

# Fractal Kinetics of Radical Polymerization of Dimethyl Diallyl Ammonium Chloride

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**ABSTRACT:** The proposed technique allows determination of variation in a macromolecular coil structure of dimethyl diallyl ammonium chloride, characterized by its fractal dimension, during polymerization. It is shown that this one factor, unaccounted for in conventional theories, determines the most important characteristics of a polymerization process: rate, output of a finite product, and molecular weight. Further, the methods of fractal kinetics allow the

quantitative description of synthesis of polymers and, in particular, give the correct shape of the conversion degree–time kinetic curve. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3140–3143, 2004

**Key words:** radical polymerization; solution; macromolecular coil, fractal dimension; irreversible aggregation

## INTRODUCTION

The kinetics of dimethyl diallyl ammonium chloride (DMAACH) polymerization in aqueous solutions has the same qualitative features and kinetics of a radical polymerization as those of other polymers.<sup>1</sup> In particular, it is expressed in sigmoidal form by the kinetic curve degree of conversion–time of reaction ( $Q-t$ ), which is commonly divided into three parts: initial, autoacceleration, and copolymerization.<sup>2</sup> For the description of a curve  $Q(t)$  a number of conventional approaches have been used, details of which were previously reported.<sup>1,2</sup> However, the indicated approaches do not take into account the structure of a basic element of synthesis of polymers in solutions—macromolecular coil—and thus of its probable variations during synthesis. It has been established<sup>3</sup> that the macromolecular coil is a fractal, whose structure (the distribution of a coil elements in space) can be described with the help of fractal  $D$ . The theory of irreversible aggregation, moreover, is intimately linked with fractal analysis, developed in detail in this study to elucidate the description of such processes as polymerization.<sup>4</sup> Use of these concepts allows a quantitative description of polymerization processes from essentially new perspectives.<sup>5,6</sup> Therefore the purpose of the present article was the development of a fractal kinetics of radical DMAACH by using models of irreversible aggregation.

## EXPERIMENTAL

Polydimethyldiallyl ammonium chloride (PDM-DAACH) was synthesized in aqueous solutions at initial concentration of monomer  $c_0 = 4.8$  mol/L (0.775 by weight). Initiation was done by thermal decomposition of ammonium persulfate with concentration of the initiator  $5 \times 10^{-3}$  mol/L. The conversion degree was determined by a calorimetric method. The used values of polymerization rates were taken from Malkanduev.<sup>7</sup>

## RESULTS AND DISCUSSION

Within the framework of the fractal analysis the polymerization kinetics is described by the following general relationship<sup>6</sup>:

$$Q \sim t^{(3-D)/2} \quad (1)$$

The formal kinetics of polymerization within the framework of conventional approaches is formulated as<sup>2</sup>

$$\frac{dQ}{dt} = -k_p(1 - Q) \quad (2)$$

where  $k_p$  is the constant rate of polymerization.

Differentiating the relationship in eq. (1) on  $t$ , we obtain<sup>6</sup>

$$\frac{dQ}{dt} \sim t^{(1-D)/2} \quad (3)$$

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The combination of relationships (2) and (3) allows us to obtain the equation for an estimation of  $D$  on kinetic parameters of the polymerization process:

$$t^{(1-D)/2} = \frac{c_1}{k_p(1-Q)} \quad (4)$$

where  $c_1$  is constant estimated from boundary conditions.

As follows from eq. (4), for an estimation of  $D$  the values  $k_p$  should be used. However, we used  $V$  values for the following reasons. As is known,<sup>1</sup> the following relationship is valid at DMDAACH polymerization:

$$V = \frac{\nu_i k_p}{k_0^{1/2} c_0 \eta_{\text{rel}}^{1/2}} \quad (5)$$

where  $\nu_i$  is the initiation rate,  $k_0$  is the constant rate of bimolecular breakage,  $c_0$  is the concentration of monomer, and  $\eta_{\text{rel}}$  is the relative viscosity of an initial solution a monomer.

From Topchiev et al.<sup>1</sup>

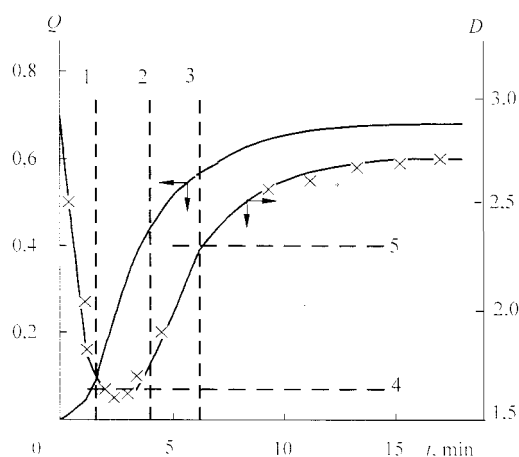
$$k_0 = k'_0 / \eta_{\text{rel}}^{1/2} \quad (6)$$

where  $k'_0$  is elementary constant rate of chain breakage under standard conditions, when the viscosity of a monomer solution is very small for constant monomer and initiator concentrations. The next equation also follows at constant polymerization temperature from eqs. (5) and (6):

$$V \sim k_p \quad (7)$$

Only the monomer is contained in the beginning stage of synthesis, which within the framework of an irreversible aggregation model can be considered as particles that are subsequently united in (macromolecular coil). As established<sup>4</sup> such a mechanism is designated the particle-cluster mechanism within the framework of indicated models and the aggregates with fractal dimension  $D \approx 2.5$  are the result of its operation. Thus the value  $c_1$  is calculated from eq. (4) with the following set of parameters:  $t = 0.5$  min;  $V = 4.8 \text{ mol L}^{-1} \text{ s}^{-1}$  and  $Q = 8.3 \times 10^{-3}$ .

In Figure 1 the dependencies  $D(t)$ , calculated by the indicated method, and  $Q(t)$ , obtained experimentally, are given. From this figure, one may observe both a strong variation of value  $D$  during the time of reaction  $t \approx 1.75$  min and a change of the aggregation mechanism. The examination of boundary conditions to estimate  $c_1$  used above can be made as follows. As previously substantiated<sup>8</sup> there is a relationship between the  $D$  value and exponent  $\alpha$  in the Mark-Kuhn-Houwink equation:



**Figure 1** Dependencies of conversion degree  $Q$  and fractal dimension  $D$  of the macromolecular coil on reaction time  $t$  for PDMDAACH ( $c_0 = 4.8 \text{ mol/L}$ , content of the initiator  $5 \times 10^{-3} \text{ mol/L}$ ,  $T = 353 \text{ K}$ ). The vertical dashed lines 1–3 indicate boundaries of polymerization stages. The horizontal dashed and dotted lines indicate value  $D$  of a macromolecular coil in dilute solution<sup>4</sup> and critical value  $D^{cr}$ .<sup>5</sup>

$$D = \frac{3}{1 + \alpha} \quad (8)$$

In turn, the Mark-Kuhn-Houwink equation for PDNDAACH has the form<sup>1</sup>

$$[\eta] = 1.12 \times 10^{-4} M^{0.82} \quad (9)$$

where  $[\eta]$  is the intrinsic viscosity and  $M$  is the viscosity-average molecular weight.

One may estimate the value  $D$  for macromolecular PDMDAACH coil in the diluted solution from eqs. (8) and (9):  $D \approx 1.65$ . This value is indicated by a horizontal dashed-and-dotted line 4 in Figure 1. As one may observe, this value  $D$  agrees well with the minimal ratio  $D$ , which increased with more concentrated solutions from eq. (4). This correspondence confirms the correct choice of boundary conditions because the value  $D$  for a macromolecular coil in the diluted solution is minimal.<sup>9</sup>

Now, by using the data of Figure 1, it is possible to give the general description of the fractal kinetics of radical PDMDAACH polymerization. There is a monomer as aggregate-forming particles (as mentioned above in the framework of irreversible aggregation models) in a solution at initial point of synthesis ( $t = 0$ ). Coalescing of these particles in clusters (in Fig. 1, stages are marked by vertical dashed lines, and the axis of coordinates is for a line 0) occurs at the first stage; that is, the process proceeds by a particle-cluster mechanism at stage 0–1 that results in formation of dense macromolecular coils with dimension  $D \approx 2.5$ , corresponding to the indicated mechanism. The rate of

reaction on this (initial) level of polymerization is small because of the rather large value of  $D$ , which directly follows from eq. (3). These clusters then begin to aggregate, forming increasing clusters (i.e., the particle-cluster mechanism is replaced by the cluster-cluster mechanism).

Recall that the degree  $N$  of polymerization reaches significant value ( $N = 200 \div 315$ ) at the beginning of the autoaccelerated stage.<sup>1</sup> At part 1-2 the value  $D \approx 1.65$ , which corresponds to the cluster-cluster diffusion-limited mechanism.<sup>4</sup> This stage responds to the autoacceleration stage (i.e., part), where the rate of reaction is maximal. Thus, within the framework of the proposed treatment the transition from an initial part to one of auto acceleration is caused by a change of the aggregation mechanism and, as a consequence, by a rapid decrease of  $D$ . In other words, line 1 in Figure 1 corresponds to the reaction by way of monomer-coil connection and on part 1-2 the reaction proceeds to completion only at the expense of arranging of macromolecular coils. The high rate of reaction on part 1-2 determines the appearance of a large number of macromolecular coils. Each of them is now in a self-similar environment that results in compactization of these coils and, therefore, in increased  $D$  values (the solution becomes "dense," by definition<sup>9</sup>). Such a process proceeds so long as the coil does not reach critical dimension  $D^{cr}$ , determined from the following equation<sup>10</sup>:

$$D^{cr} = \frac{4(d+1)}{7} \quad (10)$$

where  $d$  is the dimension of Euclidean space, in which the fractal is considered. Obviously, in our case  $d = 3$ .

The estimation by use of eq. (10) with  $d = 3$  gives  $D^{cr} = 2.29$  (horizontal dashed-and-dotted line 5 in Fig. 1). This point corresponds to the termination of stage 2-3. The examination for correctness of correspondence of transition at stage 2-3 to a "dense" solution may be done with the help of the model,<sup>9</sup> where the relationship between  $D$  and fractal dimension  $\bar{D}$  of the macromolecular coil in "dense" solution is given as

$$D = \frac{(d+2)\bar{D}}{2(1+\bar{D})} \quad (11)$$

If the value  $D$ , corresponding to the beginning of stage 2-3 ( $D \approx 1.76$ ; Fig. 1) is accepted, then we obtain from eq. (11)  $\bar{D} \approx 2.38$ , that agrees well with the above estimation.

The last stage of a curve  $Q(t)$  is the gelation, which represents formation of a cluster subtending the system (spreading from one end of a reactionary bath to another). Because PDMDAACH is a linear polymer, physical gelation—that is, macromolecular coils—act-

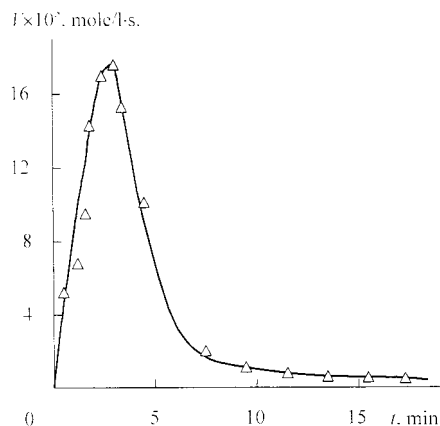


Figure 2 Dependency of rate of reaction  $V$  on time of reaction  $t$  for PDMDAACH.

ing when a cluster is subtending, are integrated within a network of macromolecular entanglements. As theoretical<sup>11</sup> and experimental<sup>12</sup> investigations have shown, the dimension  $d_f \approx 2.5$ , which is in full agreement with the data of Figure 1, corresponds to the gelation transition. The reaction of synthesis is practically terminated at this stage. As shown in a previous study,<sup>13</sup> the fractal dimension of a macromolecular coil in solution  $D$  and condensed state (gel)  $d_f$  are linked by the following relationship (for linear polymers):

$$d_f = 1.5D \quad (12)$$

If the earlier value of  $D \approx 1.76$ , corresponding to the ending of stage 1-2, is accepted as appropriate to the ending stage of the reaction, we receive  $d_f \approx 2.64$ , which again agrees with the data given in Figure 1 from eq. (12).

Another point is worth mentioning. As experimental studies<sup>1,7</sup> have shown, the output of curves  $M(t)$  on a part of saturation occurs earlier for PDMDAACH than for that of curves  $Q(t)$ . This observation is also explained within the framework of irreversible aggregation models. As is known,<sup>4</sup> the critical (maximal) radius of gyration  $R_g^{cr}$  of a macromolecular coil is determined by the relationship

$$R_g^{cr} \sim c_0^{-1/(d-d_f)} \quad (13)$$

When this condition is obtained the macromolecular coil terminates its growth and thus the increase of molecular weight stops. The further insignificant increase of  $M$  and  $Q$  can be realized only at the expense of growth of the coils, which have a less-critical radius  $R_g$  of gyration (i.e.,  $R_g < R_g^{cr}$ ).

In Figure 2 the relationship  $V(t)$  based on data from a previous study,<sup>7</sup> is shown. A comparison of Figures 1 and 2 demonstrates that dependencies  $D(t)$  and  $V(t)$

are antipate, although the maximum of dependency  $V(t)$  is expressed more sharply than the minimum on curve  $D(t)$  corresponding to it. It may be explained that the value  $V$  is determined not only by  $D$ , but also by two variables ( $t$  and  $Q$ ) according to eq. (4). Because the two indicated parameters have no extremum, the data of Figures 1 and 2 suppose that the main parameter influencing the value  $V$  is the dimension  $D$  describing the structure of the macromolecular coil. This important factor is routinely missed in conventional approaches of description of radical polymerization processes.<sup>1,2</sup>

In summary we shall consider a method of the theoretical description of a curve  $Q(t)$  within the framework of fractal kinetics based on application of eq. (1). With respect to the described process of PCM-CAACH synthesis the value  $D$  is a variable, so the increment  $Q$  ( $\Delta Q_i$ ) after termination of the arbitrarily chosen temporary interval  $t_i = t_{i-1} - t_i$ . Then for this interval it is possible to obtain

$$\Delta Q_i = \Delta t_i^{(3-D_i)/2} \quad (14)$$

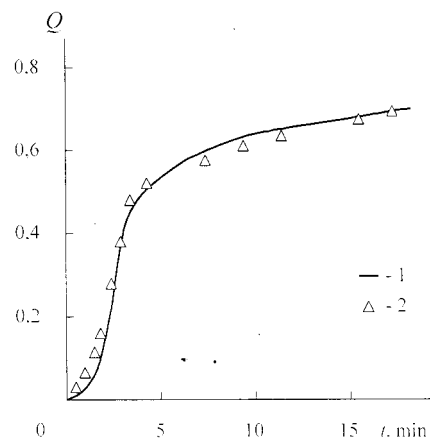
Then the value  $Q_i$ , corresponding to time  $t_i$ , was determined by summation

$$Q_i = Q_{i-1} + \Delta Q_i \quad (15)$$

In Figure 3 the comparison of kinetics curves, of experimental and calculated values within the framework of fractal kinetics  $Q(t)$ , for PDMDAACH is shown. It is obvious that there is excellent correspondence between the theory and experiment: the error does not exceed 6% (i.e., the errors of definition  $Q$  are not high).<sup>7</sup>

## CONCLUSIONS

Thus, the proposed technique allows determination of variation in a macromolecular coil structure of PDM-DAACH, characterized by its fractal dimension  $D$ , during polymerization. It is shown that this factor, not taken into account in conventional theories, determines the most important characteristics of polymerization process: rate, output of a final product, and



**Figure 3** Comparison of experimental (1) and calculated values within the framework of fractal kinetics (2) curves of conversion degree–time ( $Q$ – $t$ ) for PDMDAACH.

molecular weight. Furthermore, the methods of fractal kinetics allow the quantitative description of synthesis of polymers, particularly with respect to the correct shape of the kinetic curve  $Q(t)$ .

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