

Fractal Analysis of Polymer Molecular Weight Distribution: Dynamic Scaling

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ABSTRACT: The correctness of the molecular weight distribution (MWD) of a poly(dimethyl diallyl ammonium chloride) type was shown in the frame-work of the dynamic distribution function of the irreversible aggregation cluster–cluster model. The buildup of a generalized distribution curve confirms the possibility to describe the polymerization

processes within the framework of the mentioned model and allows one to predict the kinetics of MWD changes as the function of the initial monomer concentration c_0 and reaction time t . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2382–2384, 2003

INTRODUCTION

The basic process in many practically important cases is the formation of clusters due to the aggregation of particles.¹ To such phenomena, it is necessary to attribute the processes of polymerization, related, in the basic sense, to the formation of long-chain macromolecules from smaller molecules. A widely used method for the description of such systems is the determination of the distribution function of the sizes of clusters, which, in the physics and chemistry of polymers, is defined as a function of the molecular weight distribution (MWD).

As is known,² the macromolecular coils in a solution are fractals whose structure or, more precisely, spatial distribution of a coil's elements is characterized by its fractal dimension D . However, despite the doubtless importance, the value D gives only restricted information concerning the process of aggregation (polymerization). First, it is a static quantity and does not describe the dynamics of the aggregation process. Second, the quantity D characterizes the geometrical properties of only one cluster (macromolecular coil) and cannot be used for the description of a cluster set in the system. The last purpose needs the examination of the dynamic distribution function of cluster sizes $n_s(t)$, which is a number of clusters consisting of s unities forming, in time t .³

An interval of D values for macromolecular coils in a solution² assumes that the process of polymerization proceeds according to the aggregation cluster–cluster mechanism. The dynamic distribution function

of the cluster sizes for the mentioned mechanism was examined in a series of articles.^{3–7} The purpose of the present article was to determine the general laws of the MWD of poly(dimethyl diallyl ammonium chloride) (PDMDAACH) within the framework of the dynamic distribution function for the cluster–cluster aggregation mechanism.

EXPERIMENTAL

PDMDAACH was synthesized in water solutions at an initial monomer concentration c_0 : 1.0, 2.5, 4.05, and 5.0 mol/L (0.161–0.808 in mass). The initiation was carried out by thermal decomposition of ammonium persulfate with a concentration of the initiator of 5×10^{-3} mol/L. The conversion degree was determined by the calorimetric method. The polymerization was carried out at 333 K.

The function of the MWD for PDMDAACH was determined from the changes of a sedimentation rate according to a published procedure⁸ at a rotor rate of 6–104 rpm. All measurements were carried out at a temperature of 303 K in solutions of 1 N NaCl. The curves of the MWD for PDMDAACH at various values c_0 are given in Figure 1. The value D was determined from the following equation⁹:

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

where a is an exponent in the Mark–Houwink equation, equal to 0.82 for PDMDAACH.⁸

RESULTS AND DISCUSSION

The dynamic scaling description of the cluster-size distribution of the diffusion-limited aggregation clus-

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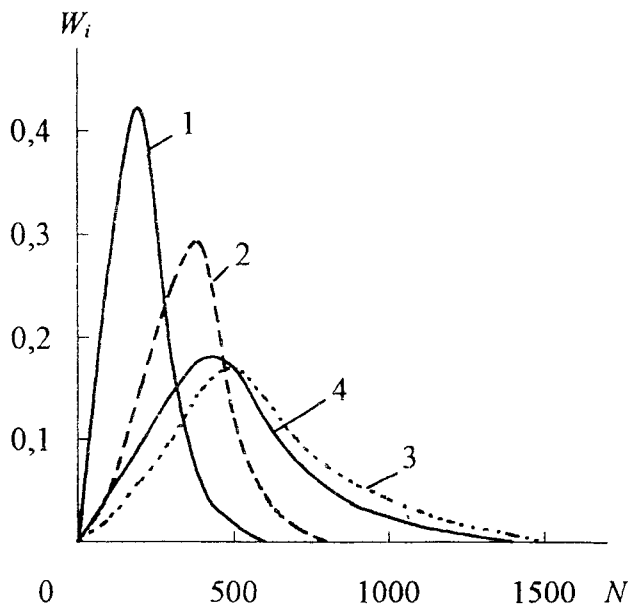


Figure 1 Curves MWD for PDMDAACH, synthesized at c_0 : (1) 1.0, (2) 2.5, (3) 4.05, and (4) 5.0 mol/L.

ter-cluster model was studied in some works.³⁻⁶ This can be applied to describe the radical polymerization of PDMDAACH for the following reason: The value $D = 1.65$ [$a = 0.82$ (ref. 8)] estimated from eq. (1) is a typical fractal dimension for aggregates forming in the diffusion-limited cluster-cluster aggregation process.¹ The applicability of this model for the description of polymerization has repeatedly proved to be true.^{7,10} On this basis for the description of the MWD for PDMDAACH, the dynamic scaling function can be used as³

$$n_s(t) \sim S^{-2tz} \tag{2}$$

where t is the reaction time, accepted as the equal gelation time, and z is an exponent.

Consider the methods of the estimation of the parameters in eq. (2). The values $n_s(t_g)$, where t_g is the gelation time, are determined from the experimental curves of the MWD, $W_i(N)$ (Fig. 1), as follows: We assume that $N = S$ and that a fraction of the polymer corresponding to S_i is equal to a summary weight fraction of the polymer W_i . By dividing W_i in S_i and multiplying, one can obtain the maximum degree of conversion Q and the value $n_s(t_g)$ or n_i for S_i . The exponent z is calculated according to the following equation¹¹:

$$z = D(1 - \alpha) - (d - 2) \tag{3}$$

where α is an exponent in the relationship for the diffusion constant D_s as a function S ($D_s \sim S^\alpha$) and d is an Euclidean space dimension, in which the fractal,

equal, in our case, to 3, is considered. The value D_s can be calculated as follows¹²:

$$D_s = \frac{kT}{6\pi\eta_0 R_g \beta} \tag{4}$$

where k is the Boltzmann constant; T , the testing temperature; η_0 , the initial viscosity of the reactionary mixture; R_g , a radius of gyration of a diffusing particle (macromolecular coil); and β , a numerical coefficient defined by the boundary conditions of the particle surface.

In turn, as was mentioned above, the value D_s within the framework of the irreversible aggregation models usually is accepted as^{3,11}

$$D_s \sim S^\alpha \tag{5}$$

From the comparison of relationships (4) and (5), it is easy to obtain

$$\alpha \sim -\ln\eta_0. \tag{6}$$

The values η_0 for the monomer solutions, used for the synthesis of PDMDAACH, were given in ref. 13.

As was pointed out,^{3,11} the value α defines a form of a distribution function. For $\alpha < -0.5$, the "bell"-shaped distribution curves having a maximum are obtained. For $\alpha > -0.5$, the monotonously decaying curves are typical. As follows from Figure 1, the experimental curves of the MWD have the maximum shape. On the basis of the absolute values η_0 , we assumed, in relationship (6), a sign of the equality, and, in this case, the values of α vary within the limits $\sim 1-3$ (values η_0 are

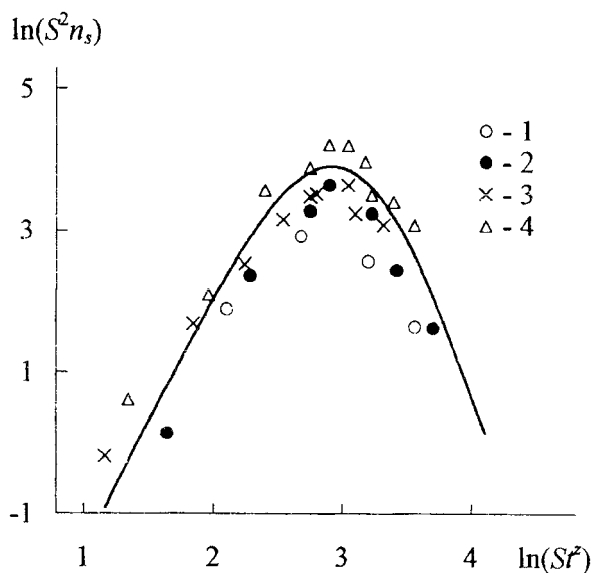


Figure 2 Generalized MWD curve in the form of functions $S^2 n_s(S t^z)$ in double-logarithmic coordinates for PDMDAACH, synthesized at c_0 : (1) 1.0, (2) 2.5, (3) 4.05, and (4) 5.0 mol/L.

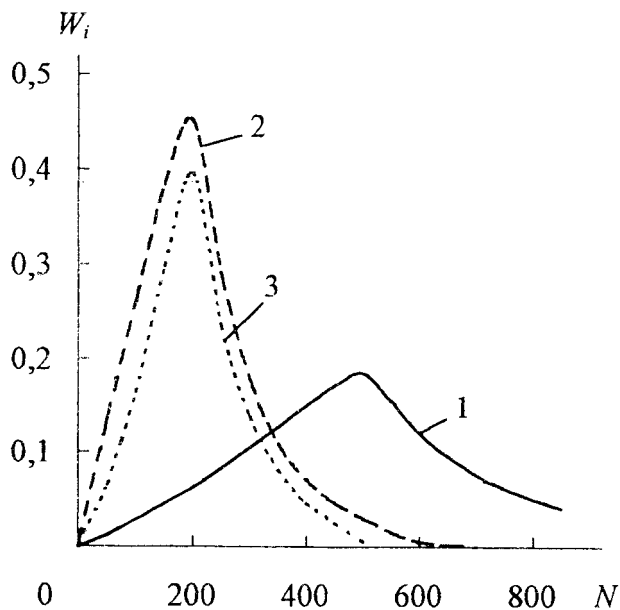


Figure 3 Experimental MWD curves at gelation time for PDMDACh, synthesized at (1) $c_0 = 4.0$ and (3) 1.0 mol/L. Calculated MWD curve at $t = 53$ min for PDMDACh, synthesized at (2) $c_0 = 4.0$ mol/L.

given in relative units¹³ and this interval completely matches the shape of the experimental MWD curves (Fig. 1). Besides, as was shown earlier,¹⁴ the position of the maximum of the curve of the MWD is determined by the relationship

$$N_{\max} \sim \frac{-\alpha}{1-\alpha} \quad (7)$$

It is not difficult to see that the increase of c_0 , given the increase of η_0 , defines the buildup of the absolute value α and increases N_{\max} , corresponding with Figure 1.

In Figure 2, the dependencies S^2n_s on St^z in the double-logarithmic coordinates for four polymers of PDMDACh, synthesized at various c_0 , are shown. As follows from the data of this figure, all four MWD curves, shown in Figure 1, are described by the unique curve. This result confirms the correctness of the use of the application of the irreversible aggregation models for the description of the polymerization process.

Using the generalized curve shown in Figure 2, it is possible to predict, theoretically, the kinetics of the MWD change as a function of time. For this purpose,

at first, we set the values $S = N$ and determine the value of St^z at arbitrary t . Then, from the diagram of Figure 2, the value S^2n_s is found corresponding to it and, according to the above-described procedure, it is defined as W_i . Then, the same calculation is iterated for another S , etc. In Figure 3, as an example, a comparison of the MWD curves for $c_0 = 4.0$ mol/L is given at $t = t_g = 108$ min and $t = 53$ min. As seen from the comparison of curves 1 and 2 in Figure 3, the decrease of t ($t < t_g$) results in a maximum MWD and lower molecular weight values and a narrower MWD. Besides, in Figure 3, the MWD curve for $c_0 = 1.0$ mol/L is given at $t = t_g$ (curve 3), and from a comparison of all three curves, it follows that the decrease of t and c_0 give a similar effect.

CONCLUSIONS

Thus, the results of the present article showed the correctness of the description the polymer of the MWD on an example of PDMDACh within the framework of the dynamic distribution function of the irreversible aggregation cluster-cluster model. It is proved by the buildup of a generalized distribution curve and allows one to predict the kinetics of the MWD change as a function of the monomer initial concentration c_0 and the reaction time t .

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