dl/g (TFA, 1g/100 ml, 25°); nmr (TFA) $\delta$ 1.06 (6 $CH_3$), $\delta$ 4.20 (4 $-OCH_2-$), $\delta$ 4.53 (4 $PhCH_2$), $\delta$ 7.3 (4 amine aromatic), $\delta$ 8.2 (2 1,2,4,5-tetrasubstituted phenyl); ir (Nujol mull) 3380 (NH), 1630 ($-C(O)O-$), 1,2,4,5-tetrasubstituted phenyl 1525 $cm^{-1}$.

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# Thermal Polymerization of Dimethylaminoethyl Methacrylate

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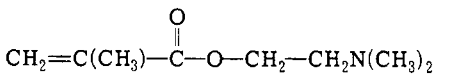
*Received October 16, 1974*

ABSTRACT: The existence of a self-catalyzed or "thermal" polymerization is reported for dimethylaminoethyl methacrylate. Evidence is provided to indicate that the polymerization is free radical in mechanism. The kinetics are observed to be: $R_p = k[\text{monomer}]^{3/2}$. A mechanism for the polymization is proposed.

The preparation of aminoalkyl acrylates was first reported in the patent literature. A British patent was awarded to E. I. du Pont deNemours and Co. in 1937 for the preparation of dimethylaminoethyl methacrylate (DMAEM) from dimethylaminoethanol and methyl methacrylate by heating in benzene in the presence of *p*-phenylenediamine as an inhibitor of polymerization and sodium methoxide.[1] In 1938, Graves prepared several monomeric amino acrylates by treating acrylyl halide with amino alcohol in the presence of a polymerization inhibitor and an inert solvent such as benzene, toluene, or dioxane.[2] A Swiss patent was issued to Voelker, Hering, and Zweifel in 1968 for the preparation of aminoacrylic esters in a high yield by the butyl orthotitanate catalyzed transesterification of isopropyl acrylate with the appropriate amino alcohol.[3,4] Agadzhanyan and Amboyan described the preparation of DMAEM in 60–80% yield by the reaction of $\beta$-chloroacyl chloride with dimethylaminoethanol.[5]



$$CH_2{=}C(CH_3){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}CH_2N(CH_3)_2$$

DMAEM

The first attempt to homopolymerize DMAEM was in 1949. It was found that benzoyl peroxide would not readily initiate the polymerization of DMAEM,[2] but that uv light[6] or azo-type initiators[7] were successful. Dimethylaminoethyl methacrylate and acrylate were radical polymerized in bulk, the acrylate giving higher initial rates.[8]

DMAEM was selected for study becuase of the presence of a tertiary amino group which could come into the vicinity of the double bond thereby exerting an effect on the polymerization reaction. The kinetics of the polymerization with azo initiator in bulk and in solution were studied by Griswold,[9] Ling,[10] and Dewey.[11] The rate law for initiated radical polymerization of DMAEM was given by the following equation.

$$R_p = k[\text{monomer}][\text{initiator}]^{1/2}$$

They observed that DMAEM polymerized without the free radical initiator at a significant rate. At 60°, DMAEM showed a self-initiation rate of polymerization of 1.2%/hr in bulk.[10] We now report an extended study of this self-initiation.

## Experimental Section

**Purification of Monomer.** The monomer, DMAEM, was donated by Rohm and Haas Co. and contained 2,000 ppm of the monomethyl ether of hydroquinone (MEHQ) as an inhibitor of polymerization for shipping.

The method described by Griswold for the extraction of the inhibitor[9] was modified. The inhibited monomer was shaken five times with solutions each 5% in sodium hydroxide and 25% in sodium chloride. The monomer was then centrifuged for 15 min to remove turbidity and stored at 0° over anhydrous sodium sulfate. The infrared spectrum of the monomer at this point showed a strong absorption band indicating the presence of water. The wet monomer was mixed with cyclohexane and stored over anhydrous calcium chloride for at least 12 hr. No detectable water then remained in the monomer solution. Where desired the cyclohexane was removed by distillation under vacuum (15 mm and 18°) without polymerization. Purified DMAEM was stored at −5° in a brown glass bottle covered with aluminum foil.

**Polymerization of Monomer.** All glassware was boiled with nitric acid, rinsed several times with distilled water, and then dried in an oven. Reaction tubes were prepared from 12-mm Pyrex tubing constricted in the center to facilitate closing the tube with a torch later. The tubes were wrapped in aluminum foil to exclude light. Samples of DMAEM were prepared by weight at desired dilutions in redistilled reagent grade cyclohexane, and approximately 3 ml of the sample was placed in each of the reaction tubes. The tubes were connected to a high vacuum manifold, frozen with liquid nitrogen, evacuated, and sealed with a torch. At zero time the tubes were placed in a constant temperature bath at 60° and each was incubated for an appropriate period of time. The reaction was stopped by freezing the tube.

**Table I**
**Thermal Polymerization of 40% DMAEM in Cyclohexane**

| Time of polymerization, hr | Absorbance at 220 nm | Corrected absorbance | % polymerization |
|---|---|---|---|
| 0 | 72.5 × $10^{-2}$ | 72.5 × $10^{-2}$ | 0 |
| 19.5 | 64.0 | 65.4 | 9.75 |
| 37.5 | 55.5 | 60.8 | 16.2 |
| 60 | 38 | 45.4 | 37.4 |
| 80 | 26 | 36.5 | 49.65 |

For assay, 1 ml of the reaction mixture was pipeted into a preweighed 10 ml volumetric flask, weighed, diluted to 10 ml with cyclohexane, and then weighed again. This process was repeated until a monomer dilution of 4 parts to 100,000 was obtained. The uv spectrum was read in matched 1-cm silica cells in a Beckman DK-2A spectrophotometer scanning down to 220 nm. The observed absorbances were then corrected for dilution variations as calculated from the weighings. Since the polymer had no appreciable absorbance down to 200 nm, percent polymerization was calculated by assuming zero absorbance represented 100% polymerization. The monomer adhered to Beer's law across the concentration range utilized.

In preliminary studies a vessel was used in which the total sample could be flushed by bubbling with nitrogen and run as a closed system. By use of nitrogen pressure, samples could be removed at intervals to observe the progress of the reaction spectrophotometrically.

## Results

The results of the preliminary experiments utilizing nitrogen flushing for oxygen removal are represented by the polymerization of 40% by weight purified DMAEM in cyclohexane (Table I). Using the freezing and evacuation technique for oxygen removal, polymerizations were run at a variety of monomer concentrations in cyclohexane. Those in the range of interest are presented in Figure 1.

Monomer samples which contained 2000 ppm MEHQ, but from which oxygen had been removed, were incubated for 24 hr at 60°. These showed small but detectable polymerization. Bulk monomer or 40% monomer in cyclohexane containing 2000 ppm and 800 ppm MEHQ respectively and from which the oxygen had not been removed did not polymerize at all at 60° in 24 hr. Monomer free of MEHQ but flushed for 30 min with oxygen at room temperature also did not polymerize measurably at 60° in 24 hr.

## Discussion

The project was originally undertaken to assess the effect of the pendant tertiary amine group of DMAEM on the polymerization. Early experiments, using bulk or solution polymerization[9-11] and 2,2′-azobis(2-methylpropionitrile) as a free radical initiator, showed that as the concentration of initiator was reduced to low levels (below 5 × $10^{-4}$ *M* in the case of bulk polymerization) the rate was clearly tending toward a minimum finite rate, rather than toward a rate of zero. In bulk this minimum rate of polymerization in the absence of initiator was reproducible under the experimental conditions used.

It was suspected that the pendant amine group could be an important factor in this thermal polymerization. It was easy to imagine the amine group bending into the vicinity of the double bond acting as an ionic catalyst. In order to pursue this possibility, the thermal polymerization was studied to determine whether it is ionic or free radical in mechanism. The technical bulletin supplied by Rohm and Haas[12] indicates that the effectiveness of MEHQ as an inhibitor of polymerization depends on its interaction with oxygen. The effectiveness of oxygen as an inhibitor was established by the several specific experiments described under the Results section. In addition, polymerizations performed without initiator using the technique of flushing with nitrogen led to lower rates of polymerization than were obtained with the freezing and evacuating technique. As a specific example, in 20 hr at 60° the solution of 40% DMAEM in cyclohexane polymerized 10% with flushing and 30% with freezing and evacuating. This difference was ascribed to less complete removal of oxygen by nitrogen flushing. The effectiveness of oxygen as an inhibitor argues for a free-radical mechanism.

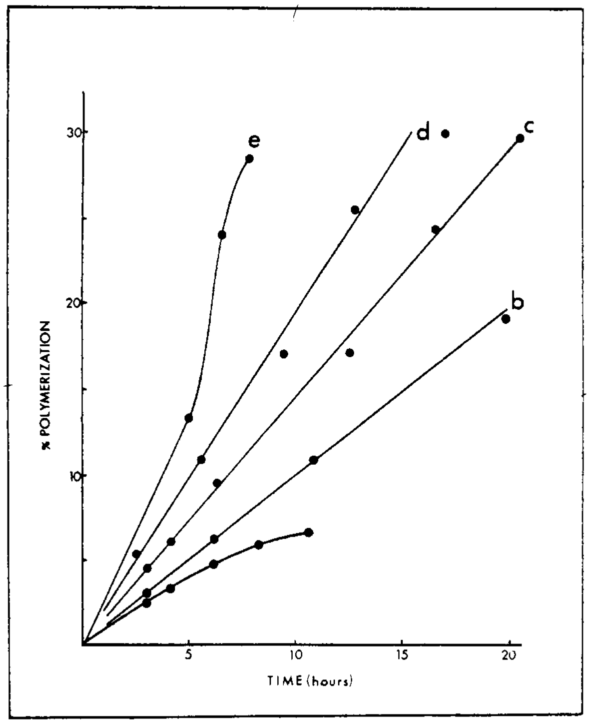


**Figure 1.** The course of the polymerization of various concentrations of DMAEM in cyclohexane at 60°: (a) 20%; (b) 30%; (c) 40%; (d) 50%; (e) 60% by weight.

To obtain further evidence pertinent to the mechanism of the thermal polymerization the reaction was run at 60° with a variety of monomer concentrations in cyclohexane. At concentrations of monomer 60% and above the rate of polymerization increased as the polymerization proceeded. This behavior is analogous to the gel effect displayed by methyl methacrylate,[13,14] and is ascribed to reduced rates of termination in the higher viscosity solution. This restricted our efforts to determine the order of the reaction with respect to monomer to the study of more dilute solutions. In the range from 20 to 60% the data were useful. Our treatment of these data indicated that the rate was proportional to the $^3\!/_2$ power of monomer concentration (Figure 2). This result is also inconsistant with the proposal that the self-catalysis was ionic.

The mechanism of the free radical initiation by which certain monomers undergo spontaneous thermal polymerization has been a subject of interest for several years. Styrene was reported in 1936 to display self-initiated polymerization,[15] and was shown to attain a rate of 0.1%/hr at 60° and 14%/hr at 127°. Methyl methacrylate (MMA) polymerizes without initiator at about 1% of that rate[16] although methyl acrylate does not exhibit thermal polymerization. Pentafluorostyrene (PFS) and 2,6-dichlorostyrene (DCS) also display thermal polymerization. PFS polymerizes at a rate of 0.028%/hr at 60°, comparable to that of styrene.[20b]

Conjecture about the mechanism for the initiator of sty-

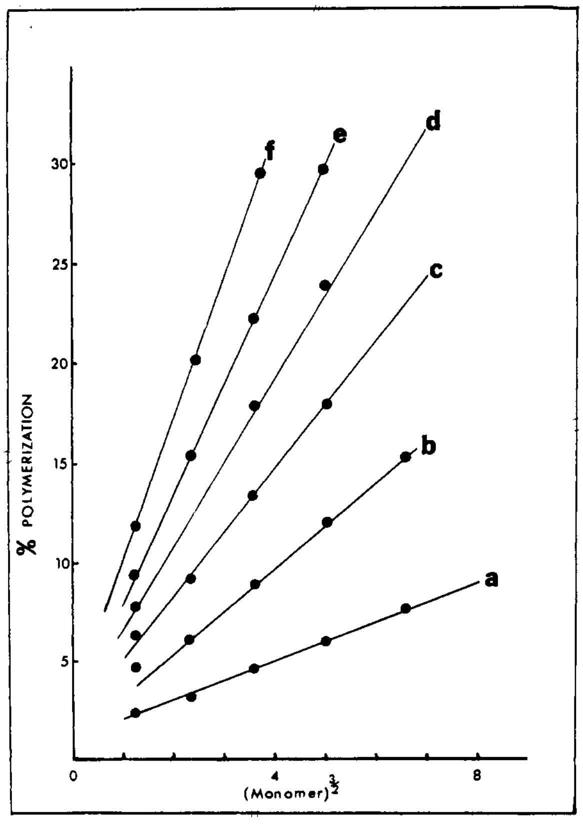


**Figure 2.** Plots of percent polymerization versus [DMAEM]$^{3/2}$ at the following time intervals in hours: (a) 3; (b) 6; (c) 9; (d) 12; (e) 16; (f) 20.

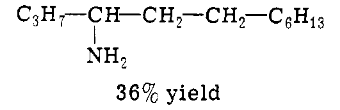
rene thermal polymerization has centered on two proposals. Flory[15d] suggested the formation of a 1,4 diradical by collision of two styrene molecules followed by propagation from both ends or transfer to monomer producing two monoradicals which would then propagate separately.

$$2ArCH{=}CH_2 \longrightarrow Ar{-}\dot{C}H{-}CH_2{-}CH_2{-}\dot{C}H{-}Ar$$

This diradical mechanism was argued against on the basis that diradicals would be more likely to cyclize than to propagate or transfer.[17] The initiation step was found to be termolecular[17c,18] and a mechanism was devised by Mayo[19] involving the formation of a Diels–Alder dimer followed by molecule-induced homolysis with another styrene to generate two monoradicals. This proposal has been supported by isolation of dimers and trimers, by kinetics studies, and by isotope studies.[17c,18,20] Pryor, however, has recently revived the 1,4 diradical as representing 0.01 to 1% of styrene thermal initiation[21] and suggests it may be the mechanism for MMA, PFS, and DCS.

The relatively high rate observed for the thermal polymerization of DMAEM imposes the requirement for an unusually favorable mechanism. Considering the similarity of the structure to that of methyl methacrylate, one is drawn to the structural difference, the pendant amine group, to explain the relatively much greater rate of polymerization of DMAEM.

It has been reported that in the presence of free radical initiators amines can be added to terminal olefins.[22,23]

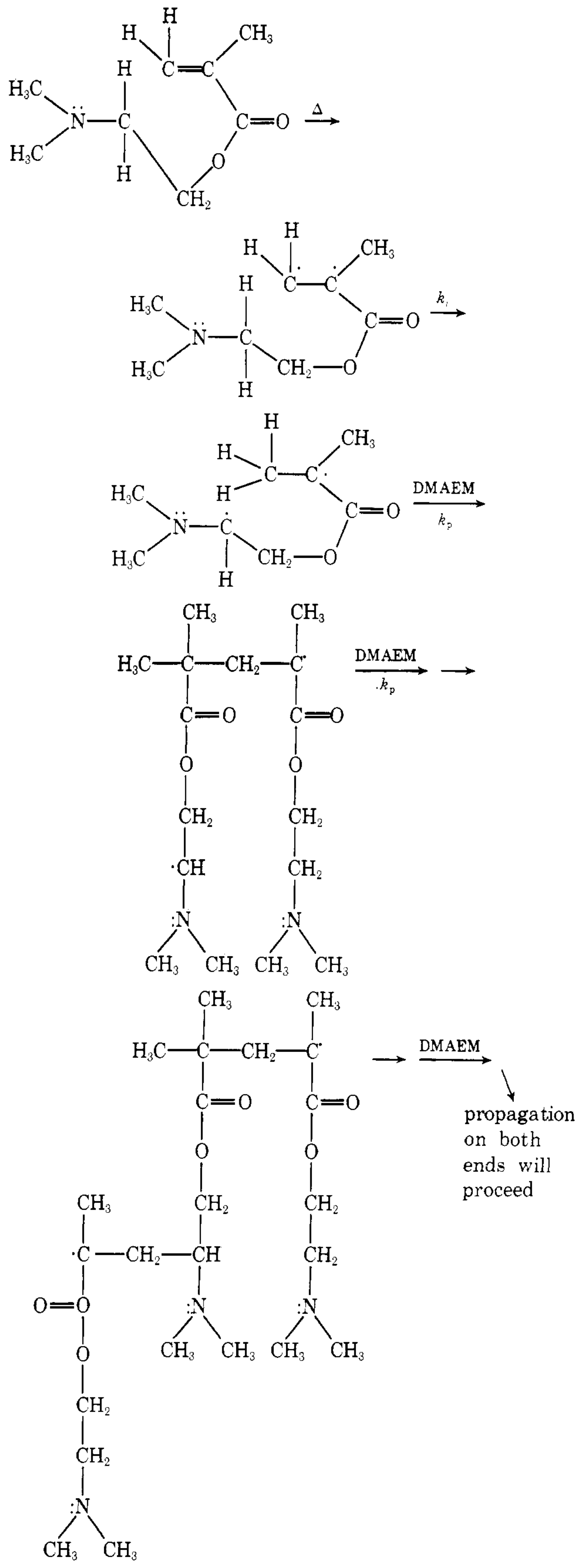


$$C_3H_7{-}CH_2{-}NH_2 + CH_2{=}CH{-}C_6H_{13} \xrightarrow[\text{tert-butyl peroxide}]{125^\circ} C_3H_7{-}\underset{NH_2}{\underset{|}{C}H}{-}CH_2{-}CH_2{-}C_6H_{13}$$

36% yield

This reaction proceeds through abstraction of hydrogen from the carbon adjacent to the amine by a radical. The selectivity for abstraction of that hydrogen is due to the great importance of polarity in the stabilization of the transition state for the formation of $\alpha$-amino radical.[24] Several $\alpha$-ami-

Scheme I



noalkyl radicals have been studied by esr.[25] Other examples of formation of the α-aminoalkyl radical include the cyclization of ethylenic amines[26] and the functioning of triethylamine as a chain transfer agent when used as a solvent for a free radical polymerization.[27]

We propose as a possible mechanism for the thermal polymerization of DMAEM the formation of stable diradical and the stabilization of that diradical by an abstraction of the hydrogen on the carbon α to the nitrogen by the terminal carbon of the double bond. The resulting stabilized diradical could then extend by the usual mechanisms of free radical propagation (Scheme I) at both free radical positions.

The formation of the diradical is favorable because each radical is stabilized by its neighboring group. The radical on the carbon α to the carbonyl group is an allylic radical, and is further stabilized by the inductive effect of the two methyl groups. The radical on the carbon α to the nitrogen is stabilized through delocalization of its spin density by the adjacent nitrogen.

We have no evidence as to whether or not the diradical could cyclize to form a γ lactone. If cyclization did take place, even if it were favored, it would be expected to produce a relatively low yield of lactone when compared to the amount of DMAEM used by polymerization reactions. If the initial diradical intermediate were in the triplet state this cyclization would not be expected to occur.

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# Polymeric Reagents. Preparation of Resins Containing Polyvinylperbenzoic Acid Units[1]

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*Received December 2, 1974*

ABSTRACT: Several synthetic routes to bead polymers containing peracid functional groups have been explored. Thus, swellable or macroreticular styrene-divinylbenzene copolymers containing approximately 1 mequiv of perbenzoic acid functional group per gram were prepared from resins containing vinylbenzoic acid, vinylbenzoyl chloride, or vinylbenzaldehyde units. The polymeric peracids were stable and could be used and regenerated several times without degradation. The use of the polymers in a simple epoxidation reaction is described.

Following the success of the Merrifield approach to the synthesis of polypeptides,[2] insoluble polymeric supports have been used successfully in the synthesis of polynucleotides[3] and polysaccharides.[4] More recently much attention has been devoted to the use of polymers as chemical reagents; thus, polymeric anhydrides,[5] oxygen-transfer resins,[6,7] Wittig resins,[8] polymeric carbodiimides,[9] N-halogenated polymers,[10] and several other interesting reagents have been prepared. Other applications of polymers in organic synthesis include the use of polymers as temporary blocking groups for the selective synthesis of symmetrical bifunctional molecules,[11] as supports in the Dieckmann condensation of mixed esters,[12] as sensitizers in photochemical reactions,[13] and as catalysts.[14]

The main advantage of polymeric reagents over their monomeric counterparts is the ease of separation of the excess reagent and by-product from the desired product of the reaction. Other advantages and properties of polymeric reagents have been reviewed recently.[15]

Polymeric peroxides were prepared as early as 1964 by Helfferich and Luten;[6] their product was a copolymer containing sulfonic as well as carboxylic acid residues and could be used to prepare α-glycols from alkenes. However, the polymers were fragile and could only be used for a few oxidation–reduction cycles. Furthermore, their use was limited to reactions in aqueous solvents. In a more recent