Cyclopolymerization Kinetics of Dimethyl Diallyl Ammonium Chloride

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ABSTRACT

A survey is made of the present knowledge about the kinetics and
mechanism of the radical cyclopolymerization of dimethyl diallyl
ammonium chloride which results in soluble, strong cationic poly-
electrolytes. The kinetic analysis, taking into consideration near-
ly complete cyclization, a linear increase of $k_p/k_t^{0.5}$ with $[M]$,
and different mechanism of initiation depending on the nature of
the initiator, leads to rate equations which fit the experimental
data well. Initiation with $S_2O_8^{2-}$ has the following peculiarities:
formation of primary radicals by redox reaction with chloride
ions and interaction with the monomer cation, additional termina-
tion by chlorine atoms, and an experimental chain transfer con-
stant to monomer which includes transfer to monomer and ter-
mination by chlorine radicals.

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INTRODUCTION

The radical polymerization of dimethyl diallyl ammonium chloride (DMDAAC) in water solution results in soluble polyelectrolytes [1, 2]. Thirty years ago this observation by Butler et al. led to the first synthesis of a linear polymer by cyclopolymerization [3] of a nonconjugated diene. Since that time cyclopolymerization has become well established and numerous dienes have been investigated. The results are discussed in several reviews [4-9], but only a few papers dealing with the cyclopolymerization of DMDAAC have been published. This is a little surprising because poly-DMDAAC is an agent for a great number of applications [10-15]. Because of its cationic charges, poly-DMDAAC is not only water soluble but also electroconductive and can interact with ions and colloids of opposite charge (the majority of organic colloids in wastewater). Therefore, its main applications are as a flocculant, retention agent, antistatic agent, and electroconductive coating. Because of its quaternary ammonium groups, poly-DMDAAC is a biocide against bacteria, algae, and fungi.

In general, cyclopolymerization of 1,6-dienes can result in polymers with five- and/or six-membered rings in the main chain [8, 9, 16]. With DMDAAC as a monomer, five-membered rings are exclusively formed. Only configurational isomers of quaternary pyrrolidinium rings were detected by ^{13}C-NMR spectroscopy [16, 17]. By varying the conditions of synthesis, e.g., change of solvent, anionic or radiation initiation, or variation of one substituent at the nitrogen atom (methyl benzyl diallyl ammonium chloride), no effects on the size of the ring and no change of the 6:1 ratio of cis- and trans-substitution at the pyrrolidinium ring were found [16]. The degree of cyclization is usually high with symmetrical 1,6-dienes [5, 8, 9, 16]. This general rule holds in the case of DMDAAC, too. Poly-DMDAAC obtained by free radical polymerization in water contains only 0.1-3% double bonds, as detected by radiochemical determination of residual double bonds with ^{203}Hg-acetate after thin-layer chromatographic separation of the hydroxymercurated products. From these results the ratio of rate constants of cyclization and of linear propagation with the formation of pendant double bonds was calculated to be greater than 10^2 mol/L [16]. Thus, poly-DMDAAC contains mainly pyrrolidinium rings, connected with $-CH_2-CH_2-$ bridges in the 3,4-position, and a small amount of pendant double bonds formed by linear chain propagation of the monomer, as shown in Fig. 1.

Investigations of the overall kinetics of radical cyclopolymerization of DMDAAC in aqueous solution using persulfate as initiator resulted in distinct deviations from the usual model of radical polymerization. With monomer concentrations up to 4 mol/L a constant exponent of initiator concentration of 0.80 ± 0.04 was found. At monomer

> 97%   < 3%

cis—trans ratio 6:1
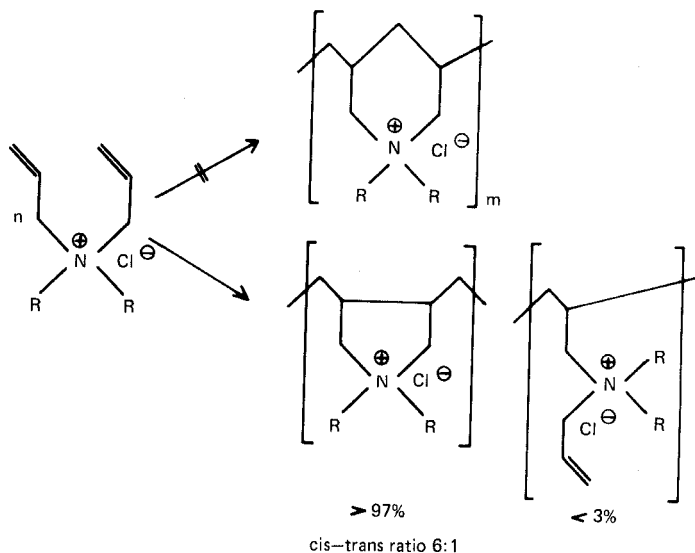
FIG. 1. Chemical structure of poly(dialkyl diallyl ammonium chlorides). $R = CH_3$, $CH_2C_6H_5$. Solvents: water, acetone, dimethylformamide, tetramethyl urea. Initiation: radical, anionic, γ-radiation.

concentrations > 1.5 mol/L a constant monomer exponent of 2.9 ± 0.2 was obtained. Thus, the overall rate equation

$$R_p = k[I]^{0.8}[M]^{2.9} \qquad (1)$$

is valid [18, 19].

The unusual exponents of [I] and [M] have been discussed in terms of an increase of the rate constant of propagation k_p with increasing monomer concentration and of degradative chain transfer [18-20], but the mechanism of this polymerization has not been completely understood until now.

EXPERIMENTAL

DMDAAC was prepared by the method of Harada [21, 22]. Polymerizations were carried out with oxygen-free solutions of the mono-

mer in bidistilled water. The kinetics were determined by a sensi-
tive method of density measurement [23] as described previously
[24, 25] and now used by several other authors [26, 27]. The method
is based on measuring the time of vibration of a capillary tube fixed
at both its ends after electronic excitation. The frequency depends
on the density of the filling. Consequently, polymerizations in the
capillary tube result in a continuous change of the time of vibration.
The continuously obtained density-time curve can be converted to a
conversion-time curve by suitable calibration. With DMDAAC it is
possible to measure conversion changes of 0.01 to 0.1%; the higher
the monomer concentration, the smaller the error. At 5% conversion
the error amounts to ±0.1 to ±1.0% [25]. In some cases we used an
automatically recording dilatometer with equivalent sensitivity [28].

Determination of the molecular weight was carried out by vis-
cometric measurements of polymer solutions in 1 $\underline{N}$ aqueous NaCl
using the relationship [29]

$$[\eta] = 1.12 \times 10^{-4} \, \overline{M}_n^{\,0.82}$$

RESULTS AND DISCUSSION

Initiation with Persulfate. Discussion of an Extended Overall Rate Equation

In order to obtain an explanation for the unusual exponents of the
experimental overall rate Eq. (1), we first made a more detailed
kinetic analysis by taking into consideration the following two experi-
mental results [20].

A Linear Increase of $k_p/k_t^{\,0.5}$ with [M] as Shown in Fig. 2

The reason may be an association of two monomer molecules sup-
ported by $\pi - \pi$ interaction and/or a decrease of electrostatic repulsion
between the growing cation radical and the monomer cation with in-
creasing ionic strength (i.e., increasing monomer concentration). As
the viscosity of aqueous solutions of DMDAAC only slightly increases
with monomer concentration, it may be concluded that k_t remains con-
stant in the investigated range of concentration and (low) conversion,
but k_p increases linearly with increasing [M]. Consequently, R_p
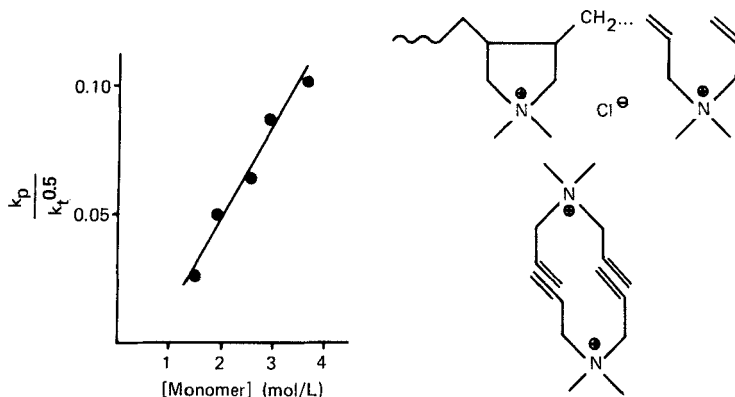should be of second-order dependence on monomer concentration.

FIG. 2. Radical polymerization of DMDAAC. Dependence of $k_p/k_t^{0.5}$ on [M] due to monomer association and/or formation of ion pairs.

Degradative Chain Transfer to the Monomer

$(k_{fM} = (2.5 \pm 0.6) \times 10^{-3}; \; 35°C) [19]$

Balance equations [20] of the different types of radicals ($P_1^{\bullet}$ = polymer radical formed by radical addition of a monomer molecule M, $P_2^{\bullet}$ = polymer radical formed by cyclization of $P_1^{\bullet}$, $M_1^{\bullet*}$ = monomer radical formed by chain transfer), assuming steady-state conditions, result in

$$R_i = k_t[P_2^{\bullet}]^2 + 2k_{tM}[P_2^{\bullet}][M_1^{\bullet*}] + k_{tMM}[M_1^{\bullet*}]^2 \qquad (2)$$

which, together with the above-mentioned balance equations, leads to

$$\left(\frac{R_i}{k_t}\right)^{0.5} = [P_2^{\bullet}] \; \frac{k_{iM}[M]/\sigma + (R_i k_t)^{0.5} + k_{fM}[M]}{k_{iM}[M]/\sigma + (R_i k_t)^{0.5}} \qquad (3)$$

an equation with only a single radical concentration.

Under steady-state conditions the usual overall rate equation of radical cyclopolymerization with complete cyclization is

$$R_p = k_c[P_1^{\bullet}] + k_{21}[P_2^{\bullet}][M] \qquad (4)$$

which can be simplified to

$$R_p = 2k_{21}[P_2^\bullet][M] \tag{5}$$

(because in this case $[P_1^\bullet] = \dfrac{k_{21}}{k_c}[P_2^\bullet][M]$)

By substitution of $[P_2^\bullet]$ with Eq. (3) and taking into consideration the experimental result (Fig. 2):

$$k_{21} = k_p = \alpha + \beta[M] \tag{6}$$

we obtain the extended overall rate equation

$$R_p = 2(\alpha + \beta[M])[M](R_i/k_t)^{0.5}[k_{iM}[M]/\sigma + (R_i k_t)^{0.5}][k_{iM}[M]/\sigma +$$

$$(R_i k_t)^{0.5} + k_{fM}[M]]^{-1} \tag{7}$$

To determine the exponents of [I] and [M], the logarithmic form of (7) has to be differentiated with respect to $\ln R_i$ and $\ln [M]$, respectively. The resulting equations illustrate that the increase of the exponents may be due to chain transfer and to the dependence of k_p on [M] according to Eq. (6); in this treatment the exponents are not constant but depend on [M]. If we assume an increase of R_i with increasing [M] according to

$$R_i = c^2[M]^2 \tag{8}$$

and additionally $\alpha \to 0$, we obtain Eq. (9) containing only constants which allow determination of a constant initiator exponent;

$$\frac{d \ln R_p}{d \ln R_i} = 0.5 + 0.5\frac{k_t^{0.5}c}{k_{iM}/\sigma + k_t^{0.5}c} - 0.5\frac{k_t^{0.5}c}{k_{iM}/\sigma + k_t^{0.5}c + k_{fM}} \tag{9}$$

which in any case must be > 0.5. For calculation of the monomer exponent, one has to combine (8) and (7), resulting for $\alpha \to 0$ in

$$R_p = [M]^3 \beta c k_t^{-0.5}(k_{iM}/\sigma + k_t^{0.5}c)(k_{iM}/\sigma + k_t^{0.5}c - k_{fM})^{-1} \tag{10}$$

and, therefore, an exponent of 3 is in good agreement with the experimental result.

There is no experimental evidence whether reinitiation by mono-
mer radicals M_1·* is important or not. If not, Eqs. (3), (7), (9), and
(10) can be simplified and the term k_{iM}/σ can be neglected, but the
conclusions are the same. In any case, the dependence $k_p \propto [M]$,
chain transfer and, eventually, a dependence $R_i \propto [M]^2$ are responsible
for the deviations of the polymerization kinetics of DMDAAC from the
ideal behavior of radical polymerization. Therefore, we started ex-
perimental investigations of the initiation reaction and the chain trans-
fer to monomer.

Kinetics and Mechanism of Initiation

The kinetics of the initiation reaction with $S_2O_8^{2-}$ as the water-
soluble initiator were investigated by two methods:

By quantitative analysis of the time-conversion curves of polymer-
ization by integral relationships.
By the well-known inhibition method.

As a convenient method for estimating the rate constant of initiator
decomposition from conversion-time data, we used the Stickler treat-
ment of overall kinetics. Stickler [31], using earlier concepts of
Walling [32] and Nishimura [33], introduced volume contraction in the
basic kinetic expression of the overall rate, resulting in

$$\frac{dx}{dt} = K[I_0]^{0.5} \frac{1-x}{(1+\epsilon x)^{0.5}} \exp\left(-\frac{k_d}{2}t\right) \tag{11}$$

where

$$K = \left(\frac{2fk_dk_p^2}{k_t}\right)^{0.5} \tag{12}$$

and ϵ = contraction constant.

After integration of Eq. (11) and developing the resulting exponen-
tial expression in a series, one obtains

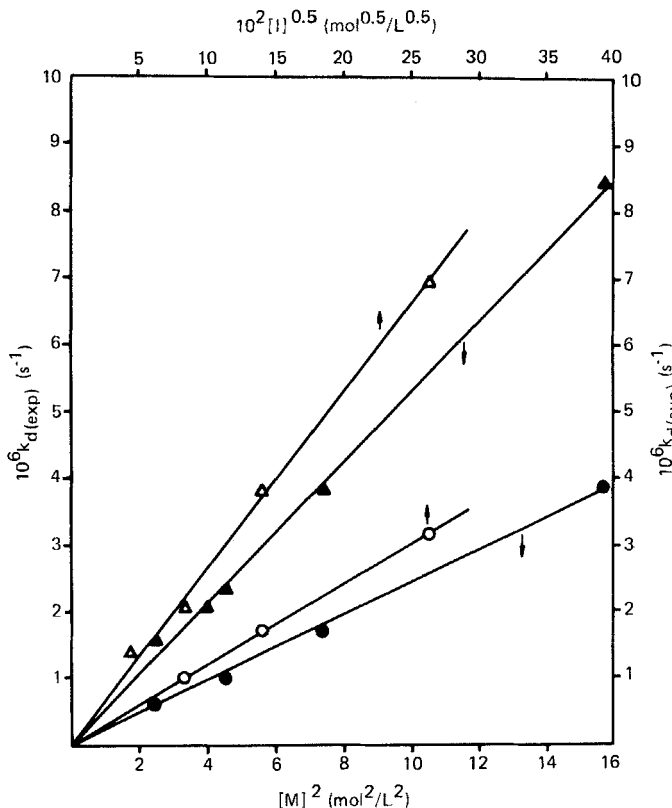$$-\frac{\ln(1-x)}{[I_0]^{0.5}t} = K - \frac{Kk_d}{4}t \tag{13}$$

FIG. 3. Rate constant of initiator decomposition $k_{d(exp)}$ vs $[I]^{0.5}$ ($[M] = 2.74$ mol/L) and $[M]^2$ ($[I] = 2 \times 10^{-2}$ mol/L). ($\circ$, $\bullet$) 35°C, ($\triangle$, $\blacktriangle$) 45°C.

which is used for graphical evaluation of K and k_d. This relationship holds for $k_dt \leqq 1$ and $x \leqq 0.2$ [31]. Contrary to the well known "dead-end-method" of Tobolsky, the integral concept established by Stickler does not require the reaction to be performed up to equilibrium.

By using the Stickler treatment, we obtained experimental values for the constants $K_{(exp)}$ and $k_{d(exp)}$ depending on concentrations of monomer and initiator [34], resulting in the relationships (Figs. 3 and 4)

$$k_{d(exp)} = k_d[M]^2[I]^{0.5} \tag{14}$$
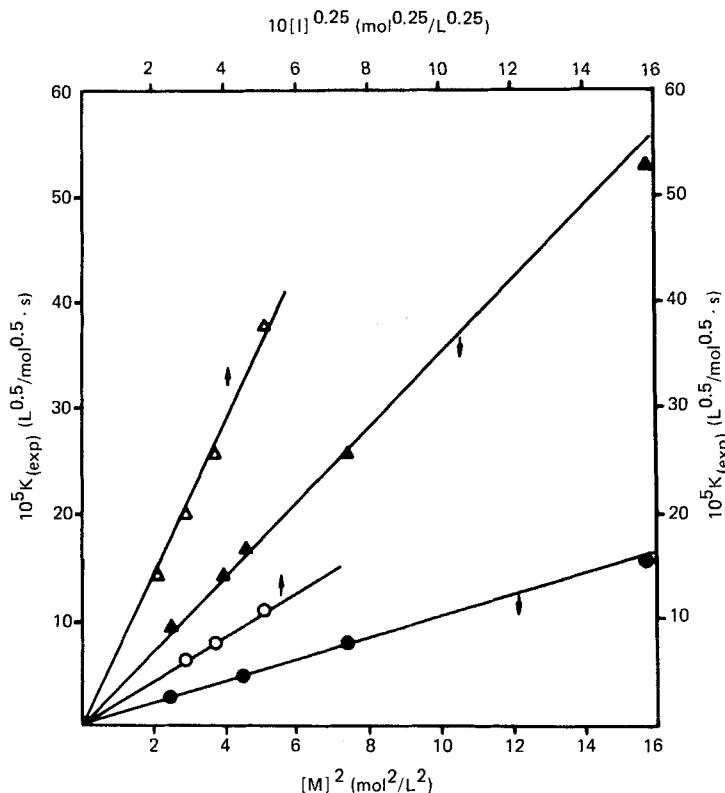
FIG. 4. Overall rate constant $K_{(exp)}$ according to Eq. (12) vs $[I]^{0.25}$ ($[M] = 2.74$ mol/L) and $[M]^2$ ($[I] = 2 \times 10^{-2}$ mol/L). ($\circ$, $\bullet$) 35°C, ($\triangle$, $\blacktriangle$) 45°C.

$$K_{(exp)} = K[M]^2 [I]^{0.25} \qquad (15)$$

With the basic rate equation for the initiation reaction of an ideal free radical polymerization,

$$R_i = 2fk_d[I] \qquad (16)$$

we obtained the following overall rate equation for the initiation step:

$$R_i = 2fk_d[I]^{1.5}[M]^2 \qquad (17)$$

There seems to be a discrepancy between the two experimentally found relationships $k_{d(exp)} \propto [M]^2$ and $K_{(exp)} \propto [M]^2$ because setting $k_{d(exp)}$ in Eq. (12) results in $K \propto [M]$. The experimentally estimated second-order relationship can easily be explained by the dependence of $k_p/k_t^{0.5}$ on [M] found by the analysis of time-conversion data by means of the Mayo equation [19] and discussed in the Introduction.

The observed decomposition rate of the initiator is higher by one order of magnitude than the rate in pure water [34], indicating rate-accelerating side reactions which we will discuss later.

Additionally, we determined the rate of initiation from inhibited polymerization. As inhibitors we used p-benzoquinone (p-BQ) and the stable free radical 2,2',6,6'-tetramethylpiperidine-N-oxide (RNO).

After the inhibition period, all polymerizations run with the expected rate, but the inhibition activity of the two inhibitors is quite different: RNO is a strong inhibitor and p-benzoquinone is a weak inhibitor. In the case of RNO we know that this inhibitor only reacts with carbon radicals with a stoichiometric coefficient of 1 [35]. Model experiments, including reactions of $S_2O_8^{2-}$ and p-BQ in the presence and absence of monomer, showed that p-BQ also only reacts with carbon radicals [34]. We determined the stoichiometric coefficient of p-BQ by comparing the rates of initiation from polymerization runs with RNO or by the Stickler method on the one hand, or with results using p-BQ as inhibitor on the other hand. This results in a marked dependence of the stoichiometric coefficient y of p-BQ on the monomer concentration. y can be calculated by

$$y = -0.217[M] + 2$$

From this equation we obtain a value of 1 at very high concentrations of monomer and the theoretical value of 2 at indefinite dilution. Similar results were described by Tüdős in the case of styrene polymerization with tetrabromoquinone as an inhibitor and discussed in terms of the theory of hot radicals [36].

In our case we assume the formation of an inhibiting species by a side reaction of the initiator with the monomer. As will be seen later, these species are chlorine atoms whose concentration is higher the higher the monomer concentration is. Thus the stoichiometric coefficient of the weak inhibitor p-BQ is lowered with increasing monomer concentration, but the coefficient of the strong inhibitor RNO is not affected. As both inhibitors only react with carbon radicals, the real concentrations of initiating radicals were estimated. The dependence of R_i on [M] and [I] as determined by inhibition experiments agree with the results of kinetic analysis by integral relationships (Fig. 5): R_i is proportional to $[M]^2$ and $[I]^{1.5}$
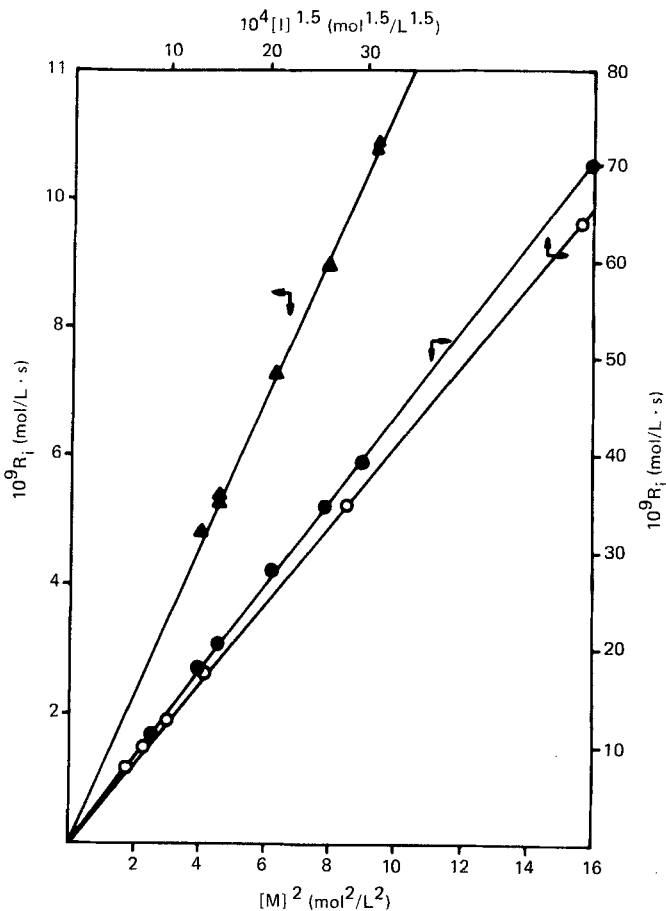
FIG. 5. Rate of initiation from inhibited polymerization. ($\blacktriangle$) [I] = 2×10^{-2} mol/L, 35°C; ($\bullet$) [I] = 2×10^{-2} mol/L, 45°C; ($\circ$) [M] = 2.8 mol/L, 45°C.

An approach to the mechanism of the initiation uses polymerization runs in the presence of additional amounts of chloride ions. Both the rate of initiation and the overall rate of polymerization increase with increasing chloride ion concentration at constant monomer concentration (Fig. 6). The increase of [Cl$^-$] can be achieved by addition of an inorganic salt, e.g., NaCl, as well as by addition of poly-DMDAAC. In both cases we get $R_i \propto$ [Cl$^-$] and, corresponding with this result, $R_p \propto$ [Cl$^-$]$^{0.5}$.
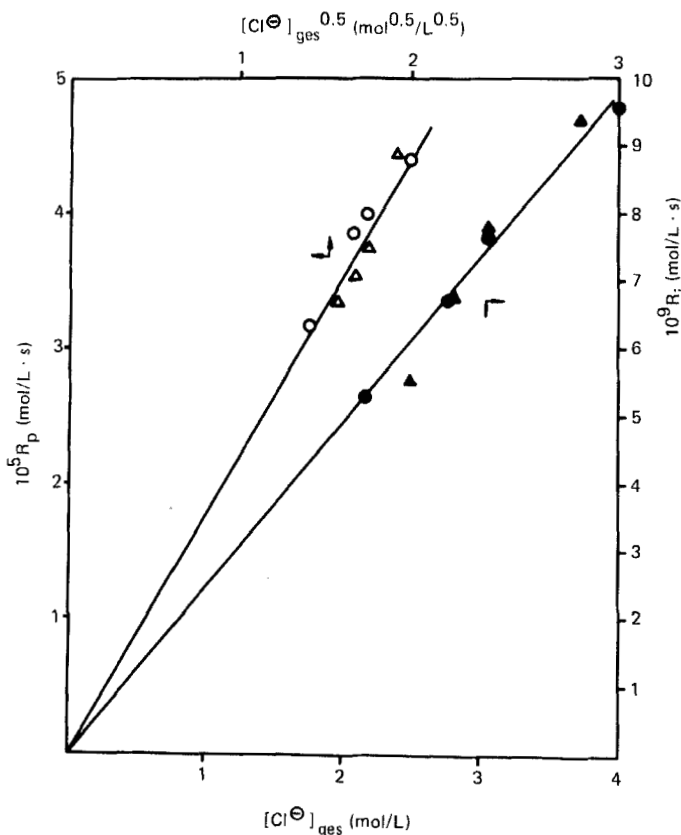
FIG. 6. Rate of initiation and overall rate of polymerization vs concentration of Cl^-, $[Cl^-]_{ges} = [Cl^-]_{monomer} + [Cl^-]_{added}$. $[I] = 2 \times 10^{-2}$ mol/L, $[M] = 2.14$ mol/L, $35°C$. ($\circ$, $\bullet$) Cl^- added as NaCl, ($\triangle$, $\blacktriangle$) Cl^- added as poly-DMDAAC.

Thus the relationship for R_i now can be written more exactly $R_i \propto [M^+][Cl^-]$, and leads to the new overall rate equation of initiation

$$R_i = k_i [M] [Cl^-][I]^{1.5} \tag{18}$$

From a mechanistic point of view it is important to consider the comparatively low value of the energy of activation of the initiation. We found 114.5 kJ/mol, in comparison to about 140 kJ/mol in the case of the decomposition of $S_2O_8^{2-}$ in water. The low value in the reaction
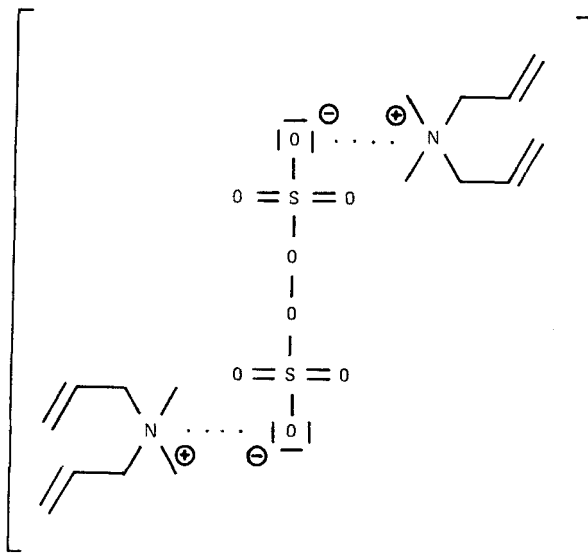
FIG. 7. Activated ion-pair complex of $S_2O_8^{2-}$ and monomer cations in the formation of primary radicals.

mixture indicates that part of the initiation could possibly be a redox reaction.

For a mechanistic explanation of the initiation with persulfate as initiator, we discuss two reactions. The first one is the formation of an intermediate complex (ion pair) between two monomer cations (or two dimer associates of the monomer) and one initiator anion (Fig. 7), reducing the O–O bond strength and thus accelerating the decomposition of the initiator:

$$S_2O_8^{2-} + 2M^+ \longrightarrow M^+ S_2O_8^{2-} M^+ \longrightarrow 2SO_4^{\cdot-} + 2M^+ \tag{19}$$
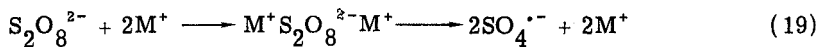
The second reaction is the redox reaction of persulfate and chloride anions, which are also associated with the monomer cation as an ion pair. This reaction results in initiating sulfate anion radicals and in both initiating and terminating chlorine atoms.

$$S_2O_8^{2-} + Cl^- \longrightarrow SO_4^{\cdot-} + Cl^{\cdot} + SO_4^{2-} \tag{20}$$
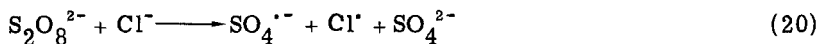
At usual temperatures, Reactions (19) and (20) run at nearly equal rates [37]. The monomolecular decomposition of $S_2O_8^{2-}$ is

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot -} \tag{21}$$

and is comparatively slow, as can be seen from numerical data for the rate of decomposition by Reactions (19)-(21) ($[M] = 1.5$ mol/L, $50°C$):

$$R_{d(19)} = 1.0 \times 10^{-7} \text{ mol/L·s}$$

$$R_{d(20)} = 1.9 \times 10^{-7} \text{ mol/L·s}$$

$$R_{d(21)} = 4.5 \times 10^{-8} \text{ mol/L·s}$$

Experimental Overall Rate Equation

Introducing the rate equation of R_i into the well-known overall rate equation of an ideal radical polymerization,

$$R_p = \frac{k_p}{k_t^{0.5}} R_i^{0.5}[M] \tag{22}$$

and considering $k_p/k_t^{0.5} = f([M])$, we obtain the rate equation of polymerization

$$R_p = k[M]^2[M^+]^{0.5}[Cl^-]^{0.5}[I]^{0.75} \tag{23}$$

In the normal case of $[M^+] = [Cl^-]$ (polymerization of the monomer without any added chloride ions), Eq. (23) can be reduced to

$$R_p = k[I]^{0.75}[M]^3 \tag{24}$$

in good agreement with the experimental rate Eq. (1). Thus the unusual exponents are mainly due to the complicated initiation reaction, but there are small differences between the experimental and theoretical exponents. The following results indicate side reactions involving chlorine atoms to be the reason for these differences.

Experimental values of R_p are somewhat lower than those calculated by Eq. (23) due to the discussed differences in the exponents. In the case of polymerizations with added NaCl, the experimental values are, contrarily, slightly higher than the calculated (Table 1). The reason may be the following. As mentioned above, increasing monomer concentration results in an increase of the rate of propagation due to the formation of associates of two monomer molecules and due to the electrolyte behavior of the monomer and the formation

TABLE 1. Experimental and Calculated Values for the Free Radical Polymerization of DMDAAC. Initiator: $S_2O_8^{2-}$. [I] $= 2 \times 10^{-2}$ mol/L, 35°C

[M] (mol/L)	[NaCl] (mol/L)	$10^9 \times R_{i(exp)}$ mol/L·s	$10^5 \times R_{p(exp)}$ mol/L·s	$10^5 \times R_{p(calc)}$ mol/L·s[a]
3.96	-	17.1	17.16	17.52
3.25	-	13.0	9.67	10.07
2.80	-	9.0	5.90	6.10
2.14	-	5.3	2.88	2.88
2.14	0.66	6.7	3.85	3.55
2.14	0.91	7.6	3.99	3.68
2.14	1.86	9.6	4.40	4.10

[a]Calculation according to Eq. (23) with $k_p/k_t = 0.028$ $L^{0.5} mol^{-0.5} s^{-0.5}$.

of ion pairs between polymer cation radical, monomer cation, and monomer anion. The formation of ion pairs, of course, will be favored upon addition of NaCl. Thus, the addition of NaCl results in an increase of the rate of polymerization for two reasons:

Mainly because of the participation of chloride ions in the initiation reaction.
To a smaller extent, because the formation of ion pairs is favored.

Formation of Chlorine Atoms and the Consequences

Combining aqueous solutions of $S_2O_8^{2-}$ and Cl^- at pH < 7 results in Cl_2, as was previously discussed by Ohme [38]. By supplementary addition of p-benzoquinone, the only reaction product is the tetrachloro derivative of benzoquinone [39]. This is proof of the formation of chlorine atoms. Exposure of a monomer solution containing a small amount of Cl_2 to UV light results only in the formation of 3,4-dichloro-methylene-pyrrolidinium chloride, but no polymer is formed [39]. Therefore, the following conclusions can be drawn:

(a) Chlorine atoms formed in the redox Reaction (20) must act as terminating agents. Therefore, we have to correct our overall rate

Eq. (23) by adding a negative term which accounts for the additional degradative termination by chlorine atoms:

$$R_p = \left(\frac{k_i k_p^{\,2}}{k_t} \right)^{0.5} [M]^2 [M^+]^{0.5} [Cl^-]^{0.5} [I]^{0.75} - A_{Cl} \tag{25}$$

(b) Initiation without formation of Cl· should lead to polymers with higher molecular weights. Actually, by initiation with water-soluble azo initiators, e.g., 4,4'-azobis(4-cyanopentanoic acid), at equal rates of polymerization the molecular weight of the polymer is more than threefold in comparison with $S_2O_8^{2-}$ initiation. For example: Rate 3.0 mol/L·s; $\bar{P}_n(S_2O_8^{2-}) = 95$, $\bar{P}_n(Azo) = 340$.

(c) As is to be expected from Mayo-plots, we obtain much lower values of the chain transfer constant to monomer in the case of azo initiators: $C_M(S_2O_8^{2-}, 35°C) = 2.5 \times 10^{-3}$ [19]; $C_M(Azo, 50°C) = 1 \times 10^{-4}$. The former value includes transfer to monomer as well as termination by chlorine atoms. The real transfer to monomer is given by the experiments with azo initiators.

(d) With any initiation without formation of Cl·, we can assume normal initiation and termination, and increasing values of k_p with increasing monomer concentration as the only unusual behavior. Therefore, the overall rate equation is

$$R_p = \left(\frac{k_i k_p^{\,2}}{k_t} \right)^{0.5} [I]^{0.5} [M]^2 \tag{26}$$

Actually, this rate equation is valid with azobis-pentanoic acid as initiator [39]. This, of course, is also strong proof of our suggestions on the mechanism of initiation with $S_2O_8^{2-}$.

The negative term $(-A_{Cl})$ in Eq. (25) is responsible for the differences in the exponents of [M] and [I] in experimental (1) and calculated rate Eqs. (23) and (24), not taking into account termination by chlorine atoms in the latter case. From a separate kinetic study [39] the following term resulted:

$$A_{Cl} = \frac{k_{deg} k_p}{2k_t} [Cl·][M]^2 \tag{27}$$

Here, only [M] is known at first. Additionally, it is possible to calculate the individual rate constants k_p and k_t from the overall rate data
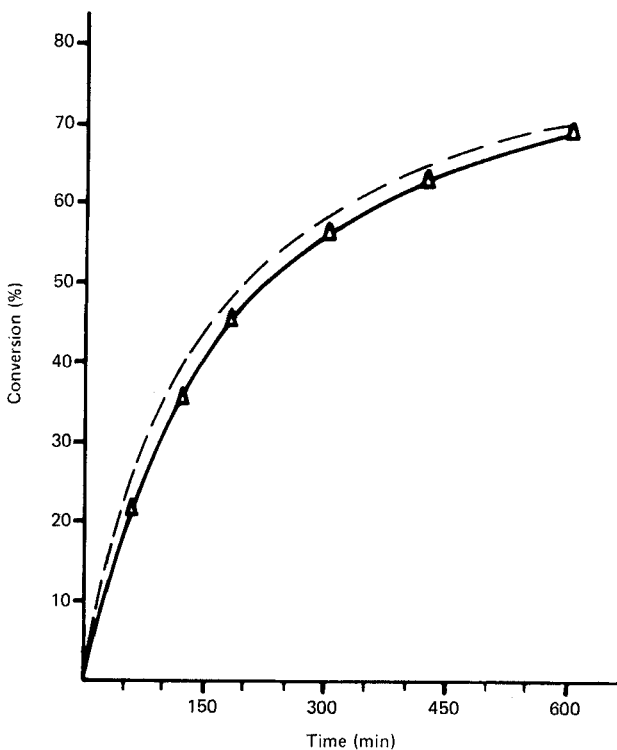
FIG. 8. Calculation of conversion vs time with different models of overall rate. $[M] = 3.97$ mol/L, $[S_2O_8^{2-}] = 2 \times 10^{-2}$ mol/L, 45°C. (—) Calculated with Eq. (25), (---) calculated with Eq. (24), ($\triangle$) experimental.

[40] by using a concept published previously [41]. Because we cannot measure the concentration of chlorine atoms, numerical values of A_{Cl} cannot be determined by the usual kinetic treatment. Therefore, we determined this value by mathematical modeling, carrying out fitting calculations with a high number of polymerization runs and so determining values for $k_{deg}[Cl^{\cdot}]$ under different conditions. The results can be shown as a comparison of time-conversion curves calculated by Eqs. (24) and (25) using $k_{deg}[Cl^{\cdot}] = 3.0$ mol/L·s and experimental data (Fig. 8), respectively. Without the degradative term A_{Cl}, calculated curves are somewhat higher than experimental values. If we take into consideration A_{Cl}, calculated kinetic curves and experimental

data are in excellent agreement. Figure 8 also demonstrates the over-
all rate Eq. (25) to be valid up to high conversions.

Initiation with Persulfate/Amine

From the discussed results one can see that in the case of DMDAAC
polymerization the usually used water-soluble initiator persulfate is
not the best one, especially with respect to the molecular weight of the
polymer. Azo initiators lead to polymers with higher molecular
weights, but only with low rates of polymerization. An increase of the
temperature of polymerization in order to increase this rate does not
result in much higher $\bar{P}_n$ values, because transfer reactions become

more important, thus limiting the degree of polymerization. There-
fore, the conclusion is drawn that we need an initiator with a high rate
of initiation at comparatively low temperature without the formation
of chlorine atoms. These conditions are achieved with persulfate/
amine redox systems [39] which are well known as polymerization in-
itiators, e.g., Ref. 30. The general results can be seen from a Mayo
plot of experimental data with dimethyl allyl amine (DMAA) as the re-
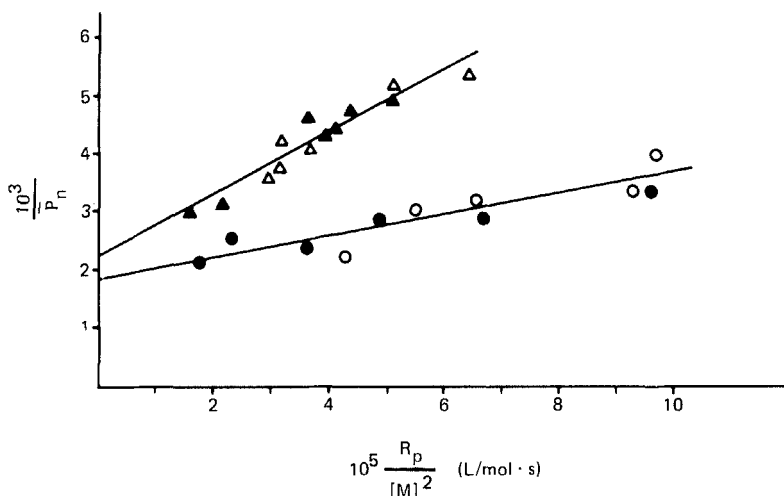ducing agent (Fig. 9). The chain transfer (intercept) is nearly as low

FIG. 9. Mayo plot of polymerization data by initiation with $S_2O_8^{2-}$/
DMAA at pH > 7, 45°C. (○) [M] = 3.94 mol/L, variation of $[S_2O_8^{2-}]$;
(●) [M] = 3.94 mol/L, variation of [DMAA]; (△) = 2.74 mol/L, varia-
tion of $[S_2O_8^{2-}]$; (▲) [M] = 2.74 mol/L, variation of [DMAA].

as with azo compounds, indicating no termination by chlorine atoms. The values of $\bar{P}_n$ and the rate of polymerization are much higher than with $S_2O_8^{2-}$ alone (Fig. 9, Table 2). Table 2 also includes results with an azo initiator. $\bar{P}_n$ values for the system $S_2O_8^{2-}$/DMAA are lower than with an azo initiator because the rate of polymerization is much higher with the persulfate/amine systems, resulting in a decrease of $\bar{P}_n$.

Investigations with different amines as a part of the initiator system resulted in different overall rate equations, indicating differences in the mechanism, mainly of initiation. The following conclusions can be drawn:

(a) Persulfate/dimethyl allyl amine (pH > 7):

$$R_p = [S_2O_8^{2-}]^{0.5}[A]^{0.25}[M]^2$$

where A = amine. There is (1) no kinetically efficient reaction of $S_2O_8^{2-}$ with Cl^-, (2) no kinetically efficient interaction between $S_2O_8^{2-}$ and monomer, and (3) additional initiation by polymeric amine radicals resulting from the reaction of amine endgroups and $S_2O_8^{2-}$.

(b) Persulfate/triethanol amine (pH > 7):

$$R_p = [S_2O_8^{2-}]^{0.65}[A]^{0.5}[M]^2$$

There is (1) no kinetically efficient interaction of $S_2O_8^{2-}$ and monomer, and (2) initiation only by $SO_4^{\cdot-}$. Monomeric and polymeric amine radicals are stabilized by intramolecular H bridges.

SYMBOLS

f	radical efficiency factor
k	overall rate constant
k_c	rate constant of cyclization reaction
k_d	rate constant of initiator decomposition
k_{deg}	rate constant of cross-termination between chain radical and chlorine atom
k_{fM}	rate constant of chain transfer to the monomer
k_i	rate constant of initiation

TABLE 2. Polymerization of DMDAAC with Different Initiators

[M] (mol/L)	$10^2 \times [S_2O_8^{2-}]$ mol/L	$10^2 \times [Azo]$ mol/L	$10^2 \times [DMAA]$ mol/L	T (°C)	$10^5 \times R_p$ mol/L·s	$\bar{P}_n$
3.96	2	-	-	35	16.75	205
3.94	0.2	-	2	45	32.00	470
3.96	-	2	-	50	9.50	845
2.74	2	-	-	35	6.09	124
2.74	0.7	-	2	45	23.71	280
2.74	-	2	-	50	4.21	553
2.14	2	-	-	35	3.10	95
2.14	-	2	-	50	2.70	343

k_{iM} rate constant of reinitiation by monomer radicals from transfer steps

k_p rate constant of propagation

k_t rate constant of termination

k_{tM} rate constant of termination by monomer radicals from transfer steps

k_{tMM} rate constant of termination between two monomer radicals

k_{21} rate constant of propagation by cyclized radicals

$\overline{M}_n$ number-average molecular weight

R_i rate of initiation

R_p overall rate of polymerization

σ proportionality factor

x   conversion

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