

# Application of the Fractional Derivative Theory to the Estimation of the End-to-End Distance of Polycarbonate Chains

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**ABSTRACT:** This study has led to two main conclusions. First, fractional derivation can be used to calculate the average end-to-end distance of a polymeric chain as precisely as other existing computational techniques. Second, knowledge of the changes in the molecular characteristics of a polymeric chain is needed for the correct calculation of the

indicated parameters. In other words, one should take into consideration the dynamics when the structure of a macromolecular coil is varied. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3765–3768, 2004

**Key words:** polycarbonates; chain; structure

## INTRODUCTION

A macromolecular coil in a polymeric solution is a fractal object, the structure (the distribution of its elements in space) of which can be described with the help of the fractal (Hausdorff) dimension ( $D_f$ ).<sup>1</sup> This allows the use of the mathematical theory of fractional derivation<sup>2–4</sup> for the description of the parameters of a macromolecular coil. Within the framework of this formalism, a capacity for the precise description of nonlinear phenomena, such as spatial correlations,<sup>4</sup> can be represented. In the past, fractional derivation has also been successfully applied to the description of the properties of polymers.<sup>5–8</sup> In this article, this approach is used for the calculation of the average end-to-end distance ( $\langle \bar{h}_s^2 \rangle^{1/2}$ ) of a polymeric chain of polycarbonate (PC) in two different solvents.

## THEORY

There are a number of methods used for the calculation of  $\langle \bar{h}_s^2 \rangle^{1/2}$ , which is an important parameter in the theory of polymeric solutions.<sup>9</sup> The following empirical relationships for PC in solutions of methylene chloride (MCh) and tetrahydrofuran (THF) can be obtained:<sup>10</sup>

$$\langle \bar{h}_s^2 \rangle^{1/2} = 0.66 M_\eta^{0.58} \quad \text{for MCh} \quad (1)$$

$$\langle \bar{h}_s^2 \rangle^{1/2} = 1.04 M_\eta^{0.53} \quad \text{for THF} \quad (2)$$

where  $M_\eta$  is the viscosity-average molecular weight.

Another method uses the following equation:<sup>9</sup>

$$[\eta] = \Phi(\alpha) \frac{\langle \bar{h}_s^2 \rangle^{1/2}}{M_\eta} \quad (3)$$

where  $[\eta]$  is the intrinsic viscosity of a solution and  $\Phi(\alpha)$  is a parameter dependent on the swelling coefficient ( $\alpha$ ) of a coil. At  $\alpha^3 > 5$ ,  $\Phi(\alpha)$  is equal to approximately  $2 \times 10^{23}$ .<sup>9</sup>

In addition to equations, an estimated value of  $\langle \bar{h}_s^2 \rangle^{1/2}$  can be obtained within the framework of fractional derivation as follows.<sup>11</sup> Let  $x = x(t)$  be the law of change of some physical property at time  $t$ . The rate of change  $x(t)$  has the following form:

$$\frac{dx}{dt} = \nu(t) \tau_0 \quad (4)$$

where  $t$  is dimensionless time and  $\tau_0$  is the characteristic time of the given process.

Equation (4) can be represented as follows:

$$D_{0+}^\nu D_{0+}^{1-\nu} x(t) = \nu(t) \tau_0 \quad (5)$$

where

$$D_{0+}^\nu f(t) = \frac{1}{\Gamma(1-\nu)} \frac{d}{dt} \int_0^t \frac{f(\tau) d\tau}{(t-\tau)^\nu} \quad (6)$$

is a Riman–Liouville fractional derivative of approximately  $\nu$  ( $0 < \nu < 1$ ).

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If we enter the notation  $D_0^{1-\nu}x(t) = h_s(t)$ , eq. (5) becomes

$$D_0^\nu h_s(t) = \nu(t)\tau_0 \quad (7)$$

The solution of eq. (7) looks like

$$h_s(t) = \frac{\tau_0}{\Gamma(\nu)} \int_0^t \frac{\nu(\tau) d\tau}{(t-\tau)^\nu} \quad (8)$$

The integral in the right part of eq. (8) is easily calculated at  $\nu(t) = \nu$ , where  $\nu$  is constant, and returning to dimensional  $t$ , we obtain the following:

$$h_s(t) = \frac{\nu\tau_0^\nu}{(1-\nu)\Gamma(\nu)} \quad (9)$$

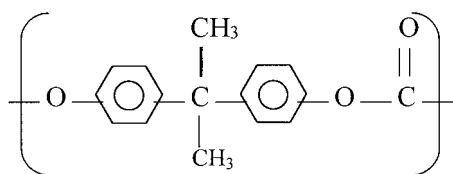
where  $\Gamma(\nu)$  is Euler's  $\Gamma$  function.

Comparing eq. (9) at  $\nu = 1/2$  with the known Einstein formula for the mean-square displacement of a particle making Brownian motion, researchers have drawn the conclusion that the value of  $h_s(t)$  can be considered  $h_s = \langle x^2 \rangle^{1/2}$ .<sup>11</sup>

A polymeric macromolecule can be divided into statistical segments of length  $l_{st}$  and one can simulate it (in an elementary case) as Brownian motion of a segment.<sup>9</sup> Then, eq. (9) can be used for the description of a polymeric chain. In this case, rate  $\nu$  can be treated as the rate of segment jumping, and  $\tau_0$  can be considered the time of one jump. If  $l_{st}$  is equal to  $\nu\tau_0$  and  $t$  is equal to  $\tau_0 N_{st}$  (where  $N_{st}$  is the number of statistical segments in a chain), we obtain the following:<sup>11</sup>

$$\langle \bar{h}_s^2 \rangle^{1/2} = \frac{l_{st} N_{st}^{1-\nu}}{(1-\nu)\Gamma(\nu)} \quad (10)$$

We have chosen PC because it is a very well studied polymer for which Mark-Kuhn-Houwink equations have been obtained for various solvents. PC has the following chemical structure:



The purpose of this article is the calculation of  $\langle \bar{h}_s^2 \rangle^{1/2}$  according to eqs. (1)–(3) and (10) and the subsequent comparison of the results for samples of PC solutions in two solvents (MCh and THF). For this purpose, five molecular weights (MWs) for PC have been arbitrarily chosen: 2.5, 5.0, 7.5, 10.0, and  $12.5 \times 10^4$ . With eqs. (1) and (2), the empirical values of  $\langle \bar{h}_s^2 \rangle^{1/2}$  are calculated for the indicated MWs. When eq. (3) is used for the

determination of the  $[\eta]$  values (dL/g) corresponding to the indicated MWs, the following Mark-Kuhn-Houwink equations are used:<sup>10</sup>

$$[\eta] = 1.11 \times 10^{-4} \text{ MW}^{0.82} \quad \text{for MCh} \quad (11)$$

$$[\eta] = 3.99 \times 10^{-4} \text{ MW}^{0.70} \quad \text{for THF} \quad (12)$$

This allows us to calculate  $\langle \bar{h}_s^2 \rangle^{1/2}$  according to eq. (3). When eq. (10) is used, the parameters  $l_{st}$ ,  $N_{st}$ ,  $\nu$ , and  $\Gamma(\nu)$  should be defined.  $l_{st}$  can be determined as follows:<sup>12</sup>

$$l_{st} = C_\infty l_0 \quad (13)$$

where  $C_\infty$  is the characteristic ratio of chain statistical flexibility<sup>9</sup> and  $l_0$  is the length of the skeletal bond of the main chain equal to 1.25 Å for PC.<sup>13</sup>

In this article, two variants of  $C_\infty$  are used. The first (static) is based on the application of a literature value of  $C_\infty$  for PC (2.4).<sup>12,13</sup> The second (dynamic) variant supposes that the value of  $C_\infty$  depends on the structure of the macromolecular coil in solution, that is,  $D_f$ , and in this case,  $C_\infty$  can be determined as follows:<sup>14</sup>

$$D_f = 2 - 4 \left( \frac{2}{C_\infty^2 S} \right)^{1/2} \quad (14)$$

where  $S$  is the cross-section area of a macromolecule ( $30.7 \text{ \AA}^2$ )<sup>15</sup> for PC.

In turn,  $D_f$  can be calculated with the following equation:<sup>16</sup>

$$D_f = \frac{3}{1+a} \quad (15)$$

where  $a$  is the index in the Mark-Kuhn-Houwink equation [0.82 for MCh and 0.70 for THF; see eqs. (11) and (12), respectively].

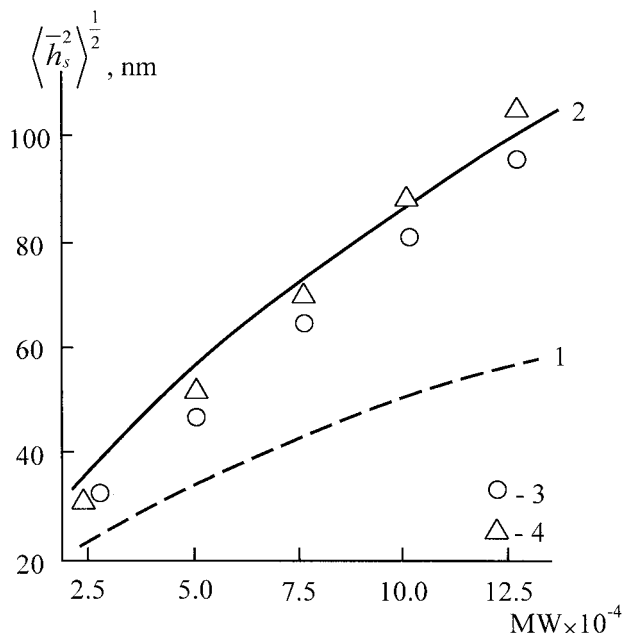
The volume of a macromolecule ( $V_m$ ) can be determined with known MW values as follows:<sup>17</sup>

$$V_m = \frac{\text{MW}}{\rho N_A} \quad (16)$$

where  $\rho$  is the density of a polymer ( $1.20 \times 10^3 \text{ kg/m}^3$  for PC<sup>17</sup>) and  $N_A$  is Avogadro's number.

Furthermore, it is possible to calculate the length of a macromolecule ( $L_m$ ) as  $V_m/S$  and  $N_{st}$  as  $L_m/l_{st}$ .

As shown in ref. 2, the fractional exponent  $\nu$  correlates with the fractal dimension of Cantor's set and indicates a fraction of the system, the status being kept for the entire evolution time  $t$ . Cantor's set is considered in one-dimensional Euclidean space ( $d = 1$ ), and so its fractal dimension is  $d_f < 1$  by virtue of the fractal definition. For fractal objects in Euclidean spaces with



**Figure 1** Dependence of  $\langle \bar{h}_s^2 \rangle^{1/2}$  on MW for a solution of PC in MCh: (1) eq. (1) with a constant value of  $C_{\infty}$ , (2) eq. (3) with a constant value of  $C_{\infty}$ , (3) eq. (10) with a constant value of  $C_{\infty}$ , and (4) eq. (14) with an estimated value of  $C_{\infty}$ .

higher dimensions ( $d > 1$ ) like  $\nu$ , one should accept  $d_f$  or<sup>7,8</sup>

$$\nu = d_f - (d - 1) \tag{17}$$

where  $d$  is the dimension of the Euclidean space in which the fractal is considered.

We consider the physical sense and definition of the value of a fractional exponent  $\nu$  in the given context. The transition to the condensed polymeric state occurs at  $D_f = 2.5$ .<sup>1</sup> This means that the limiting value of  $\nu$  is reached at this value of  $D_f$ , equivalent to  $d$ , and then we obtain the following:<sup>7</sup>

$$\nu = D_f - (2.5 - 1) \tag{18}$$

or

$$\nu = D_f - 1.5 \tag{19}$$

At last,  $\Gamma(\nu)$  can be calculated as follows:<sup>18</sup>

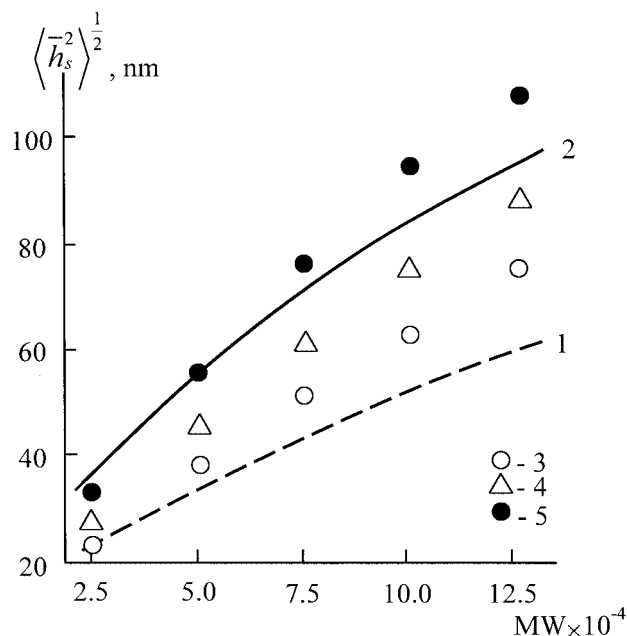
$$\Gamma(\nu) = \left(\frac{\pi}{2}\right)^{1/2} \nu^{-\nu} e^{-\nu} \tag{20}$$

**RESULTS AND DISCUSSION**

Figure 1 presents a comparison of the relationships of the  $\langle \bar{h}_s^2 \rangle^{1/2}$  (MW) values, calculated by the three indicated methods, for solutions of PC in MCh. A good

correspondence (within a limit of 8%) for the values of  $\langle \bar{h}_s^2 \rangle^{1/2}$  calculated with eqs. (11) and (12) with the use of a dynamic variant of an estimation of  $C_{\infty}$  [eq. (14)] has been obtained. The application of the statistical variant  $C_{\infty}$ , when it is constant, increases the error of the calculated values up to approximately 12%. As for the empirical equation, eq. (1), it produces values of  $\langle \bar{h}_s^2 \rangle^{1/2}$  much lower than the estimations of eqs. (11) and (12).

A similar picture is obtained for solutions of PC in THF (Fig. 2), although the disagreement of the calculated results of eqs. (11) and (12) and eq. (14) is a little bit greater, approximately 17%. The error in the estimation of  $D_f$  may be the reason. Therefore, reducing  $D_f$  from 1.765 to 1.70 (i.e., 3%) results in the best correspondence of the indicated calculations (Fig. 2): the average disagreement is reduced to 11.5%. It is necessary to mark the other important feature of the relationships of  $\langle \bar{h}_s^2 \rangle^{1/2}$  and MW, calculated with eq. (10): they grow faster than similar dependences calculated with eq. (11) at large MWs. At large MWs, the macromolecular coil becomes more compact, and this results in a decrease in exponent  $a$  in the Mark-Kuhn-Houwink equation and, according to eq. (15), to an increase in  $D_f$ .<sup>9</sup> The estimations have shown that for solutions of PC in MCh, when  $D_f$  increases from 1.648 to 1.681, that is, 2% (or  $a$  decreases from 0.820 to 0.785),  $\langle \bar{h}_s^2 \rangle^{1/2}$  decreases from 107.4 to 99.6 nm; that is, the indicated difference is eliminated.



**Figure 2** Dependence of  $\langle \bar{h}_s^2 \rangle^{1/2}$  on MW for a solution of PC in THF: (1) eq. (1) with a constant value of  $C_{\infty}$ , (2) eq. (3) with a constant value of  $C_{\infty}$ , (3) eq. (10) with a constant value of  $C_{\infty}$ , (4) eq. (14) with an estimated value of  $C_{\infty}$ , and (5)  $D_f = 1.70$ .

We now return to the correctness of using  $\Phi(\alpha) = 2 \times 10^{23}$  in eq. (3). The value of  $\alpha$  is connected to  $D_f$  by the following equation:<sup>19</sup>

$$D_f = \frac{5\alpha^2 - 3}{3\alpha^2 - 2} \quad (21)$$

For values of  $D_f$  obtained with eq. (15) for solutions of PC in MCh and THF ( $D_f = 1.648$  or  $1.764$ , respectively),  $\alpha^3$  is 2.5–25, and this enables the use of the indicated coefficient  $\Phi(\alpha)$ .

### CONCLUSIONS

The results of this article allow us to make two main conclusions. First, fractional derivation can be used to calculate  $\langle \bar{h}_s^2 \rangle^{1/2}$  of a polymeric chain as precisely as other existing computational techniques. Second, knowledge of changes in the molecular characteristics of a polymeric chain is needed for the correct calculation of the indicated parameters. In other words, one should take into consideration the dynamics when the structure of a macromolecular coil is varied.

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