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THE DEPENDENCE OF THE CHAIN BRANCHING DEGREE ON MOLECULAR WEIGHT: FRACTAL ANALYSIS

The fractal analysis methodology allows the clear structural identification of both chemical and physical factors controlling a chain branching degree. The effective number of branching centers per one macromolecule m is controlled by four factors: polymer molecular weight, MW , maximal "chemical" density of reactive centers, c_{ch} , dimension of non-screening surface of macromolecular coil, d_w , and its fractal dimension, D . The presented research allows the determination of the critical value, $D_{cr} = 1.10$, the lower of which branching degree is equal to zero (i.e., branching does not occur).

Key words: polyhydroxyether; branching; structure; non-screening surface; critical dimension.

The branching degree of polymeric chain can be characterized by several parameters [1]. One of them is a number of branching centers per one macromolecule m . The branching degree, g , determined from the scaling relationship [1,2], serves as another parameter:

$$m \sim MW^g \quad (1)$$

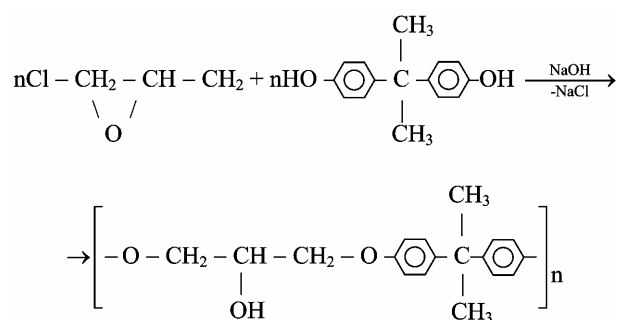
where MW is the polymer molecular weight.

As a rule, the value $g < 1$ [1] means that the number of branching centers is not proportional to the length of macromolecule or its polymerization degree, N . From the chemical point of view, such an effect is difficult to explain, as each monomer link in a macromolecule has the same probability of branch formation, and then one can expect $m \sim N$. However, in the real conditions of polymer(s) synthesis there are a number of causes which can in principle cause the ratio m/N to decrease. One of such reasons can be the fact that the branching reactive centers, formed in initial stages of synthesis, are proved to be "buried" inside a macromolecular coil and, consequently, are less accessible [2]. This situation defines the necessity of the macromolecular coil structure allowance. As already known [3], a macromolecular coil in solution is fractal and its structure (more exactly, distribution in space of its links) can be characterized by a

fractal dimension, D . Therefore, the purpose of the present paper is description of macromolecular coil structure influence on the accessible for reaction number of branching centers at polymer molecular weight change. This description will be fulfilled within the framework of fractal analysis [4] on the example of polyhydroxyether synthesis [5].

EXPERIMENTAL

Polyhydroxyether (PHE) was synthesized by one-step method, namely, by a direct interaction of epichlorohydrin and 4,4'-dioxidiphenylpropane (DPP) according to the scheme [5]:



To obtain PHE by a hetero-phase method, the optimal values of four factors were used: the duration of synthesis was 4 h, duration of epichlorohydrin addition was 50 s, DPP concentration was 0.70 mol/l and the sodium hydroxide concentration was 1.15 mol/l. Sodium hydroxide was used as the activator of polymer formation process and as agent of dehydrohalogenation [5].

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The synthesis was made at three temperatures: 333, 338 and 343 K, since with such conditions branched polymers are obtained [6]. The dependences of the produced viscosity, η_{red} , and the conversion degree, Q , on the reaction duration, t , at mentioned T , as reported by Beeva and coworkers [5], were accepted. The macromolecular coil fractal dimensions, D , at these T s are equal to 1.98, 1.89 and 1.69, respectively [6].

The produced viscosity, η_{red} , was determined for 0.50 % PHE solution in chloroform on Ubbelode viscosimeter at 298 K.

RESULTS AND DISCUSSION

Besides the characteristics indicated above, only one more parameter, the branching factor, g' , can be used for estimation of polymer branching degree, which is determined as follows [7]:

$$g' = \frac{\overline{R}_\theta^2}{\overline{R}_{l,\theta}^2} \quad (2)$$

where \overline{R}_θ^2 and $\overline{R}_{l,\theta}^2$ are average gyration radii of the branched polymer and its linear analog in θ -solvent, respectively, at the same values of molecular weight, MW , and Kuhn segment size characterizing the chain thermodynamic rigidity [1].

In the ref. 6, the following fractal equation for g' estimation was obtained:

$$g' = MW^{\frac{2(D_{l,\theta} - D_\theta)}{D_{l,\theta} D_\theta}} \quad (3)$$

where D_θ and $D_{l,\theta}$ are fractal dimensions of the macromolecular coil of a branched polymer and its linear analog in θ -solvent, respectively. The values D_θ and $D_{l,\theta}$ for PHE, synthesized at $T = 333$ K, are equal to 2.249 and 2.0, respectively [6].

Equation (3) supposes that g' depends on the molecular weight. Parameters g' and m are connected according to the following relationship [1,7]:

$$g' = \left[\frac{4m}{9\pi} + \left(1 + \frac{m}{7}\right)^{0.5} \right]^{-0.5} \quad (4)$$

The dependence m vs. MW for $T = 333$ K in log-log coordinates is shown in Fig. 1, which proves to be linear, and from its slope the value $g \approx 0.272$ can be calculated. The dependences for the two remaining temperatures are similar and therefore they are not shown. The small g value supposes that macromolecular coil structure strongly influences the m value and this effect can be estimated quantitatively as follows. As it is known [8], one of the main features of

the fractal object structure is strong screening of its internal regions by the surface. Therefore, the reaction sites of the macromolecular coil accessible for branching are disposed either on its surface or near it. The number of such sites, M_u , is described according to the following scaling relationship [8]:

$$M_u \sim R_g^{d_u} \quad (5)$$

where R_g is coil gyration radius, d_u is a dimension of non-screening surface of a macromolecular coil (accessible for the reaction).

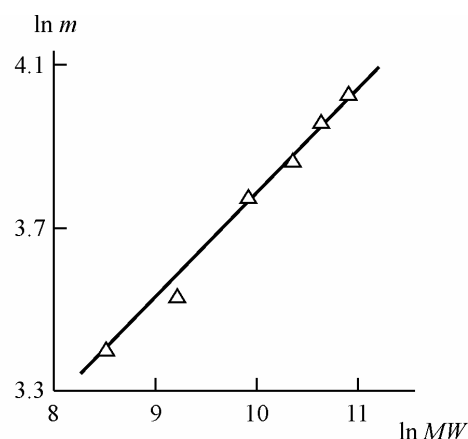


Fig. 1. The dependence of the number of branching center per one macromolecule, m , on the molecular weight, MW , for PHE synthesized at 333 K.

The dimension d_u is determined according to the following equation [8]:

$$d_u = (D - 1) + \frac{d - D}{d_w} \quad (6)$$

where d is dimension of Euclidean space in which fractal is immersed (it is obvious that in our case $d = 3$) and d_w is the dimension of the random walk over fractal, determined according to Aharony-Stauffer rule [9]:

$$d_w = D + 1 \quad (7)$$

Besides, it is well known [10] that in case of various chemical reaction proceedings, including synthesis of polymers, the so-called steric factor ρ ($\rho \leq 1$) plays an essential role, showing that not all collisions of reacting molecules occur with the proper orientation of these molecules for the formation of chemical bonds. The value ρ is connected with R_g as follows [4]:

$$\rho \sim \frac{1}{R_g} \quad (8)$$

Thus, it can be assumed that the number of macromolecular coil sites open for branching formation, m , will be proportional to the product ρM_u or:

$$m \sim \frac{R_g^{d_u}}{R_g} \sim R_g^{d_u-1} \quad (9)$$

In its turn, the value R_g can be estimated from the known values MW . For PHE, the monomer link molecular weight, m_0 , determined from its chemical constitution, is equal to 284. This makes it possible to determine the value of the monomer link(s) number per macromolecular coil, N :

$$N = \frac{MW}{m_0} \quad (10)$$

Then, the value R_g can be calculated according to the equation [11]:

$$R_g \approx 37.5N^{\frac{1}{D}} \quad (11)$$

The dependence of m vs. $R_g^{d_u-1}$ according to the relationship (9) is shown in Fig. 2. As one can see, it is linear and has an expected feature: m increase with $R_g^{d_u-1}$. The extrapolation of this plot to $m = 0$ gives $R_g^{d_u-1} \approx 2.4$, which corresponds to the smallest size of PHE macromolecule for beginning of the branching. This size is equal to $\approx 9.9 \text{ \AA}$. It is possible to estimate PHE volume for monomer link, V_0 , according to the equation [12]:

$$V_0 = \frac{m_0}{\rho N_A} \quad (12)$$

where ρ is the polymer density (for PHE, $\rho \approx 1.15 \text{ g/cm}^3$ [5]) and N_A is Avogadro's number.

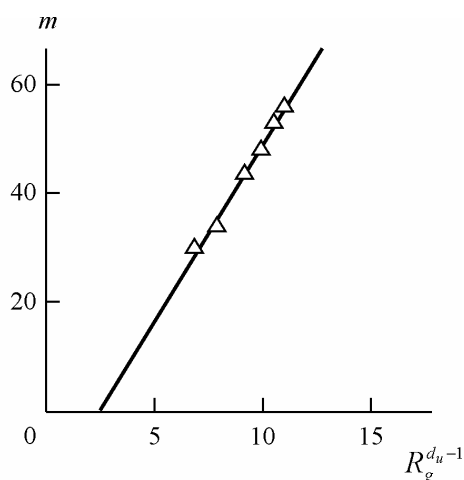


Fig. 2. The dependence of branching center number per one macromolecule, m , on the composite parameter $R_g^{d_u-1}$, for PHE synthesized at 333 K.

Then, believing that the cross-sectional area of PHE macromolecule is equal to 30.7 \AA^2 [13] and using the volume $V_0 \approx 410 \text{ \AA}^3$, calculated according to

the Eq. (12), the monomer link length for PHE, l_0 , can be estimated to be equal to $\approx 13.4 \text{ \AA}$. The comparison of the smallest value R_g and l_0 indicates that PHE chain branching process begins already at the initial synthesis stage.

We note that the dependences m vs. MW with fractional exponent $q < 1$ are typical for other polymers as well. In ref. 7, the of Mark-Kuhn-Houwink constant for θ -solvent in the case of branched polyarylate ($D-1$) and its linear analogs have been reported, which allows calculation of intrinsic viscosities $[\eta]_\theta$ and $[\eta]_{l,\theta}$, for arbitrary MW . Then, the value of g' can be estimated according to the relationship [7]:

$$\frac{[\eta]_\theta}{[\eta]_{l,\theta}} = (g')^{2-a} \quad (13)$$

where a is an exponent in Mark-Kuhn-Houwink Equation for a linear analog in θ -solvent ($a = 0.5$ [7]).

Knowing the values of g' , magnitudes of m can be calculated according to the Eq. (4). The estimations have shown, that for polyarylate ($D-1$) MW increases from 5×10^4 to 10×10^4 , while m increases from 2.0 up to 2.8, which corresponds to $g \approx 0.66$.

Taking into consideration that gyration radius, R_g , scales to MW as follows [4]

$$R_g \sim MW^{\frac{1}{D}} \quad (14)$$

from relationship (9) one obtains:

$$m \sim MW^{\frac{d_u-1}{D}} \quad (15)$$

The comparison of the relationship (1) and (15) allows derivaton of the following equation:

$$g = c_{ch} \frac{d_u-1}{D} \quad (16)$$

The proportionality coefficient, c_{ch} , in the Eq. (16) has a clear physical significance: it defines the maximal density of "chemical" branching centers per one macromolecule. Parameter $(d_u-1)/D$ defines the density decrease by macromolecular coil structural features for PHE value $c_{ch} \approx 1.41$. The values of g , $(d_u-1)/D$ and $c_{ch}((d_u-1)/D)$ for PHE at three synthesis temperatures, T , are listed in Table 1. Good correspondence of the first and the third parameters from the indicated ones is indicated.

For branched polyacrylate ($D-1$) the value of D can be determined according to the following equation [14]:

$$D = \frac{3}{1+a} \quad (17)$$

Table 1. Experimental and theoretical branching degree of PHE at different synthesis temperatures

T/K	g	$\frac{d_u-1}{D}$	$c_{ch} \frac{d_u-1}{D}$
333	0.272	0.193	0.270
338	0.229	0.145	0.203
343	0.130	0.105	0.147

Further, according to the Eqs. (6) and (7), by using $a = 0.36$ [7] and $D \approx 2.20$, d_u can be determined and c_{ch} can be calculated for $(D-1)$ according to the Eq. (16). In this case, $c_{ch} \approx 3.22$, *i.e.*, maximal “chemical” branching center density for $(D-1)$ is much higher than for PHE.

To conclude, the integral dependence of m on chemical and physical factors can be written as:

$$m \sim MW^{c_{ch} \frac{d_u-1}{D}} \quad (18)$$

The dependence corresponding to the relationship (18) is shown in Fig. 3. As one can see, this correlation is linear and passes through the origin. This is the case asserting that all factors controlling the value of m are taken into consideration.

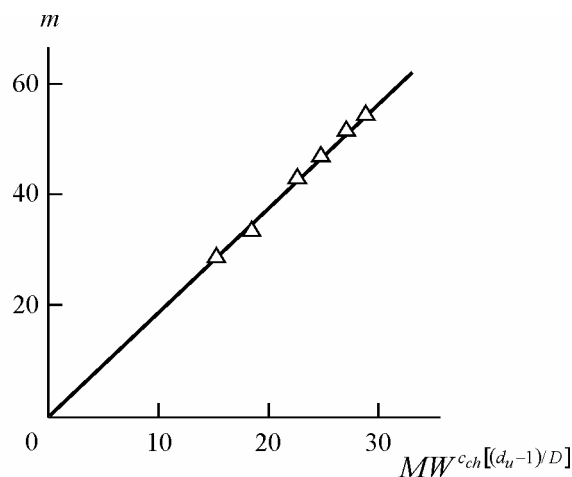


Fig. 3. The dependence of the number of branching centers per one macromolecule, m , on composite parameter $MW^{c_{ch} \frac{d_u-1}{D}}$ for PHE synthesized at 333 K.

CONCLUSIONS

The fractal analysis methods are efficient for clear structural identification of both chemical and physical factors, controlling a chain branching degree. The number of effective branching center(s) per one macromolecule, m , is controlled by four factors: polymer molecular weight, MW , maximal “chemical” density of reactive centers, c_{ch} , dimension of non-screening surface, d_u , of macromolecular coil and its fractal dimension, D . The Eq. (16) determines the critical value D (D_{cr}), the lower of which $g = 0$ (*i.e.*, branching does not occur): $D_{cr} = 1.10$.

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