

Molecular Weight Distribution of Poly(Dimethyl Diallyl Ammonium Chloride): Analysis Within the Framework of Irreversible Aggregation Models

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ABSTRACT: The results of the present study have shown that the molecular weight distribution of polydimethyldiallyl ammonium chloride is simulatable and predictable within the framework of the irreversible cluster–cluster aggregation model. The shape and position of a curve of molecular weight distribution are influenced by a number of factors, for example, by macromolecular coil structure, stochastic contribution of a coil environment to polymerization intensity, and level of coil destruction during polymer-

ization. These factors can be linked by simple relationships to technical characteristics of the polymerization process, which is especially important for fractal applications of the proposed theoretical model. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3144–3147, 2004

Key words: radical polymerization; macromolecular coil structure; fractal analysis; molecular weight distribution; cluster–cluster mechanism

INTRODUCTION

With respect to the concepts of the nature of a molecule and its molecular weight (MW), high molecular weight substances have characteristics that are qualitatively different from those of polymers produced from low molecular weight substances.¹ This difference is closely linked with the fact that polymers are a mixture of macromolecules with different molecular weights (mixture of polymer–homologs). The value of MW determined by a distinctly unique method depends on the degree of polydispersity, the type of function of molecular weight distribution (MWD), and the method of experimental definition of MW² for such mixtures. Therefore a complete description of the molecular weight characteristics of a polymer requires knowledge of its MWD.

As is well known,³ the macromolecular coils in a solution are fractals, whose structure—or, more precisely, the spatial distribution of coil elements—is characterized by its fractal dimension D . However, despite its unquestioned importance, the value D gives only limited information about an aggregation (polymerization) process. First, it is a static value and does not describe the dynamics of an aggregation process. Second, the value D characterizes geometrical properties of only one cluster (macromolecular coil) and cannot be used for the description of a set of clusters.⁴ Thus, both classical and fractal approaches

indicate the need for MWD analysis in determination of the characteristics both for polymers and for the polymerization process.

D value intervals for macromolecular coils in a solution³ assume that the polymerization process proceeds according to the mechanism of irreversible cluster–cluster aggregation. The functions of distribution for the indicated mechanism were investigated in a number of studies.^{4–6} The purpose of the present article is the theoretical description of MWD functions within the framework of a theoretical approach⁶ and determination of the factors influencing the shape of these functions, using the example of polydimethyldiallyl ammonium chloride (PDMDAACH).⁷

EXPERIMENTAL

PDMDAACH was synthesized in aqueous solutions at various initial concentrations of monomer c_0 : 1.0, 2.5, 4.0, and 5.0 mol/L (0.161 ÷ 0.808 by weight). Initiation was carried out by thermal decomposition of ammonium persulfate with initiator concentration of 5×10^{-3} mol/L. The polymerization was carried out at 353 K.

The MWD functions for PDMDAACH were determined from measurements of rate of sedimentation by a previously described procedure⁸ at a rotor rate of 6×10^4 rpm. All measurements were executed at $T = 303$ K in 1N NaCl solutions.

The value of D for PDMDAACH was determined from the following relationship⁹:

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

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where α is an exponent in the Mark–Kuhn–Houwink equation, which for PDMAACH is about 0.82.⁸

The computer simulation of theoretical MWD curves was completed on an IBM PC with software written in BASIC.

RESULTS AND DISCUSSION

In a previous study⁶ the theoretical treatment of a cluster–cluster aggregation was proposed that accounted for the existence of coalescing of particles or of clusters (monomer or macromolecular coil) to aggregate in actual polymerization processes, and their disconnection (destruction) was reported.

Macromolecules are in a random environment— influencing the processes of aggregation or destruction in dilute polymeric solution—that is described by a stochastic equation⁶:

$$\tilde{N} = \lambda N^a - N^b + \xi_t N^a \quad 0 < a < b \quad (2)$$

where N is the number of particles in the aggregate (polymerization degree), a and b are exponents describing the processes of aggregation and destruction, accordingly ($\xi_t = c_t/m$, where c_t is the stochastic contribution to intensity of the aggregation process attributed to the influence of an environment, $\langle c \rangle$ is its average value, and m is a coefficient).

The value of λ was determined by the following expression⁶:

$$\lambda = \langle c \rangle / m \quad (3)$$

Following Shiyan,⁶ we believe that the reference times of random effects for the fractal aggregation process of macromolecules are much less than the reference times of the aggregation itself and, consequently, it is possible to present ξ_t as white noise of intensity $\langle \xi_t^2 \rangle = \sigma^2$.

The exponent a in the case of cluster–cluster aggregation is linked with fractal dimension D of a macromolecular coil according to the following relationship⁶:

$$a = \frac{2D - d}{D} \quad (4)$$

where d is the dimension in Euclidean space, in which the fractal is considered (as in our case 3).

Equation (2) allows us to obtain a density of probability $P_S(N)$, which for a stationary solution looks like⁶

$$P_S(N) = AN^{-a} \exp\{2\lambda N^{1-a}[1 - (1-a)N^{b-a} / \lambda(b+1-2a)] / (1-a)\sigma^2\} \quad \text{for } a \neq 1 \quad (5)$$

where a is the normalization constant.

As in eq. (5) the value of λ has no effect on $P_S(N)$, and the indicated relationship supposes three basic parameters acting on distribution $P_S(N)$: a , b , and ξ^2 . Each of the indicated parameters characterizes a def-

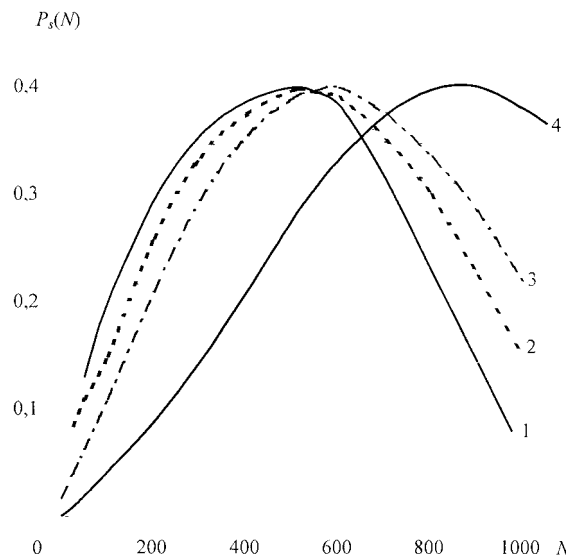


Figure 1 Simulation of MWD curves according to eq. (5) for $D = 1.50$ (1), 1.65 (2), 1.80 (3), and 2.0 (4). $b = 1$, $\sigma^2 = 0.25$.

inite feature of the polymerization process. The exponent a is thus essentially determined by the structure of the macromolecular coil, which directly follows from eq. (4). The value b characterizes the type and intensity of the destructive processes. Parameter σ^2 is determined by the stochastic contribution to a polymerization process and it is possible to assume dependency σ^2 from c_0 : the greater the initial concentration of a monomer, the larger the probability of random collisions. All experimental MWD curves have the universal shape that supposes low mobility for coils in solution or $\sigma^2 < \frac{2}{3}$.⁶

We shall first consider the general aspects of influence of the three indicated parameters on the form of MWD curves. For this purpose we shall construct theoretical dependencies $P_S(N)$ with a serial variation when only one of the indicated parameters varies, whereas the other two are constant. In Figure 1 the curves $P_S(N)$ are shown for the case when the fractal dimension D is variable, whereas for a coil (or variable a) both σ^2 and b are constants. In Figures 1–3 the normalization constant A was chosen so that the maximal magnitude P_S was equal to about 0.4 for all curves $P_S(N)$. As follows from the data of Figure 1, the increase in D results in displacement of a maximum of distribution in the higher N . This tendency is most strongly expressed for $D = 2$, corresponding to the Θ -condition.³ For experimental MWD curves the greatest value of N , corresponding to a maximum of MWD distribution, was obtained for $c_0 = 4.0$ mol/L where $N = 550$. As may be observed from $P_S(N)$ curves, shown in Figure 1, the indicated value of N corresponds to $D = 1.65$, which agrees with the calculated value of D by eq. (1). This result demonstrates that the coil contraction reported by Bityurin et al.¹⁰ up to Θ -conditions at enough high c_0 is not realized in practice.

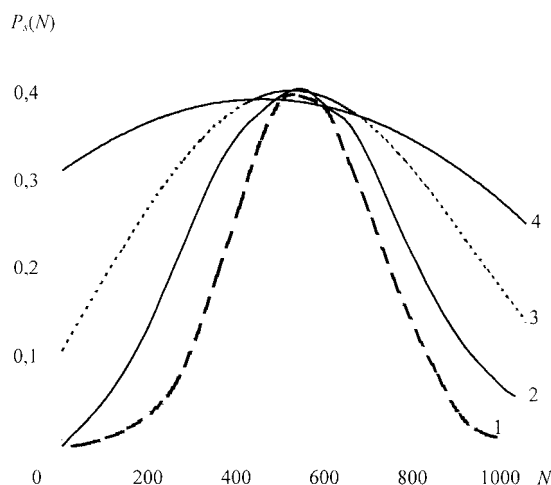


Figure 2 Simulation of MWD curves according to eq. (5) for $\sigma^2 = 0.05$ (1), 0.10 (2), 0.25 (3), and 0.60 (4). $b = 1$, $D = 1.65$.

In Figure 2 the theoretical $P_S(N)$ curves are shown when σ^2 is variable and both D and b are constants. As follows from the diagram of this figure, the value σ^2 exerts a primary influence on the width of MWD. Strictly monodisperse distribution can be obtained only at $\sigma^2 = 0$. The increase of the stochastic contribution in polymerization intensity results in symmetrical broadening of MWD relative to its maximum.

The theoretical curves $P_S(N)$ are shown in Figure 3, where b is variable and both D and σ^2 are constants. The value $b = 1$ means availability of the channel of disintegration for each bond in a cluster. When the greatest portion of bonds is fixed ($b = 0.2$), the maximum in an investigated interval $N = 0 \div 1000$ is not generally reached. At $b = 0.5$ (half of the bonds are fixed) the $P_S(N)$ curve is fixed at a maximum, but with obvious asymmetry at large N . Further increases of b

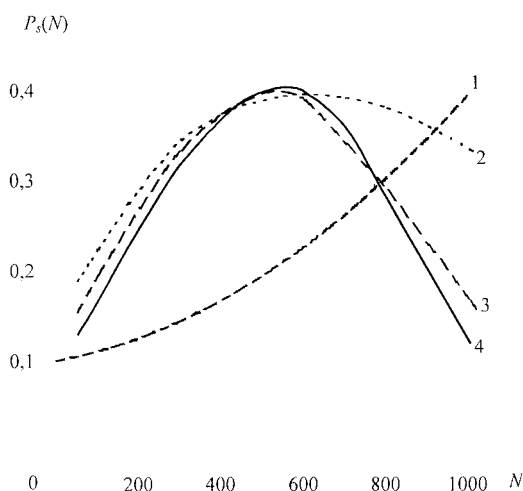


Figure 3 Simulation of MWD curves according to eq. (5) for $b = 0.2$ (1), 0.5 (2), 1.0 (3), and 2.0 (4). $D = 1.65$, $\sigma^2 = 0.25$.

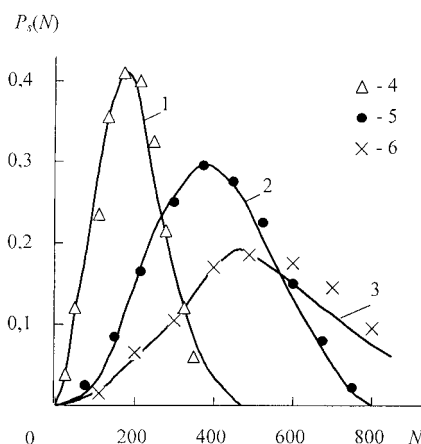


Figure 4 Comparison of experimental (1–3) and calculated [according to eq. (5) (4–6)] MWD curves for PDMDAACH at $c_0 = 1.0$ (1, 4), 2.5 (2, 5), and 4.0 (3, 6) mol/L.

means—as should be expected—a decrease in the fraction of clusters with large N (high-molecular fraction).

The comparison of experimental and theoretical MWD curves has shown that these curves for PDMDAACH, synthesized at $c_0 = 4.0$ and 5.0 mol/L, are simulated directly at the following parameters of a $P_S(N)$ curve: $D = 1.65$ ($a \approx 0.182$), $\sigma^2 = 0.25$, and $b = 1$. The model for $c_0 = 4.0$ mol/L is given in Figure 4 (curve 3), from which good conformity to both the theory and experiment may be observed. When MWD curves of such direct modeling at $c_0 = 1.0$ and 25 mol/L prove to be unsatisfactory (because the position of a maximum on the MWD curve corresponds to $N_{\max} = 175$ and 375), the theoretical curves at such low values of N_{\max} are not attained (Figures 1–3). Nevertheless, to achieve agreement between the theory and the experiment by use of renormalization is possible for these curves, which is attributed to the automodality of $P_S(N)$ distribution on the variable $\tilde{N} = N/N_0$.⁶ Simultaneously it is required to execute the renormalization of white noise of intensity σ^2 as follows⁶:

$$\sigma^2 \rightarrow \sigma_0^2 = \sigma^2 N_0^{2a-1-b} \quad (6)$$

The indicated renormalization is performed by definition of N_0 under conditions at which \tilde{N} is equivalent to the theoretical value N_{\max} and N is the experimental value of this parameter. Figure 4 shows excellent agreement between experimental and theoretical MWD curves for PDMDAACH, synthesized at $c_0 = 1.0$ and 2.5 mol/L, thus confirming the correctness of the indicated renormalization. In turn, this renormalization shows one of the basic properties of fractals—their automodality.¹¹

It was previously established⁵ that the MWD curve for cluster–cluster aggregation depends on the diffusive characteristics of a system in many respects, that is, on

mobility of clusters expressed by their rate ν . The value ν can be expressed by the following simple equation⁵:

$$\nu = m^\beta \quad (7)$$

where m is mass of the cluster.

In turn, the value of an exponent β determines the position of a maximum from the MWD curve⁵:

$$N_{\max} = \frac{-\beta}{1-\beta} \quad (8)$$

One should expect that the mobility of clusters ν will be higher concomitantly with less viscosity of an initial monomer solution η_0 , for which values for PDMDAACH are adduced in Topchiev et al.¹² This supposition was confirmed by the relationship $\nu(\eta_0^{-2})$ shown in Figure 5, which is linear and passes through on origin.

As mentioned above, one should expect an increase of the stochastic contribution in polymerization intensity or white noise σ^2 in the growth process of monomer initial concentration c_0 . This supposition confirms the relationship $\sigma^2(c_0^{1/2})$ shown in Figure 6, which is also linear and passes through an origin. The data of Figures 5 and 6 demonstrate that the parameters of the eq. (5) can be expressed through technical characteristics of the polymerization process, for example, c_0 and η_0 .

CONCLUSIONS

Thus, the results of the present study have shown that the MWD of PDMDAACH is possible to simulate and predict within the framework of the irreversible cluster-cluster aggregation model. The shape and posi-

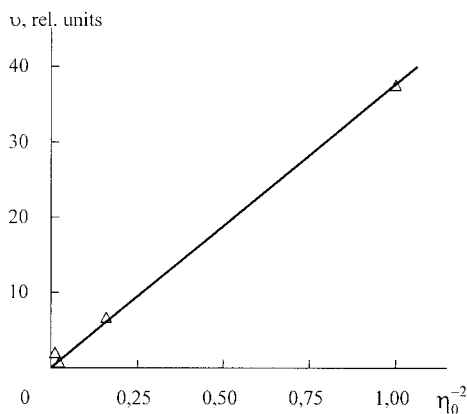


Figure 5 Relationship between mobility of macromolecular coil ν and initial viscosity of monomer solution η_0 for PDMDAACH.

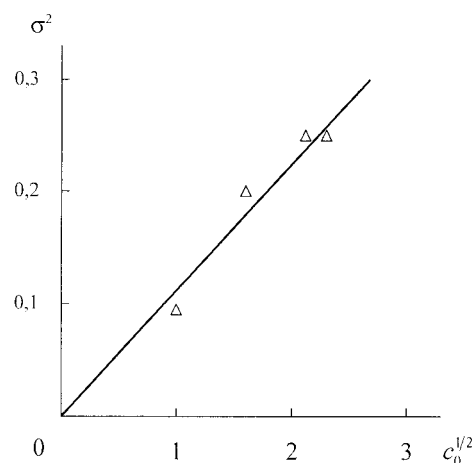


Figure 6 Relationship between the white noise of polymerization intensity σ^2 and initial concentration of monomer c_0 for PDMDAACH.

tion of the MWD curve are influenced by a number of factors, such as macromolecular coil structure, stochastic contribution of a coil environment to a polymerization intensity, and level of destruction of a coil during polymerization. These factors can be linked by simple relationships to technical characteristics of the polymerization process (e.g., c_0 and η_0), which is especially important for the practical applications of the proposed theoretical model.

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