Gas Diffusion in Branched and Crosslinked Polymers: A Model of Treelike Clusters

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ABSTRACT: The correctness of the fractal model of treelike clusters for describing the diffusion processes in branched (crosslinked) copolymers is shown. As in the fractal model of gas transport processes, for the copolymers investigated, the main role of diffusivity was to change the connectivity of the macromolecule, characterized by its spectral dimension. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3571–3573, 2006

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INTRODUCTION

In previous articles,[1–3] it was shown that for grafting copolymers produced by irradiation of polyethylene, in the swelling of various vinyl monomers, permeability decreased with an increase in the content of the copolymers styrene, acrylonitrile, and vinylpyridine. This supposition was made because the grafting of these monomers occurred only in the amorphous regions of the polyethylene. It appeared that polymers with relatively nonpermeable regions acted as an excluder for the running gas volume.[3]

An analogous effect was observed by the authors[3] in irradiation grafting of polyacrolein (PAL) to poly(vinyltrimethyl silane) (PVTMS). In this case it was supposed that the decrease in diffusivity, D, was a result of the increase in the density of the transversal crosslinking of PVTMS macromolecules by PAL chains. In the articles mentioned above, the explanation for the experimentally observed effect was given on the qualitative level. The quantitative explanation of a pointed decrease in grafting copolymer permeability can be advanced within the limits of the fractal model of gas transport processes, where D is determined by[5]

$$D = D_0' f_g (d_h / d_m)^{2(D_t - d_s)/d_s}, \qquad (1)$$

where D_0 is the universal constant, which is equal to 3.8×10^{-7} cm^2/s; f_g is the relative free volume; d_h and d_m are the diameters of the free-volume microvoid and the gas-penetrant molecule, respectively; D_t is the dimension of the structure of the controlling processes of gas transport; and d_s is the spectral dimension of the structure characterizing the degree of connectivity.[6]

In fact, the decreased membrane permeability shown reported previously[1–4] resulted from the formation of branched (crosslinked) macromolecules. This resulted in an increase in d_s[6] and, as follows from eq. (1), in a decrease in D. However, more fractal treatment of this effect is possible, which would consider the branched macromolecule as some type of treelike structure.[7] Such a model has been successful in describing polyethylene thermodegradation,[8] and in the present study it was used to describe the diffusion process in the grafting copolymers investigated.

EXPERIMENTAL

The diffusion processes of N$_2$ and O$_2$ in the grafting copolymers at irradiation of polyethylene (PE) produces swelling in various vinyl monomers, of which styrene, acrylonitrile, and vinylpyridine were investigated in the present study.[1] The values of permeability to gas, P, for N$_2$ and O$_2$ were taken from a previous article.[3] To calculate diffusivity, D, according to the known P, the following equation[3] was used:

$$D = \frac{P}{\sigma}, \qquad (2)$$

where σ is the solubility coefficient, estimated according to the PE data from Tochin et al.[9] It was surmised that σ was independent of the content of the grafting

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component, C_g, as gas solubility of polymers is determined mainly by the nature of the gas.[3]

The values of diffusivity, D, reported in the literature for PVTMS-PAL compositions with PAL contents of 9.9 and 20.6 wt % for three gases (Kr, Xe, and CO_2)[4] also were used in the present study.

RESULTS AND DISCUSSION

As a theoretical model for the description of diffusion processes in the above-mentioned grafting copolymers, a treelike cluster was used consisting of a root or a beginning, an infinite skeleton, and branching from it finite "dead" ends.[7] If a gas-penetrant molecule got into such a dead end (branch, transversal bond) it became immobile and was excluded from the next diffusion process. The probability of getting gas-penetrant molecules into a dead end, $p_0(l)$, was determined by[7]

$$p_0(l) = 1 - \frac{A}{l^\alpha}, \tag{3}$$

where A is the constant, l is the distance from root to particle, and the exponent α is determined according to the following equation[7]:

$$\alpha = d_l - d_l^s, \tag{4}$$

where d_l and d_l^s are the chemical ("spreading") dimensions of the macromolecule and its skeleton, respectively.

The values d_l and d_l^s were determined with the help of following equations[7]:

$$d_s = \frac{2d_l}{1 + d_l}, \tag{5}$$

$$d_s = \frac{2d_l}{2 + d_l - d_l^s}. \tag{6}$$

Therefore, the key parameter for calculation of chemical dimensions d_l and d_l^s is the spectral dimension, d_s, and therefore its determination is considered in more detail. As is known,[5] diffusion of gases in polymers occurs on a molecular level, and therefore, given that d_s was adopted as the spectral dimension of the macromolecule, its value could change within the interval 1.0–1.33.[6] For linear chains, $d_s = 1.0$ was accepted, and for strongly branched (crosslinked) macromolecules, $d_s = 1.33$ was accepted.[6] On the basis of previously reported data[1–4] it would be expected that for the initial linear PE and PVTMS, $d_s = 1.0$, and with an increase in C_g d_s would increase the limits of the above-mentioned interval. For a more exact estimation of d_s, the following procedure was used. First, the
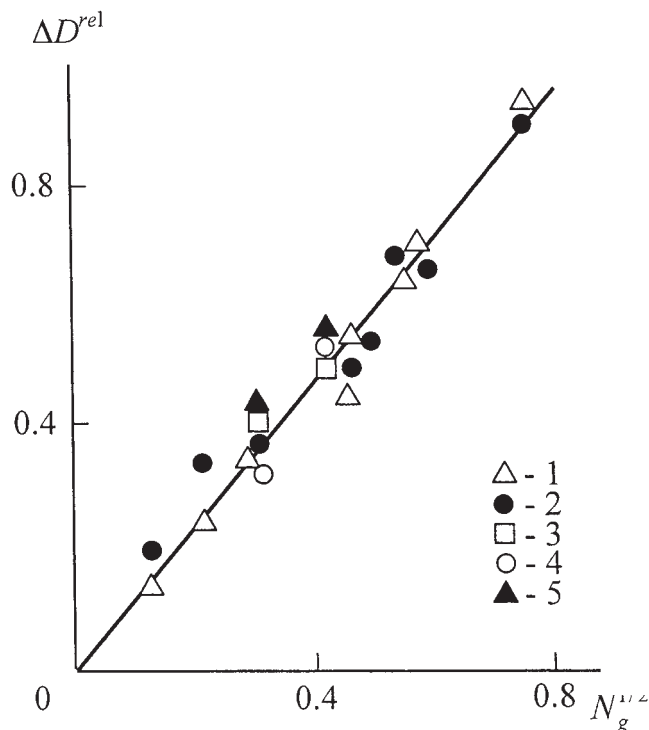

Figure 1 (1) Dependence of relative reduction in diffusivity, ΔD^{rel}, on content of the grafting component, C_g, for N_2 in PE copolymers; (2) dependence of ΔD^{rel} on C_g for O_2 in PE copolymers; (3) dependence of ΔD^{rel} on C_g for Kr in PVTMS–PAL composites; (4) dependence of ΔD^{rel} on C_g for Xe in PVTMS–PAL composites;, and (5) dependence of ΔD^{rel} on C_g for CO_2 in PVTMS–PAL composites.

relative reduction in diffusivity, ΔD^{rel}, was determined according to the formula

$$\Delta D^{rel} = \frac{D_0 - D}{D_0}, \tag{7}$$

where D_0 and D are the diffusivities of initial polymer (PE or PVTMS) and the grafting copolymer, respectively.

After that, the dependence $\Delta D^{rel}(C_g)$ was plotted, which was approximately quadratic in form. For linearization of the last, this correlation was replotted in coordinates ΔD^{rel}- $C_g^{1/2}$ (Fig. 1). As Figure 1 shows, the data for the three grafting vinyl monomers (styrene, acrylonitrile, and vinylpyridine) lie on a straight line. Such correlation shows that a decrease in D is independent of the chemical nature of the monomer and determines only content, C_g, that is, the degree of branching (crosslinking) of the initial polymer macromolecules. On the basis of the plot shown in Figure 1, the decrease in D with an increase in C_g can be described analytically by a simple equation:

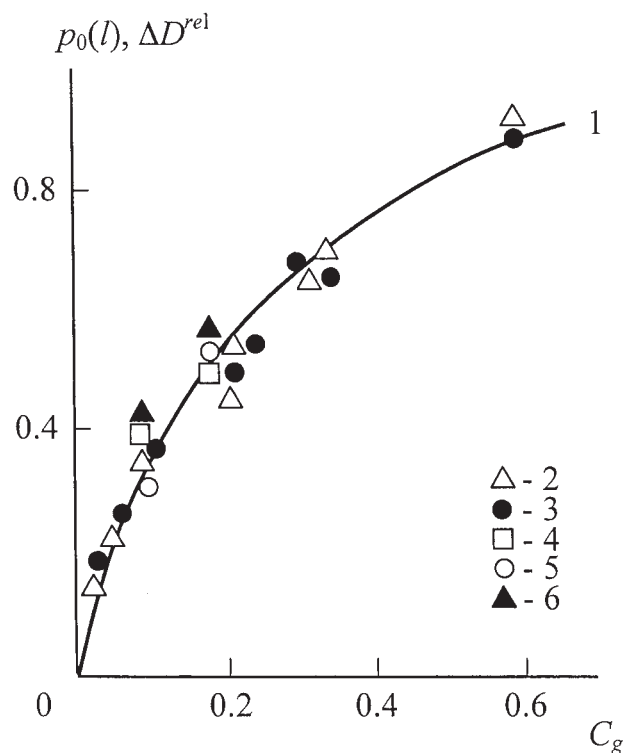$$\Delta D^{rel} = 1.16 \, C_g^{1/2}. \tag{8}$$

Figure 2 Comparison of (1) the probability of the gas-penetrant molecules going into a "dead" end, $p_0(l)$; with (2) relative reduction in diffusivity, ΔD^{rel}, on the grafting component, C_g, content for N_2 in PE copolymers; (3) ΔD^{rel} of C_g for O_2 in PE copolymers; (4) ΔD^{rel} of C_g for Kr in PVTMS–PAL composites; (5) ΔD^{rel} of C_g for Xe in PVTMS–PAL composites; and (6) ΔD^{rel} of C_g for CO_2 in PVTMS–PAL composites.

Then, supposing that d_s is linearly dependent on C_g, that $d_s = 1.0$ for linear PE and PVTMS, and that $d_s = 1.33$ for the PE copolymer with $C_g = 0.60$, the d_s of copolymers studied can be estimated with the following equation:

$$d_s = 1.0 + 0.43\, C_g^{1/2}, \qquad (9)$$

which shows an increase in d_s (an increase in the degree of macromolecule connectivity[6]) with an increase in the degree of branching (crosslinking) of the copolymer chain.

It is obvious that for macromolecules as the skeleton, it is necessary to estimate its linear analog, that is, the linear chain of the initial polymer (PE or PVTMS).

In this case, $d_s = 1.0^6$, and according to eqs. (5) and (6), $d_l = 1.0$ and $d_l^s = 1.0$.

Further, accepting eq. (3) with $A = 1.40$ and $l = 10$ relative units, $p_0(l)$ can be calculated and compared with the relative reduction in diffusivity, ΔD^{rel}, which is shown in Figure 2. The physical sense of such a comparison is obvious: the greater the probability of getting a gas-penetrant molecule into a dead end, $p_0(l)$, the more such molecules become immobile and are excluded from the diffusion process and the exclude from the diffusion process and the smaller D. As follows from the data shown in Figure 2, the theoretical curve of $p_0(l)$ and the experimental points of ΔD^{rel} as a function C_g agreed very well.

The model[7] was obtained for aggregates without loops, and the correspondence of the theory with the experimental results, shown in Figure 2, suggests that branched and crosslinked macromolecules should be considered aggregates without loops.

CONCLUSIONS

The results of this study have verified the correctness of the fractal model of treelike clusters for the description of diffusion processes in branched (crosslinked) copolymers. As in the fractal model of gas transport processes, for the copolymers investigated, the main role of diffusivity was to change the connectivity of the macromolecule, characterized by its spectral dimension.

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