

Modeling of Solid State Polymer Properties at the Stage of Synthesis: Fractal Analysis

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ABSTRACT: The genetic relationship between the polymer structures in solution and the condensed state are discovered within the framework of fractal analysis. It allows us to predict and model the properties of polymers already at the stage of synthesis, using the representation of a cluster model of the amorphous polymer state. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1137–1140, 2002

Key words: polymer; properties; fractal dimension; macromolecular coil; cluster model; solution

INTRODUCTION

It is well known that the structure and properties of products obtained from polymer solutions essentially depend on the nature of the solvent, as concentrated solutions already include structures similar to the simple types of the solid polymer structures. But such suppositions stay on the qualitative level, and at present there are no analytical correlations known to connect the structures of the macromolecular coil (MC) in a solution and a solid polymer to each other or to polymer properties. The development of modern physical conceptions, such as fractal analysis, in recent years gives us a base from which to work on this problem. The MC in a solution is a fractal^{1,2} with a fractal dimension of D ; the spatial structure of the coil is therefore defined by two groups of factors: these are interactions between the polymer and the solvent and the interactions between coil elements itself.¹ Changing the medium, which surrounds the MC (e.g., changing the size of a solvent molecule, the transition to the

bulk state, etc.), leads to a change in its structure, characterized by the value D . The aim of this work is, first, to analyze the connection between the MC structures and the solid polymer, and second, to define the influence of the solid polymer on one of the most important polymer properties—its glass transition temperature. This interrelation will be obtained within the framework of the fractal analysis, using the cluster model of the structure of the polymer's amorphous state³ on the sample of amorphous glassy copolymers (aromatic copolyethersulfonformals).⁴

RESULTS AND DISCUSSION

Aromatic copolyethersulfonformals (PESFs) were obtained with the nonequilibrium polycondensation in solution.⁴ The copolymers with weight-average molecular weights (\bar{M}_w) $\sim 5\text{--}11 \times 10^4$ were used. The values of \bar{M}_w depended on the relation between the copolymer's components. For the calculation of the intrinsic viscosity (η), the following correlation was used:⁵

$$[\eta] = \frac{(\eta_{sp}/C)}{1 + K_\eta \eta_{sp}}, \quad (1)$$

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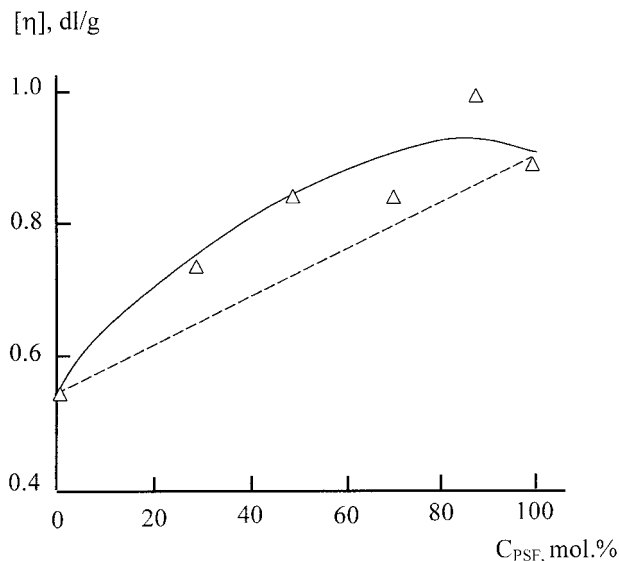


Figure 1 The dependence of characteristic viscosity $[\eta]$ on the content of sulfone C_{PSF} for the solution's aromatic copolyethersulfonformals in symm-tetrachloroethane.

where η_{sp} is the specific viscosity, C is the concentration of the polymer in the solution, and K_{η} is the coefficient equal to 0.28.

The fractal dimension D of MC in the solution was defined with the use of the following correlation:⁶

$$D = \frac{5([\eta]/[\eta]_{\theta})^{2/3} - 3}{3([\eta]/[\eta]_{\theta})^{2/3} - 2}, \quad (2)$$

where $[\eta]$ and $[\eta]_{\theta}$ is the intrinsic viscosity of the PESF in the θ -(1,4-dioxane) and good (symm-tetrachloroethane [TCE]) solvents, respectively.

As can be seen above, both the type of solvent from which the solid polymer was obtained and the structure of the polymer chain will influence the structure of the solid polymer and, consequently, its properties. Both of the pointed factors influence D , and as we used only the data for PESF solutions in TCE, it is obvious that the structure of the chain will be the main influence on the change in D . The dependence $[\eta]$ on the content of polysulfon fragments, C_{PSF} , in PESF, shown in Figure 1, revealed the inadditivity of correlation $[\eta]$ (\bar{N}_{PSF}). It is known⁷ that the value of $[\eta]$, with other conditions equal, characterizes the compactness of MC, and its increase means the lowering of macromolecular coil compactness. Analytically, it is expressed by the fractal relation:²

$$R_g \sim N^{1/D}, \quad (3)$$

where R_g is the radius of coil gyration and N is the degree of polymerization.

The calculation of D according to eq. (2) confirmed this hypothesis. The dependence of D on the content of formal in PESF, as shown in Figure 2, is also inadditive, and the D values of copolymers are lower than the additive dependence. Thus, Figures 1 and 2 permit us to observe the change in the structure of the MC of PESF in TCE depending on the content of several components. However, how these changes influence the structure of the polymer in the bulk state? The value D with the calculation of interaction of the excluded volume can be defined as:²

$$D = \frac{d_s(d+2)}{d_s+2}, \quad (4)$$

where d_s is the spectral (fracton) dimension of the coil, characterizing the degree of its connection,⁸ and d is the dimension of an Euclidean space, in which the fractal is examined. In our case, $d = 3$.

As all examined PESFs are linear polymers, for them, d_s should be taken to be equal to 1.⁸ The transition of gelation or the transition to the condensed state characterizes the change in the surroundings of MC and how now, instead of by molecules of the solvent, it is surrounded by anal-

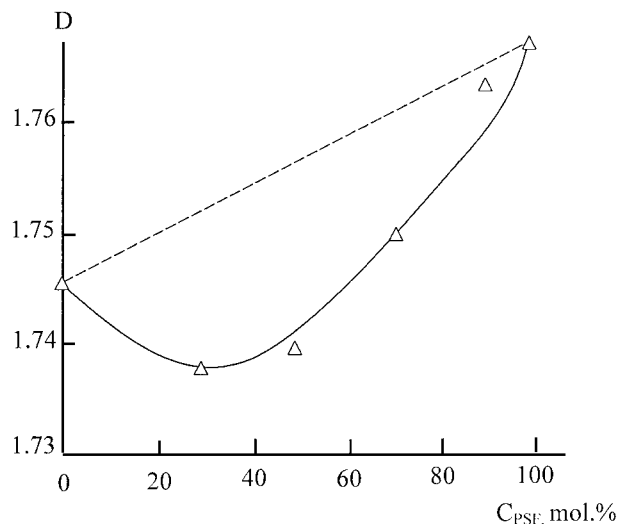


Figure 2 The dependence of the fractal dimension D on the content of formal C_{form} for the solution's aromatic copolyethersulfonformals in symm-tetrachloroethane.

ogous coils. It leads to a change in the fractal dimension, and its value, d_f for the condensed state is defined as follows:²

$$d_f = d_s(d + 2)/2. \quad (5)$$

The combination of eqs. (4) and (5) with the conditions mentioned above ($d_s = 1$ and $d = 3$) gives the following result for linear polymers:

$$d_f = 1, 5D. \quad (6)$$

Eq. (6) clearly shows the genetic interrelation between the structure of the products of the reaction (the coil in the solution) and the condensed state of the polymers. To obtain the analytical interrelation between the structure and properties of the polymers, it is necessary to define the concrete quantitative model of the structure. The cluster model of the structure of the polymers in an amorphous state³ was used in this article. The concept of local order is based on this model. The relative fraction of the closely packed segments in clusters (ϕ_{cl}) is a parameter of order in a strict physical sense of this term and is connected with the glass transition temperature (T_g) with the following percolation correlation:^{9,10}

$$\phi_{cl} \approx 0.03(T_g - T)^{0.55}, \quad (7)$$

Within the framework of the cluster model, the glass transition is considered to be a thermofluctuational decomposition of clusters at T_g .¹¹ In addition, the fractal concepts interrelate with the cluster model; thus, the correlation of the main characteristics of these models is given as follows:¹²

$$d_f = d - 6 \times 10^{-10} \left(\frac{\phi_{cl}}{SC_\infty} \right)^{1/2}, \quad (8)$$

where S is the area of the cross section of a macromolecule, expressed in meters squared, and C_∞ is a characteristic ratio, which is the index of the flexibility of the chain.¹³

The values of S for the fragments sulfone and formal, which are the components of PESF, were set equal to 35 and 23 Å², respectively,¹⁴ and the values of S for the copolymers were estimated according to the addition law. The values of C_∞ were calculated by following equation:¹²

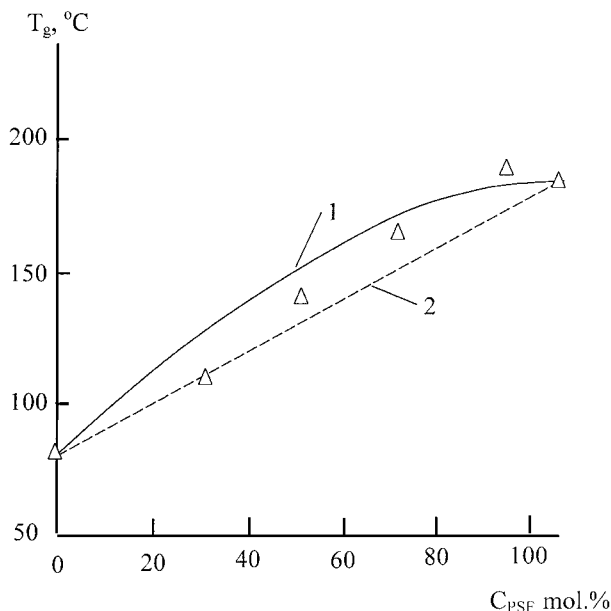


Figure 3 The dependence of the glass transition temperature T_g on the content of formal C_{form} for aromatic copolyethersulfonformals. 1 = experimental data, 2 = calculation by eqs. (5)–(9).

$$C_\infty = \frac{d_f}{d(d - d_f)} + \frac{4}{3}. \quad (9)$$

The combination of eq. (6) divided by eq. (9) permits us to calculate the value T_g , proceeded only from the structure of MC in the solution, characterized by D , and from the molecular parameter S . The experimental and calculated values of T_g obtained with the methods proposed in this article (Fig. 3) correspond well (divergence between them does not increase even 4%). We should mention that the comparison of Figures 2 and 3 with the use of the scheme of calculation accounted above demonstrates the way of getting copolymers with the value of T_g above additive. The values of D must be lower than the values of the additives. In addition, the reason for increasing T_g when introducing bulky side substituents into the polymer chain¹⁵ leads to the essential growth of S and, therefore ϕ_{cl} , according to eq. (8), thus causing T_g to increase, according to eq. (7).

The main reason for the increase of D , as far as the concentration of formal increases (Fig. 2), is the decrease of the chain rigidity of the copolymer, which, from the chemical point of view, is caused by the decrease of the content of the rigid and strongly polar diphenylsulfone fragments, resulting from their substitution for methene

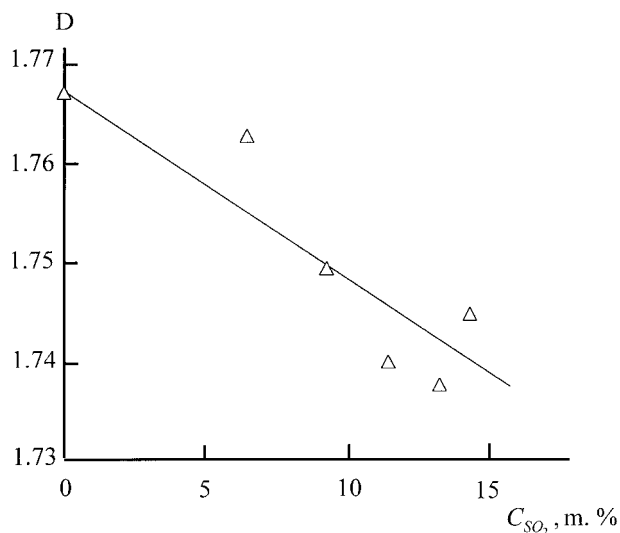


Figure 4 The dependence of the fractal dimension D on the content of groups SO_2 C_{SO_2} for the solution's aromatic copolyethersulfonformals in symm-tetrachloroethane.

groups, which increase the flexibility of macromolecules. The dependence of D on the presence of groups of SO_2 for the analyzed copolymers (Fig. 4) confirms the assumption made above.

These results demonstrate the genetic interrelation of the structure of the products of synthesis (MCs in the solution) and the bulk state of polymers. This interrelation creates the possibility for prognosticating and modeling the properties of the polymers already at the stage of synthesis.

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