

Description of the Structure of Branched Polyphenylquinoxaline Macromolecular Coil within the Framework of Fractal Theory

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ABSTRACT: The applicability of fractal analysis for a quantitative description of a structure of a macromolecular coil of branched polymers is shown. The important aspect of the offered treatment is a type of interaction between macromolecule elements (repulsion or attraction). One of the more important factors was the structure of this macromol-

ecule characterized by its fractal dimension. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3574–3577, 2006

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INTRODUCTION

As is known¹ and generally used now, the traditional methods of determining branched polymer macromolecular coils are connected with the necessity of their hydrodynamic properties being compared with the linear analog properties of the same molecular weight. Theories for this purpose are complicated, often non-unique, and sometimes do not allow quantitative estimations of a branched polymer structure. Therefore, the purpose of the present study was to describe the structure of a macromolecular coil of branched polymers within the framework of fractal analysis,² using as an example branched polyphenylquinoxaline (PPQX) with various degrees of branching in the two solvents.

EXPERIMENTAL

Data from Korshak et al.³ on branched PPQX with a varying fraction of polyfunctional components, γ , in the range of 0–0.04 (Table I) were used. Table I lists the parameters of the Mark–Houwink–Sakurada equation in two solvents: chloroform and *N*-methylpyrrolidone.³ The values of the spectral dimension, d_{sr} , of PPQX macromolecular coils (Table I) from Dolbin and Kozlov⁴ were accepted. The fractal dimension

of the solvent molecules, δ_f , was determined according to the equation⁴

$$\delta_f \approx 1.58(\delta_s^{1/2} - 2.83), \quad (1)$$

where δ_s is the solubility parameter of the solvent, which was 8.7 (cal/sm³)^{1/2} for chloroform and 11.6 (cal/sm³)^{1/2} for *N*-methylpyrrolidone.⁵

RESULTS AND DISCUSSION

As is known,² the phantom (which does not account for excluded volume interactions) fractal dimension of a macromolecular coil, d_f , is given by

$$d_f = \frac{2d_s}{2 - d_s}, \quad (2)$$

and the swollen (which accounts for excluded volume effects) fractal dimension of the same coil, D_f , is determined by²

$$D_f = \frac{d_s(d + 2)}{d_s + 2}, \quad (3)$$

where d is the dimension of Euclidean space in which the fractal is examined (in our case, apparently $d = 3$).

The experimental estimation of dimension D_f allowed construction of the following simple equation:⁶

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TABLE I
Parameters of the Mark–Houwink–Sakurada Equation, $[\eta] = K_v M^a$, and Spectral Dimension, d_s , for Statistically Branched Poliphenylquinoxaline

γ	d_s	Chloroform		<i>N</i> -methylpyrrolidone	
		$K_v \times 10^4$	a	$K_v \times 10^4$	A
0	1.0	7.94	0.64	12.9	0.57
0.0067	1.10	2.30	0.72	25.0	0.47
0.01	1.15	2.51	0.71	32.0	0.44
0.02	1.23	4.91	0.63	43.3	0.41
0.04	1.30	7.40	0.57	55.4	0.38

$$D_f = \frac{3}{1 + a'} \quad (4)$$

where a is an exponent in the Mark–Houwink–Sakurada equation (see Table I).

Eq. (3) gives the value D_f in solvents consisting of point (zero-dimensional) molecules, which have the fractal dimension $\delta_f = 0$.² From eq. (1) it follows that the condition $\delta_f = 0$ is achieved for $\delta_s \leq 8.0$ (cal/sm³)^{1/2}. As δ_s values for the solvents used were larger than this value, for them, $\delta_f > 0$. From eq. (1) it could be estimated that the value of δ_f would be ~ 0.19 for chloroform and ~ 0.91 for *N*-methylpyrrolidone. In this case the D_f was determined from the following equation²:

$$D_f = \frac{d + 2}{2 - (\delta_f - 2)/\delta_f} \quad (5)$$

Figure 1 shows the dependence of D_f and d_f on d_s for all cases considered. The dependence $D_f(d_s)$ for real polymers should be between curves $d_f(d_s)$ and $D_f(d_s)$, where D_f is determined according to eq. (3), curves 1 and 2, respectively. For PPQX macromolecular coils in *N*-methylpyrrolidone this condition was really carried out, and, in addition, the experimental values of D_f [eq. (4)] were in excellent agreement with the calculations of D_f using eq. (5), where $\delta_f = 0.91$ and d_f is calculated according to eq. (2). At the same time, the data for PPQX macromolecular coils in chloroform estimated according to eq. (4) were lower than $D_f(d_s)$ for the swollen coils, though eq. (3) assumes they would have the minimum value of D_f ($\delta_f = 0$). The $D_f(d_s)$ for the swollen coils (curve 2 in Fig. 1) did not agree with the experimental results. To explain this disagreement, the definition of eq. (5) by Vilgis² should be considered. It was assumed that the fractal molecules of the solvent screen excluded volume interactions, that is, a decrease in the degree of repulsion interactions between macromolecule elements. Therefore, the increase in δ_f would lead to an increase in D_f . Then α , which is equal to²

$$\alpha = \frac{\delta_f}{d_f} \quad (6)$$

would be incorporated. In eq. (6), δ_f is a phantom fractal dimension of the solvent molecules.

The screening interaction is approximated by two-body interactions²:

$$U^{(2)} \sim (v/N)M^2/R^d = (v/r^{\delta_f})M^2/R^d, \quad (7)$$

where $U^{(2)}$ is the energy of interaction of a two-body repulsion, v is a parameter of the excluded volume, N is the degree of polymerization, M is the molecular weight, and r and R are the gyration radii of the solvent molecule and a macromolecular coil, respectively.

Then $U^{(2)}$ was minimized, and the final result was²

$$F/kT = (R/R_0)^2 + vM^{2-\alpha}/R^d, \quad (8)$$

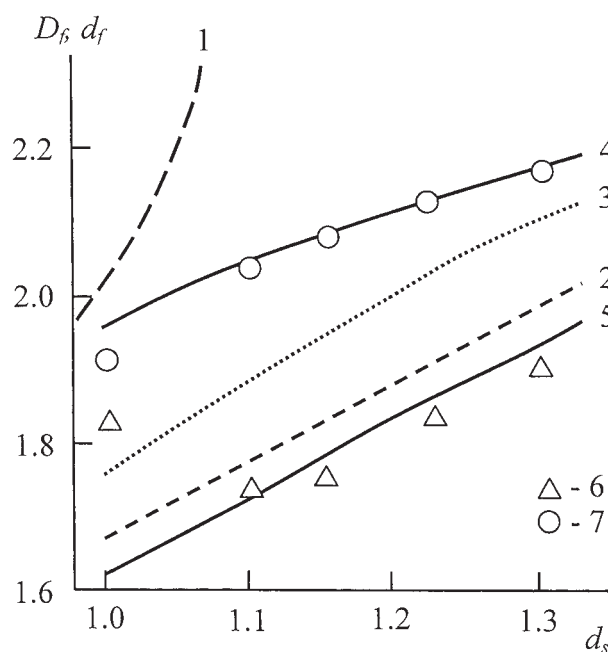


Figure 1 Dependences of swollen D_f and phantom d_f fractal dimensions of a macromolecular coil PPQX on the spectral dimension, d_s : (1) from eq. (2); (2) from eq. (3); (3) from eq. (5) for chloroform; (4) from eq. (5) for *N*-methylpyrrolidone; (5) from modified eq. (5) for chloroform; (6) from eq. (4) for chloroform; and (7) from eq. (4) for *N*-methylpyrrolidone.

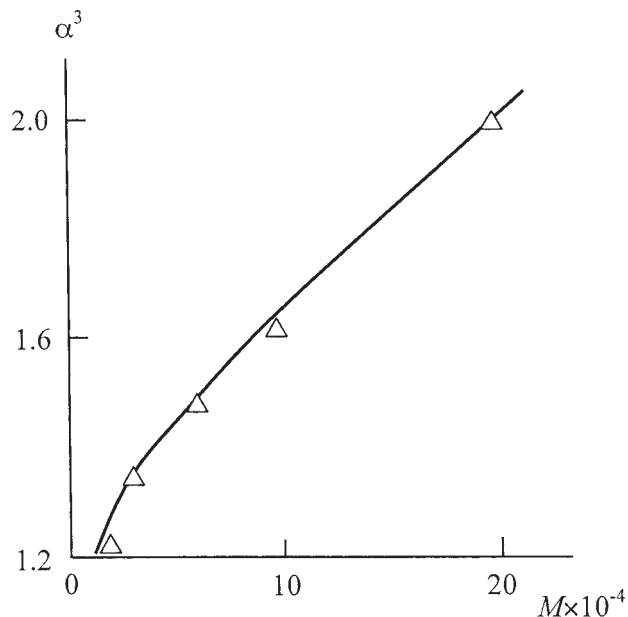


Figure 2 Dependence of the excluded volume factor, α^3 , on the molecular weight of PPQX.

where F is the free energy, k is the Boltzmann constant, T is the temperature, and R_0 is the gyration radius of the coil in ideal conditions.

The final result of this treatment was eq. (5) or, if the spectral dimension d_s was used, the following equation²:

$$D_f = \frac{d_s(d+2)}{(1-\alpha)d_s+2}. \quad (9)$$

It is easy to see that in this treatment the possibility of screening attraction interactions between macromolecule elements is not allowed. This effect should produce a decrease in coil compactness and a reduction in the D_f value, which was observed for PPQX coils in chloroform (Fig. 1). The simplest method for incorporating this effect is the replacement of the plus sign before δ_f in eq. (5) by a minus sign or the replacement of the minus sign before α in eq. (9) by a plus sign. Calculating D_f according to these modified eqs. (5) and (9) showed excellent correspondence with the experimental results (curve S, Fig. 1). This allowed the assumption that the chloroform molecules screened attracted interactions between the branches of PPQX macromolecules but did not screen them for the main chain of a polymer [the experimental value D_f for linear PPQX corresponded well with a calculation according to eq. (5) or eq. (9) at $d_s = 1$, Fig. 1]. If this is true, then the molecular weight, M , would increase proportional to the increase in the number of branches in the macromolecular coil, which should amplify the effect expressed by the factor of excluded volume, α^3 , which was determined by:³

$$\alpha^3 = \frac{[\eta]_{ch}}{[\eta]_{mp}}, \quad (10)$$

where $[\eta]_{ch}$ and $[\eta]_{mp}$ are the intrinsic viscosities of polymer in chloroform and *N*-methylpyrrolidone, respectively.

Figure 2 shows dependence $\alpha^3(M)$ plotted according to the data of Korshak et al.,³ which confirmed the above assumption. It was assumed that α^3 was uniquely connected with the fractal dimension of a macromolecular coil, D_f , by the following relationship⁷:

$$D_f = \frac{5\alpha^2 - 3}{3\alpha^2 - 2}. \quad (11)$$

Eq. (11) enabled the estimation of an excluded volume factor for each of the solvents [which means it differed from eq. (10)]. The values of dependence α^3 on the branching component fraction, γ , for PPQX are shown in Figure 3. As had been expected, an extreme change in $\alpha^3(\gamma)$ in the PPQX solutions—for chloroform and monotone a reduction in α^3 and for *N*-methylpyrrolidone an increase in γ —was observed.

The maximum dependence, $\alpha^3(\gamma)$, reported by Korshak et al.³ was explained only qualitatively. It was assumed that the first portion of this dependence (up to the maximum) resulted from the increased density of the links in a coil for a thermodynamically good solvent at branching, which should have increased α^3 .

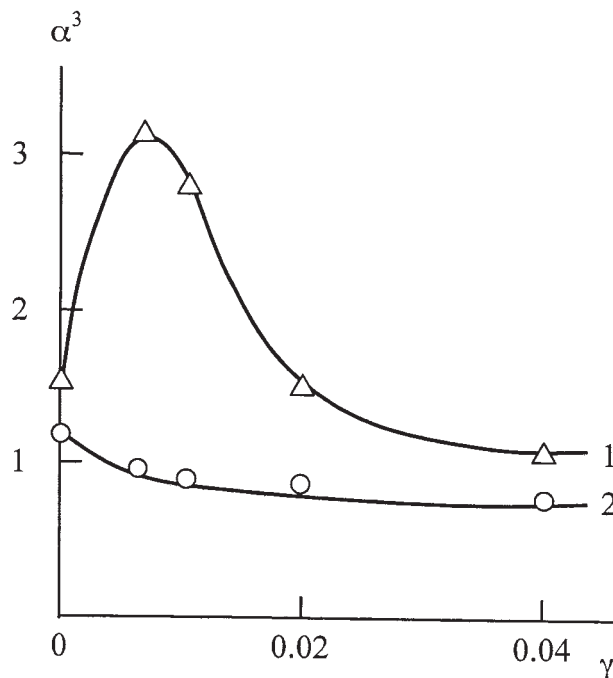


Figure 3 Dependence of the excluded volume factor, α^3 , on the branching component fraction, γ , for PPQX solutions in (1) chloroform and (2) *N*-methylpyrrolidone.

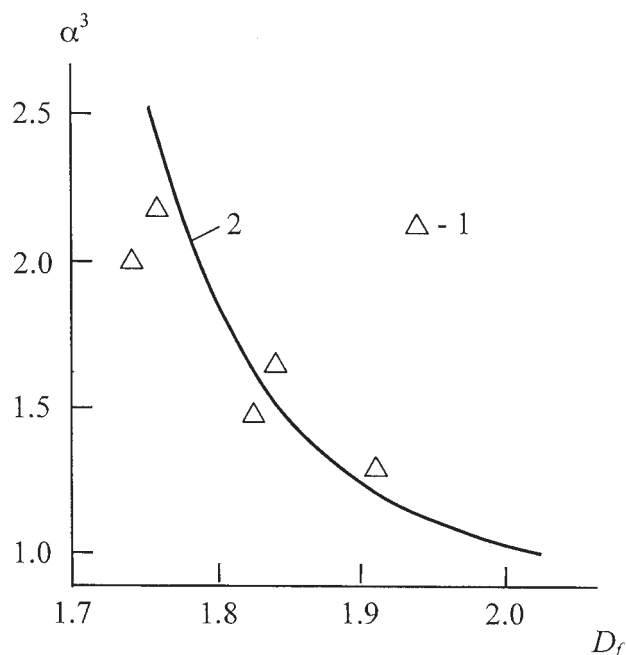


Figure 4 Comparison of the dependences of the excluded volume factor, α^3 , on fractal dimension, D_f , of a macromolecular coil calculated according to (1) eq. (10) and (2) eq. (11) for PPQX at $M = 2 \times 10^5$.

The second portion of the curve resulted from the increased structural rigidity with an increased degree of branching connected with a decrease in the inter-nodal distance. Within the framework of the fractal model, a general quantitative treatment of this effect

can be achieved. Figure 4 shows a comparison of the values of α^3 (D_f), in which the values of α^3 were determined theoretically according to eq. (11) and experimentally according to eq. (10). As can be seen, a good correspondence between these values was obtained.

CONCLUSIONS

The results of the present study showed the applicability of fractal analysis to a quantitative description of a structure of a macromolecular coil of branched polymers. The most important aspect of the treatment was the type of interaction between the macromolecule elements (repulsion or attraction). Another of the more important factors was the structure of the macromolecule characterized by its fractal dimension.

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