ag/AgCl at 2 mm glassy carbon electrodes. Quinone detection was also confirmed by ultraviolet detection at 210 nm. MEHQ was determined by liquid chromatography with oxidative electrochemical detection. A mobile phase of acetonitrile /water 30/70 (v) containing 0.02M HClO<sub>4</sub> was used at a flow rate of 1.0 mL/min. A Whatman Partisil ODS 10, 4.6 × 250 mm column was used for separation and the liquid chromatograph was a Bioanalytical Sciences BAS-200 with a thin layer cell. Detection was configured to simultaneously acquire electrochemical and ultraviolet responses.

Samples were prepared for analysis by fracturing the glass NMR tube and combining the contents with a known volume of 5% (w/w) Na<sub>2</sub>SO<sub>4</sub> solution (15–100 mL). The mixture was homogenized using a mechanical blender and the solution was allowed to stand for 10 min. Each sample was diluted 1 : 10 with a solution prepared by mixing equal volumes of 5% (w) Na<sub>2</sub>SO<sub>4</sub> and 30/70 acetonitrile/water. The diluted solution was filtered through a 0.45 μm Nylon-66 syringe filter and deoxygenated for 5 min with helium prior to injection. MEHQ was quantified by external standard analysis using a three level calibration.

For determination of MEHQ in commercial superabsorbent products, 0.100 ± 0.020 g of sample

was dissolved in 5.0 mL of 5% Na<sub>2</sub>SO<sub>4</sub>, to which was added 5.0 mL of 30/70 acetonitrile/water. The solution was filtered as above and injected.

### Molecular Weight Analysis

Molecular weights were determined by size-exclusion chromatography as described previously using polyethylene oxide standards.<sup>14</sup>

### Sodium Persulfate Analysis

Sodium persulfate was determined by liquid chromatography with electrochemical detection using the procedure of Reim et al.<sup>15</sup>

### Gel Polymerizations

The reactions were performed under an atmosphere of nitrogen in a purged 2 L glass-jacketed resin pot fitted with a stainless steel agitator and baffle assembly. The acid solutions were prepared in a 1 L beaker by adding reactants in the following order: water (408.44 g), VERSENEX 80 (1.00 g), 5% polyvinyl alcohol solution (1.50 g), trimethylpropane triacrylate (1.60 g), and acrylic acid (319.04 g). The stirred acid solution was then neutralized slowly with aqueous sodium carbonate (152.65 g sodium carbonate, and 381.63 g water), added via a separatory funnel. Using a delivery tube, the resulting monomer solution was drawn into the 30°C resin pot by vacuum while maintaining agitation, then the delivery tube was replaced with a dip tube and the stirred solution was sparged with nitrogen for 1 h. The dip tube was removed and the reaction was treated, under positive nitrogen pressure, consecutively with the following aqueous initiator solutions, each loaded in a separate syringe: (1) 10% solution of sodium persulfate (5.10 g); (2) after 2 min elapsed time, a 10% solution of sodium erythorbate (0.64 g). The reactor port was capped and polymerization begun. The temperature of the jacket was increased at a rate that matched that of the exotherm, until a peak reaction temperature of 85°C was achieved, at which time the reaction was prevented from exceeding 85°C by pulling a vacuum, and cooling the reactor jacket to 65°C. Once the reaction exotherm stopped, the vacuum was shut off and the water bath was set to 65°C. Then the nitrogen blanketed product was allowed to stir for 3 h. The resulting white crumbly polymer was dried for 16 h at 100°C. The dried polymer was

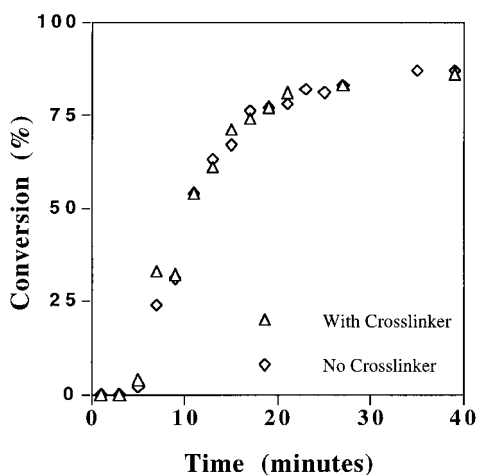
ground and screened into a narrow size fraction using U.S.A. Standard Sieves. Unreacted monomer,<sup>16</sup> soluble polymer content,<sup>17</sup> and centrifuge capacity<sup>18</sup> (swelling in 0.9% NaCl solution) were determined on the products using particles larger than a #50 screen and smaller than a #30 screen.

## RESULTS AND DISCUSSION

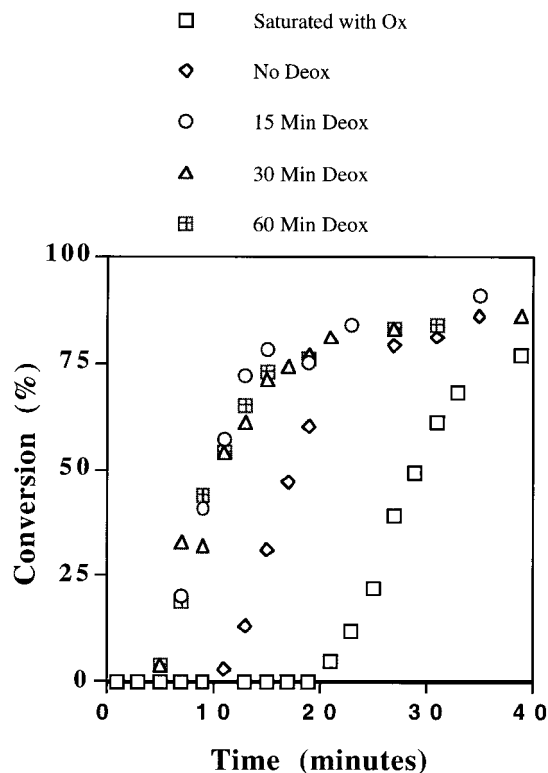
### Polymerization Rate Measurements Using <sup>1</sup>H-NMR

In one series of control experiments the rate of polymerization of a crosslinked polyacrylic acid system was compared to that of one without crosslinking. The absence of crosslinker did not reduce the rate of polymerization (Fig. 3). The high rates of polymerization of acrylic acid gave no evidence of a "gel effect" from crosslinking, at least during the first 90% conversion. It is possible that the very high molecular weights formed in this system function as "effective" crosslinks to reflect a Tromsdorff effect (slowing termination with a subsequent increase in radical concentration) throughout the course of the polymerization. It is also possible that association of the monomer with the solvent (water) through hydrogen bonding is the key element in the high polymerization rates of acrylic acid.<sup>19</sup>

The length of deoxygenation time was important for the removal of oxygen. Figure 4 shows the conversion vs. time plots taken from <sup>13</sup>C-NMR spectroscopy of samples made from the same poly-



**Figure 3** Rates of polymerization of 32% solids, 65% neutralized acrylic acid solutions at 55°C with (5000 ppm TMPTA) and without crosslinker, both containing 1600 ppm sodium persulfate (BOAA).



**Figure 4** Polymerization rate and inhibition time as a function of deoxygenation conditions.

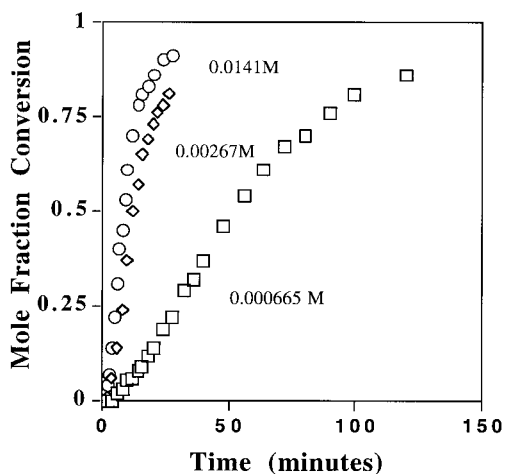
merization mixture and deoxygenated for times ranging from 0 to 60 min by bubbling nitrogen at 4.0 mL/min through 0.8 g of solution in 5 mm NMR tubes. One sample was saturated with oxygen by being aerated for 70 min. The ultimate rates of the reaction show little dependence on the deoxygenation conditions but the magnitude of the induction time depends strongly on the deoxygenation conditions. Deoxygenation for 15 min or more gave essentially equivalent kinetic data. For the remaining experiments, samples were deoxygenated for 30 min or longer. The fact that the presence of oxygen did not diminish (significantly) the rate of reaction, but rather lengthened the induction period, indicated that oxygen was an inhibitor rather than a retarder for this polymerization, consistent with the cited art. Slow leaks of air into a reaction would result in a polymerization that appears retarded.

The rates of polymerization for neutralized acrylic acid at five concentrations of MEHQ were easily obtained using the NMR technique at 55°C (Table I). The conversion time plots are shown in Figures 5 and 6 for the lowest (0 ppm) and highest

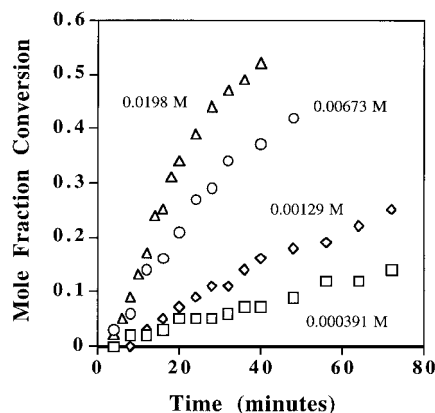
**Table I Initiator and Conversion Data for 65% Neutralized Acrylic Acid Feed Mixtures Polymerized at 55°C**

[MEHQ]	[Persulfate] (mol/L)	Pseudofirst-Order Rate Constants $k_{prop}[R\cdot]$ ( $s^{-1}$ )
0 ppm	0.000665	0.0181
	0.0141	0.139
177 ppm	0.000273	0.00472
	0.00163	0.0329
	0.00433	0.0568
	0.00872	0.0963
577 ppm	0.000232	0.00227
	0.00154	0.0259
	0.0220	0.1195
1941 ppm	0.000423	0.00381
	0.00138	0.0116
	0.00451	0.0365
	0.0104	0.0582
4844 ppm	0.000391	0.00199
	0.00129	0.00426
	0.00673	0.0154
	0.0198	0.0247

(4844 ppm) levels of MEHQ. As expected, the rate of polymerization increased with increasing persulfate content for all monomer mixtures with the varied MEHQ content. The relative rate of polymerization of the feed mixtures at any given initiator content was reduced with increasing MEHQ addition. In polymerizations where the mode of termination of the growing chain is by mutual



**Figure 5** Rate of polymerization of acrylic acid containing 0 ppm of MEHQ at varied sodium persulfate [NPS] levels.



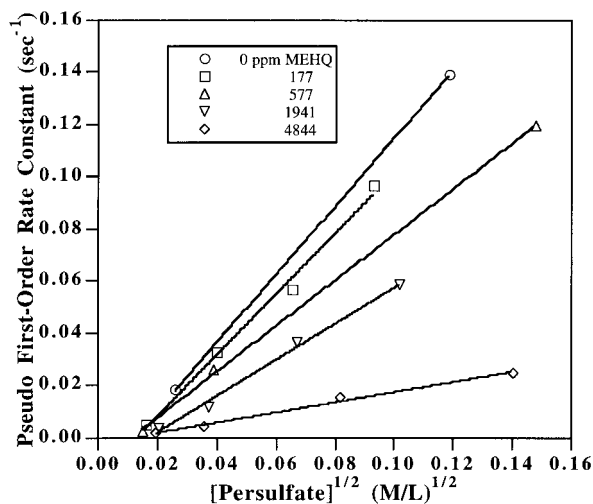
**Figure 6** Rate of polymerization of acrylic acid containing 4844 ppm of MEHQ at varied sodium persulfate [NPS] levels.

coupling of the growing polymeric radicals, the initial rate of polymerization is proportional to the square root of the initiator concentration. This square root proportionality was observed in this work and was not affected by the potential termination of growing chains by MEHQ, regardless of the MEHQ concentration or percent conversion. This will be discussed in more detail later.

To obtain the best rate values from these data, the initial slopes of the  $\ln(M_0/M)$  vs. time curves were used rather than of the conversion vs. time curves. These pseudofirst-order plots are linear for longer times, even if the reaction order is greater than one in monomer. This allows the use of more points and yields more accurate estimates of rates. The slopes of such curves can be considered pseudofirst-order constants equal to  $k_{prop}[R\cdot]$ . The values obtained are given in Table I and plotted in Figure 7.

**Direct Measurement of MEHQ and Sodium Persulfate Concentrations**

Commercial samples of polyacrylic acid superabsorbents produced by several companies were analyzed for MEHQ. Levels ranging from 16 to 84 ppm were found (Table II). Presumably the amounts found represent the amount remaining of the initial approximately 200 ppm present in commercial glacial acrylic acid used in the process. These amounts are surprisingly high, considering the fact that several thousand ppm of free radical initiators were used in the polymerization of these products, and show that significant polymerization can occur in the presence of



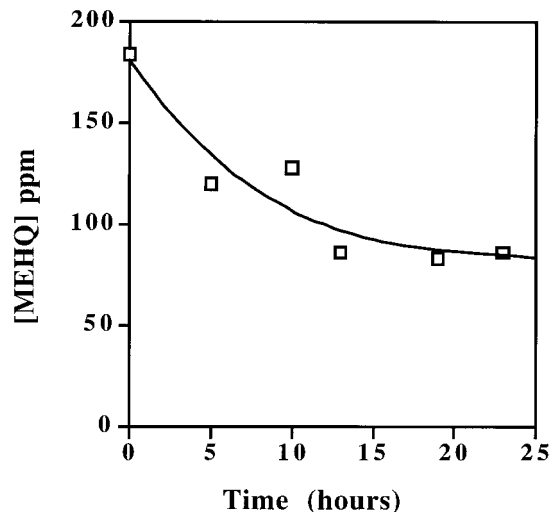
**Figure 7** Effect of MEHQ on the rate of polymerization of acrylic acid.

MEHQ, once oxygen is removed. MEHQ does not have to be consumed by the initiator in order for acrylic acid to polymerize.

The rate of consumption of MEHQ in an isothermal (55°C) acrylic acid polymerization was determined by an ampoule polymerization experiment. Glass ampoules (2 mm i.d.) were loaded with a 65% neutralized feed mixture (33.8% solids, 1600 ppm sodium persulfate) and deoxygenated by bubbling nitrogen through the solution for 30 min. The MEHQ decreased from 184 ppm (based on acrylic acid) to 85 ppm during the first 13 h of reaction at 55°C and plateaued thereafter. Continued decomposition of the persulfate did not further reduce the concentration of the MEHQ (Fig. 8). The monomer conversion to polymer was greater than 90% after 13 h. Qualitative assessment of the products showed a simultaneous decrease in the MEHQ concentration and the appearance of products attributable to an oxidation

**Table II** MEHQ Content of Commercial Superabsorbent Resins

Company	[MEHQ] (ppm)
Company A	16
Company B	32
Company C	84
Company D	67
Company E	46
Company F	46



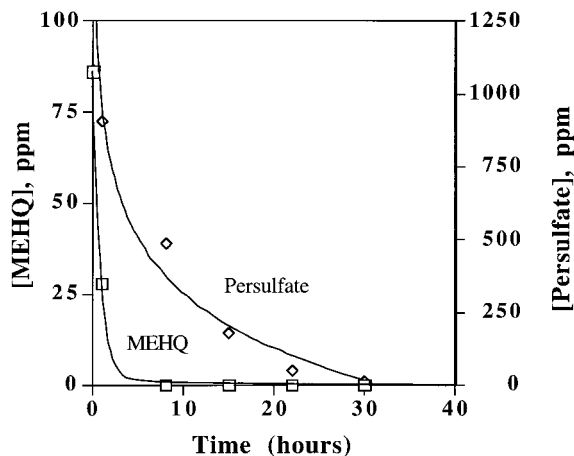
**Figure 8** Decrease in MEHQ content of a 65% neutralized acrylic acid feed mixture polymerized at 55°C.

process. The oxidation products are presumably formed through reactions between the remaining oxygen, radicals, and MEHQ during the initial part of the process. The MEHQ level in the reaction decreases initially and then reaches a plateau, probably partially depending on the initial level of oxygen present. Simultaneous acquisition of ultraviolet and oxidative and reductive electrochemical response allowed specific detection of hydroquinone and quinone species in the acrylate matrix during various stages of polymerization, but only the MEHQ concentration was quantified. Levy found that MEHQ was completely consumed when acrylic acid and AIBN were heated in the presence of oxygen without any polymerization occurring.<sup>20</sup> He ascribed a conventional inhibition mechanism to explain his results.

The fate of MEHQ and the rate of decomposition of sodium persulfate were studied in the absence of monomers. Ampoules were loaded with a water solution containing 86 ppm of MEHQ and 1079 ppm of sodium persulfate and placed in a 70°C water bath (without deoxygenation) and samples removed and analyzed for MEHQ and sodium persulfate over a 30-h period. Within 8 h the MEHQ was not detectable (less than 1 ppm). The persulfate decomposed slightly more slowly than the rate observed in buffered water. In the absence of monomer, MEHQ is rapidly oxidized by sodium persulfate as seen in Figure 9, via the Elbs reaction.

Because of the selective nature of electrochemical detection, only compounds that oxidized at 700





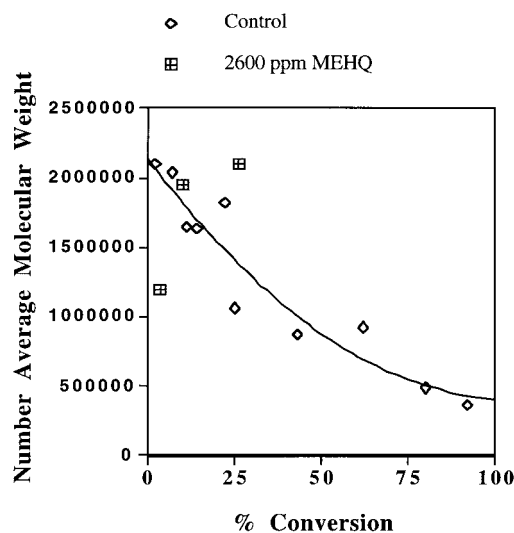
**Figure 9** Reaction of MEHQ with sodium persulfate (without deoxygenation) in water at 70°C buffered with 0.01M NaHCO<sub>3</sub>.

mV were detected. MEHQ was present in the mixture at time = 0 and at time = 1 h, but its concentration decreased to nondetectable levels within 8 h. Interestingly, three new unidentified, oxidizable compounds were detected with  $t_r = 3.1, 5.6,$  and 7.8 min. The respective concentrations of these unidentified intermediates increased during the first hour of polymerization and then decreased to nondetectable levels within 8 h. By 8 h yet another oxidizable compound was detected,  $t_r = 4.7$  min, whose concentration increased with polymerization time until the experiment was terminated (30 h). A similar pattern was observed in the simultaneous ultraviolet detector responses at 210 nm. In addition, a nonelectroactive reaction product was detected at  $t_r = 4.2$  min. A peak matching the retention time of benzoquinone ( $t_r = 3.8$  min) was observed in the simultaneous reductive electrochemical detector responses at  $t = 0$  h and whose concentration decreased to nondetectable levels between 1 and 8 h. Similar oxidative components were also observed in the polymerization study where monomer was present. No attempt was made to identify the intermediates. It is postulated that these species are oxidation and condensation products of MEHQ because this would be consistent with the Elbs reaction and most of the intermediates are more strongly retained on the reverse phase column than MEHQ.

### Molecular Weight Measurements

The effect of MEHQ on the molecular weight (MW) of the polyacrylic acid was studied at 55°C

by loading 2 mm glass ampoules with a 65% neutralized feed mixture containing 1600 ppm sodium persulfate with a total solids content of 33.8%. One sample was spiked with 2600 ppm MEHQ and one sample (control) contained the standard 177 ppm of MEHQ. The ampoules were deoxygenated for 60 min and placed in a water bath. Samples were withdrawn over a 90-min time period and analyzed for MW after hydrolysis with NaOH solution as previously described.<sup>14</sup> The conversion vs. time relationship was determined by polymerizing the same feed mixture in the NMR. The control produced polymer of very high MW at low conversion that then decreased with conversion. The feed mixture containing 2600 ppm MEHQ produced lower MW initially, but the MW did not decrease initially with conversion. The MW appeared to remain relatively constant and actually increased to a value greater than that of the control (Fig. 10 and Table III). This effect on MW is not consistent with the normal retarder effect, which reduces the rate of polymerization by terminating growing polymer chains. It is consistent with direct reaction of initiator with MEHQ. Fewer chains are thus initiated and grow to a higher MW. The low initial MW of the sample containing 2600 ppm MEHQ may be due to quinone, which is formed in the early stage of the reaction and reacts directly with the grow-



**Figure 10** Number-average molecular weight vs. conversion of polyacrylic acid polymerized at 55°C, 65% neutralized, and 1600 ppm sodium persulfate containing 177 ppm MEHQ (control) and 2600 ppm MEHQ.

**Table III Molecular Weight of Polyacrylic Acid**

[MEHQ] (ppm)	Time (min)	$M_n^a$	% Conv <sup>b</sup>
177	5	2,100,000	2
177	8	2,033,000	7
177	10	1,639,000	11
177	12	1,636,000	14
177	16	1,819,000	22
177	20	1,058,000	25
177	30	872,000	43
177	40	917,000	62
177	60	480,000	80
177	90	359,000	92
2600	10	1,197,000	3
2600	20	1,940,000	10
2600	40	2,100,000	26

<sup>a</sup> Number average molecular weight of polymer prepared at 55°C, 65% neutralized, 1600 ppm sodium persulfate, and 33.8% solids.

<sup>b</sup> Determined by parallel NMR experiment.

ing polymer chains. The concentration of quinone decreased after the initial stage of the reaction.

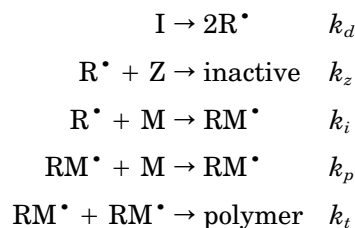
### Kinetic Model

The mechanism for inhibition/retardation implies that, if the inhibition constant  $z (=k_z/k_p)$  is large, significant polymerization will not occur until the species "Z" is completely consumed (induction period), at which time the rate is normal (inhibition). If the effect is milder ( $z$  is smaller), polymerization occurs from the outset but at a reduced rate (retardation). Initial observations of the acrylic acid system were the following: (1) in degassed runs, polymerization began almost immediately. (2) The rate was lowered by the addition of MEHQ. (3) MEHQ was found in the polymer after essentially total conversion. All of these factors indicate that MEHQ behaves like a retarder in this system. In other words, the reaction described in eq. (1) would be significant but would not prevent considerable "normal" polymerization from occurring. Referring to eq. (2), this would be a situation in which the third term ( $k_z[Z][M^*]$ ) dominates the second term ( $2k_t[M^*]^2$ ) sufficiently to reduce the rate by lowering the radical concentration. This, in turn, would imply that  $[M^*]$ , and, hence, the polymerization rate would depend on the first power of initiator. In addition, one would expect chain termination by a small molecule [eq. (1)] to result in half the average molecular weight

seen with normal recombination of growing polymer chains.

However, the rates of polymerization given in Table I depend approximately on the half power of the initiator, just as would be expected for an uninhibited reaction. Furthermore, molecular weights show either little change with increased inhibitor level or actually appear to increase (Table III).

These deviations from the expected retardation behavior can be accommodated by a mechanism where the radical originating from the initiator fragment has a noticeably different reactivity with the monomer (or the inhibitor) than do polymer-based radicals. Thus, we propose the following reaction scheme:



In this scheme the rate constant for addition of the initiator fragment to the monomer,  $k_i$ , is not necessarily equal to the propagation constant  $k_p$ . This might be due to a "cage effect," in which the initiator fragment must "break out" of a solvent cage by reacting with monomer. To describe the kinetic implications, first consider the concentration of growing polymer radicals  $[RM^*]$ , to be at steady state.

$$\begin{aligned}
 \frac{d[RM^*]}{dt} &= 0 = k_i[R^*][M] - 2k_t[RM^*]^2 \\
 [RM^*] &= \sqrt{\frac{k_i[R^*][M]}{2k_t}}
 \end{aligned}$$

Because the concentration of the initiator fragment  $[R^*]$  is also at steady state,

$$\begin{aligned}
 \frac{d[R^*]}{dt} &= 0 = 2k_d[I] - k_z[R^*][Z] - k_i[R^*][M] \\
 [R^*] &= \frac{2k_d[I]}{k_z[Z] + k_i[M]}
 \end{aligned}$$

Substitution into the expression for  $[RM^*]$  yields

**Table IV Interpolated Values of  $k_p[\text{RM}\cdot]$  at Fixed Initiator Concentrations, [I]**

MEHQ		$k_p[\text{RM}\cdot]$			
(ppm)	(mol/L)	[I] = 0.0016	[I] = 0.0032	[I] = 0.0064	[I] = 0.010
0	0	0.037	0.065	0.090	0.115
177	0.000425	0.033	0.056	0.080	0.103
577	0.00138	0.028	0.044	0.061	0.080
1941	0.00466	0.016	0.030	0.045	0.060
4844	0.0116	0.008	0.010	0.015	0.017

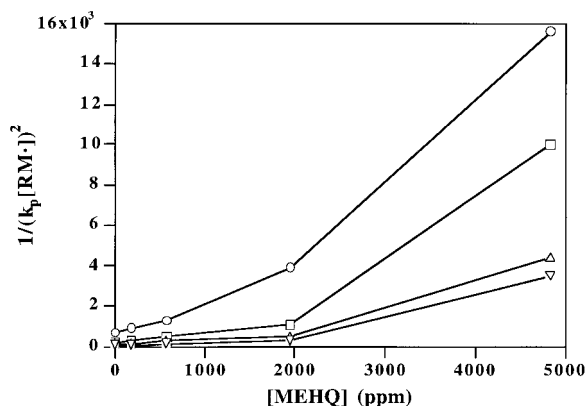
$$[\text{RM}\cdot] = \left( \frac{k_d[\text{I}]}{k_t} \right)^{1/2} \left( \frac{k_i[\text{M}]}{k_z[\text{Z}] + k_i[\text{M}]} \right)^{1/2}$$

Inverting and squaring this equation results in the following relation,

$$\frac{1}{[\text{RM}\cdot]^2} = \frac{k_t}{k_d[\text{I}]} \left( 1 + \frac{k_z[\text{Z}]}{k_i[\text{M}]} \right). \quad (7)$$

The pseudofirst-order rate constants in Table I are equal to  $k_p[\text{RM}\cdot]$ . A plot of  $1/(k_p[\text{RM}\cdot])^2$  vs.  $[\text{Z}]$  at various  $[\text{I}]$  would allow the determination of  $k_z/k_i$ . Because the data in Figure 7 represent several runs, at fixed levels of inhibitor and varying levels of initiator, interpolated values for the pseudorate constants at fixed initiator values were determined. These interpolations are given in Table IV. The plot of all the data in the form representing eq. (7) is given in Figure 11.

It is apparent that these are not linear plots; indeed, they appear almost second order. How-

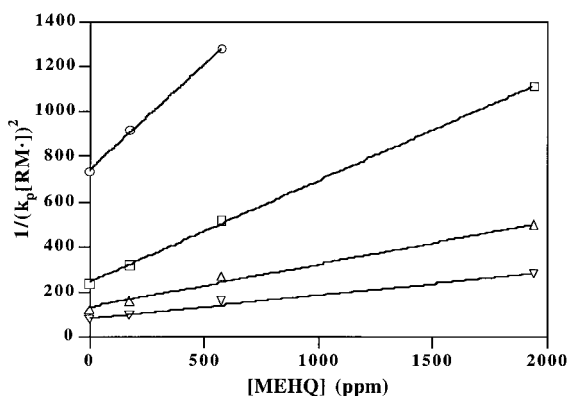


**Figure 11** Dependence of inverse square of rate on initiator concentration (all data).  $\circ$  [I] = 0.0016; [I] = 0.0032;  $\triangle$  [I] = 0.0064;  $\nabla$  [I] = 0.010.

ever, the first four levels of inhibitor are nearly linear. It is reasonable that at very high levels of inhibitor the model may break down. High quinone levels at the higher MEHQ concentrations would be expected to add an additional inhibiting effect by the direct termination mechanism. The revised plot showing the lower inhibitor levels is given in Figure 12.

The inhibition constant,  $k_z/k_i$  for any data set (value of  $[\text{I}]$ ), can be obtained by dividing the appropriate slope in Figure 12 by the corresponding intercept and correct for the initial monomer concentration (constant at 4.5 mol/liter). The values are given in Table V.

These values are remarkably constant. They are rather high if compared to the values for the inhibition constant  $z (= k_z/k_p)$  given by Odian.<sup>2</sup> It should be noted, however, that  $k_i$  in this system is probably significantly smaller than  $k_p$ . If  $k_i$  were equal to or greater than  $k_p$ , there would be no apparent effect on the kinetics because nothing would react with the initiator fragment but monomer. Because  $k_i$  must be smaller than  $k_p$ ,  $k_z/k_i$



**Figure 12** Portion of Figure 11 at MEHQ concentrations below 2000 ppm.  $\circ$  [I] = 0.0016; [I] = 0.0032;  $\triangle$  [I] = 0.0064;  $\nabla$  [I] = 0.010.

would be larger than the value expected for  $k_z/k_p$ . This is the case and thus internally consistent.

#### Superabsorbents Prepared with Varied MEHQ Content in the Monomer

Laboratory batch polymerizations were conducted with feed compositions containing 10 ppm, 177 ppm, and 2600 ppm MEHQ (BOAA). The acid containing 10 ppm MEHQ was prepared by recrystallization of glacial acrylic acid. The properties of the materials are shown in Table VI. The polymerization rate reduction caused by high levels of MEHQ (Fig. 7) delayed the peak exotherm from 21 min (10 ppm MEHQ) to 46 min (2000 ppm MEHQ) and resulted in higher levels of residual acrylic acid at the end of the polymerization. The level of soluble polymer in the three samples containing from 10 to 2600 ppm of MEHQ was not significantly different, but the centrifuge capacity decreased as the MEHQ level was increased, even though the crosslinker concentration was constant, consistent with the formation of higher MW polyacrylic acid (Table VI).

#### CONCLUSIONS

The effects of MEHQ on the polymerization of acrylic acid under conditions similar to the commercial production of polyacrylic acid superabsorbents were determined. Oxygen has been shown to be an inhibitor while MEHQ functions as a retarder in the polymerization of acrylic acid. The mechanism of MEHQ retardation appears to be through direct reaction with initiator fragments and not by termination of growing polymer chains. By this mechanism, the rate of polymerization is reduced, but the molecular weight is not. An inhibition constant for MEHQ in acrylic acid at 55°C was determined to be in the range of

**Table V Ratio of Rate Constants at Various Initiator Concentrations**

Interpolated [I]	$k_z/k_i$
0.0016	2405
0.0036	3506
0.0064	2711
0.01	2409
0.0144	2523

**Table VI Properties of Superabsorbents Made with Varied MEHQ Content**

[MEHQ] (ppm)	Centrifuge Capacity (g/g)	Soluble Polymer (%)	Residual Monomer (ppm)
10	30.7	1.9	320
177	26.1	2.1	650
2600	24.6	2.8	8090

2400–3500, based on a modified definition, which accounts for the effect being through a direct reaction of the initiating species and MEHQ. The initial rate of polymerization of acrylic acid at all levels of MEHQ was shown to be proportional to the half power of the initiator concentration. From 8–42% of the MEHQ present in commercial glacial acrylic acid is not consumed during polymerization and remains in polyacrylic acid superabsorbent resins. In the absence of monomers, MEHQ is rapidly consumed by direct reaction with sodium persulfate, presumably by way of the Elbs reaction. The NMR technique used in this study to monitor kinetics is versatile and should be useful for studying other systems.

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#### REFERENCES

1. G. G. Blauer, *Trans. Faraday Soc.*, **56**, 606 (1960).
2. G. Odian, *Principles of Polymerization*, 2nd ed., Wiley-Interscience, New York, 1981, p. 243.
3. G. C. Eastmond, in *Comprehensive Chemical Kinetics*, Vol. 14A, C. H. Bamford and C. F. H. Tipper, Eds., American Elsevier, New York, 1976.
4. J. Brandup and E. H. M. Immergut, McDowell, W., *Polymer Handbook*, J. Brandup and E. H. M. Immergut, Eds., Wiley-Interscience, New York, 1975.
5. A. A. Yassin and N. A. Risk, *Polymer*, **19**, 57 (1978).
6. A. A. Yassin and N. A. Risk, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1475 (1978).
7. A. A. Yassin and N. A. Risk, *Eur. Polym. J.*, **13**, 441 (1977).
8. L. B. Levy, *J. Polym. Sci.*, **23**, 1505 (1985).
9. K. K. Georgieff, *J. Appl. Polym. Sci.*, **9**, 2009 (1965).

10. K. Elbs, *J. Prakt. Chem.*, **48**, 179 (1893).
11. S. M. Sethna, *Chem. Rev.*, **49**, 91 (1951).
12. C. E. Barnes, *J. Am. Chem. Soc.*, **67**, 217 (1945).
13. J. J. Kurland, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1139 (1980).
14. S. S. Cutié and S. J. Martin, *J. Appl. Polym. Sci.*, **55**, 605 (1995).
15. J. D. McLean and R. E. Reim, *Am. Lab.*, **March**, 122 (1983).
16. S. S. Cutié, W. C. Buzanowski, and J. A. Berdasco, *J. Chromatogr.*, **513**, 93 (1990).
17. S. S. Cutié, G. J. Kallos, and P. B. Smith, *J. Chromatogr.*, **408**, 349 (1987).
18. S. K. Byerly, D. G. Iwanski, and S. R. Kellenberger, Eur. Pat. Appl. 532002 A1 (to Kimberly-Clark Corporation) (1992).
19. A. Chapiro and J. Dulieu, *Eur. Polym. J.*, **13**, 563 (1977).
20. L. B. Levy, *J. Polym. Sci., Part A*, **30**, 569 (1992).