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Dielectric Dispersion of Dilute Solution Polymers

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ABSTRACT: It is well-known that polymers in dilute solution generally exhibit two separate dielectric dispersions. By assuming that the end-to-end vector relaxes negligibly over times for which the high-frequency dispersion occurs, we are able to show that the high- and low-frequency dispersions have relative strengths $1 - \Gamma$ and Γ, respectively, where $\Gamma = \langle \mu\cdot\mathbf{r}\rangle^2\langle\mu^2\rangle^{-1}\langle r^2\rangle^{-1}$ and where μ and $\mathbf{r}$ are respectively the net dipole moment and the end-to-end vector of the chain. This result is equally true for chains with or without excluded volume. We also work out the excluded-volume behavior of the quantity Γ, obtaining $\Gamma = [\alpha_r^2/\alpha_\mu^2]\Gamma_0$, for α_r and α_μ expansion factors of $\mathbf{r}$ and μ, respectively, and for Γ_0 the unperturbed value of Γ.

1. Introduction

As is well-known, polymers in dilute solution exhibit at most two dielectric dispersions.[1-3] These two dispersions vary in relative strength depending on the value of the quantity $\langle\mu\cdot\mathbf{r}\rangle$, for μ the net dipole moment of the molecule and for $\mathbf{r}$ the end-to-end vector of the molecule. Whenever $\langle\mu\cdot\mathbf{r}\rangle \neq 0$, a low-frequency, molecular-weight-dependent dispersion is observed which relaxes via the motion of the end-to-end vector of the chain. At higher frequencies a dispersion is observed that relaxes that portion of the dipole moment not coupled to the end-to-end vector.

With only the assumption that the molecule is sufficiently long that, first, it follows Gaussian statistics when unperturbed and, second, that the two dispersions occur in well-separated time domains (more specifically, that the fast relaxation is complete before the end-to-end vector has had time to change appreciably), we can show that the fraction of the total dipole moment relaxing via the low-frequency dispersion is

$$\Gamma = \langle\mu\cdot\mathbf{r}\rangle^2\langle\mu^2\rangle^{-1}\langle r^2\rangle^{-1} \tag{1}$$

This result is valid for any magnitude of the excluded volume. Furthermore, we can show that the excluded-volume behavior of this quantity is controlled by

$$\Gamma = \alpha_r^2\alpha_\mu^{-2}\Gamma_0 \tag{2}$$

where $\alpha_r^2 = \langle r^2\rangle\langle r^2\rangle_0^{-1}$ and $\alpha_\mu^2 = \langle\mu^2\rangle\langle\mu^2\rangle_0^{-1}$.

In deriving these two results, we make use of some mathematical techniques first introduced by Doi[4] in his study of the effects of excluded volume on $\langle\mu^2\rangle$. In the interest of presenting a self-contained derivation and because we find it necessary to generalize Doi's arguments slightly, we review his results in the next section and obtain expressions for the effect of excluded volume on $\langle\mu^2\rangle$ and on $\langle\mu\cdot\mathbf{r}\rangle$. In section 3 we derive a result for the mean dipole moment in an ensemble with $\mathbf{r}$ fixed. In section 4 we derive eq 1 and 2.

2. Relationships between $\langle\mu^2\rangle$, $\langle\mu\bullet\mathbf{r}\rangle$, and $\langle r^2\rangle$

Nagai and Ishikawa[5] computed the excluded-volume behavior of $\langle\mu^2\rangle$ to third order in the excluded-volume perturbation expansion and concluded that the following equation holds to at least third order:

$$(\alpha_\mu^2 - 1) = \Gamma_0(\alpha_r^2 - 1) \tag{3}$$

Here α_μ and α_r are the expansion factors defined above and Γ_0 is the unperturbed value of the ratio defined in eq 1. Subsequently, Doi[4] demonstrated that eq 3 is generally valid. We apply Doi's technique in this section to obtain an additional expression relating $\langle\mu\cdot\mathbf{r}\rangle$ to $\langle r^2\rangle$ and in the next section to obtain another result.

Let $\mathbf{x}_j$ represent the end-to-end vector of the jth chain segment and let μ be the total dipole moment of the chain. Assume that the chain contains N segments total. Let $P(\mu,\mathbf{x}_1,\mathbf{x}_2...,\mathbf{x}_N)$ be the multivariate probability density obeyed by μ and all the $\mathbf{x}_j$, and let $P_0(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)$ be its unperturbed value. Let $\tilde{\mathbf{P}}(\mathbf{k}_\mu,\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_N)$ and $\tilde{\boldsymbol{P}}_0(\mathbf{k}_\mu,\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_N)$ be the Fourier transforms of P and P_0, respectively, defined, for example, as

$$\tilde{P}(\mathbf{k}_\mu,\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_N) = \int d\mathbf{x}_1 \int d\mathbf{x}_2 ... \int d\mathbf{x}_N\, P(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) \exp[i\mathbf{k}_\mu\cdot\mu + i\textstyle\sum\mathbf{k}_j\cdot\mathbf{x}_j] \tag{4}$$

We also introduce the following three distribution functions:

$$P_\mu(\mu) = \int d\mathbf{x}_1 \int d\mathbf{x}_2 ... \int d\mathbf{x}_N\, P(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) \tag{5}$$

$$P_r(\mathbf{r}) = \int d\mu \int d\mathbf{x}_1 \int d\mathbf{x}_2 ... \int d\mathbf{x}_N\, P(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) \times \delta(\mathbf{r} - \textstyle\sum\mathbf{x}_j) \tag{6}$$

$$P_{\mu r}(\mu,\mathbf{r}) = \int d\mathbf{x}_1 \int d\mathbf{x}_2 ... \int d\mathbf{x}_N\, P(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)\, \delta(\mathbf{r} - \textstyle\sum\mathbf{x}_j) \tag{7}$$

These have Fourier transforms $\tilde{P}_\mu(\mathbf{k}_\mu)$, $\tilde{P}_r(\mathbf{k}_r)$, and $\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r)$. These various Fourier transforms are all interrelated as follows:

$$\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r) = \tilde{P}(\mathbf{k}_\mu,\mathbf{k}_1{=}\mathbf{k}_2{=}\mathbf{k}_3{=}...{=}\mathbf{k}_r) \tag{8}$$

$$\tilde{P}_r(\mathbf{k}_r) = \tilde{P}_{\mu r}(0,\mathbf{k}_r) \tag{9}$$

$$P_\mu(\mathbf{k}_\mu) = \tilde{P}_{\mu r}(\mathbf{k}_\mu,0) \tag{10}$$

Finally we note that

$$P(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) = Q(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)\, P_0(\mu,\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) \tag{11}$$

where Q is $\exp[-\beta U(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)]$ up to a normalization factor and where $U(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)$ is the perturbing hamiltonian that carries the excluded-volume interaction. It follows that $\tilde{P}$ and $\tilde{P}_0$ re related by the following convolution integral:

$$\tilde{P}(\mathbf{k}_\mu,\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_N) = (2\pi)^{-3N}\int d\mathbf{q}_1 \int d\mathbf{q}_2 ... \int d\mathbf{q}_N\, \tilde{P}_0(\mathbf{k}_\mu,\mathbf{k}_1,-\mathbf{q}_1,\mathbf{k}_2-\mathbf{q}_2,...,\mathbf{k}_N-\mathbf{q}_N)\, \tilde{\mathbf{Q}}(\mathbf{q}_1,\mathbf{q}_2,...,\mathbf{q}_N) \tag{12}$$

or

$$\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r) = (2\pi)^{-3N}\int d\mathbf{q}_1 \int d\mathbf{q}_2 ... \int d\mathbf{q}_N\, \tilde{\mathbf{P}}_0(\mathbf{k}_\mu,\mathbf{k}_r-\mathbf{q}_1,\mathbf{k}_r-\mathbf{q}_2,...,\mathbf{k}_r-\mathbf{q}_N)\, \tilde{Q}(\mathbf{q}_1,\mathbf{q}_2,...,\mathbf{q}_N) \tag{13}$$

$\tilde{\mathbf{P}}_0$ is a generating function for the moments $\langle\mu^2\rangle_0$, $\langle\mu\cdot\mathbf{x}_j\rangle_0$, and $\langle x_j^2\rangle_0$. Therefore, to second order it must obey

$$\tilde{\mathbf{P}}_0(\mathbf{k}_\mu,\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_N) = 1 - k_\mu^2\langle\mu^2\rangle_0/6 - (1/3)\sum_j\langle\mu\cdot\mathbf{x}_j\rangle_0\mathbf{k}_\mu\cdot\mathbf{k}_j - (1/6)\sum_j\langle x_j^2\rangle_0 k_j^2 \tag{14}$$

But since $\tilde{P}_0$ must also be Gaussian for large N, we can write

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$$\tilde{P}_0(\mathbf{k}_\mu,\mathbf{k}_1,\mathbf{k}_2,\ldots,\mathbf{k}_N) = \exp[(-1/6)(NC_{\mu\mu}k_\mu^2 + 2\sum_j C_{r\mu}\mathbf{k}_\mu\cdot\mathbf{k}_j + \sum_j C_{rr}k_j^2)] \quad (15)$$

where at large N, $\langle\mu^2\rangle_0 = NC_{\mu\mu}$, $\langle\boldsymbol{\mu}\cdot\mathbf{r}\rangle_0 = NC_{r\mu}$, and $\langle r^2\rangle_0 = NC_{rr}$.

We now consider an expression of the form

$$\tilde{P}_0(\mathbf{k}_\mu,\mathbf{k}_r-\mathbf{q}_1,\mathbf{k}_r-\mathbf{q}_2,\ldots,\mathbf{k}_r-\mathbf{q}_N) = A(\mathbf{k}_\mu,\mathbf{k}_r,\mathbf{k}_\mu',\mathbf{k}_r')\ \tilde{P}_0(\mathbf{k}_\mu',\mathbf{k}_r'-\mathbf{q}_1,\mathbf{k}_r'-\mathbf{q}_2,\ldots,\mathbf{k}_r',\mathbf{q}_N) \quad (16)$$

In other words, we define A as the quotient of the two $\tilde{P}_0$'s and ask what conditions $\mathbf{k}_\mu$, $\mathbf{k}_r$, $\mathbf{k}_\mu'$, and $\mathbf{k}_r'$ must satisfy if A is to depend on them but not on any of the $\mathbf{q}_j$. A little algebra indicates that if we require

$$C_{r\mu}(\mathbf{k}_\mu - \mathbf{k}_\mu') + C_{rr}(\mathbf{k}_r - \mathbf{k}_r') = 0 \quad (17)$$

then

$$A = \exp((1/6)[NC_{\mu\mu}(k_\mu'^2 - k_\mu^2) + 2NC_{r\mu}(\boldsymbol{\mu}'\cdot\mathbf{k}_r' - \mathbf{k}_\mu\cdot\mathbf{k}_r) + NC_{rr}(k_r'^2 - k_r^2)]) \quad (18)$$

satisfies eq 16. To proceed, multiply both sides of eq 16 by $(2\pi)^{-3N}\tilde{Q}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and integrate over $\mathbf{q}_1$, $\mathbf{q}_2$, etc. The result is

$$\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r) = A(\mathbf{k}_\mu,\mathbf{k}_r,\mathbf{k}_\mu',\mathbf{k}_r')\ \tilde{P}_{\mu r}(\mathbf{k}_\mu',\mathbf{k}_r') \quad (19)$$

which holds, of course, whenever A is given by eq 18 and whenever eq 17 is satisfied. This is the most general form of the Doi scaling law and is a very useful expression relating $\tilde{P}_{\mu r}$ at different values of its arguments. An important special case is obtained by setting $\mathbf{k}_\mu' = 0$

$$\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r) = \exp\left[\frac{-NC_{\mu\mu}}{6}k_\mu^2 + \frac{NC_{r\mu}^2}{6C_{rr}}k_\mu^2\right]\tilde{P}_r[\mathbf{k}_r + (C_{r\mu}/C_{rr})\mathbf{k}_\mu] \quad (20)$$

and we obtain the original Doi scaling law if we also set $\mathbf{k}_r = 0$:

$$\tilde{P}_\mu(\mathbf{k}_\mu) = \exp\left[\frac{-NC_{\mu\mu}}{6}k_\mu^2 + \frac{NC_{r\mu}^2}{6C_{rr}}k_\mu^2\right]\tilde{P}_r[(C_{r\mu}/C_{rr})\mathbf{k}_\mu] \quad (21)$$

Equation 20 provides a relationship between $P_{\mu r}$ and P_r, and likewise, eq 21 relates P_μ and P_r.

Recalling that to second order in $\mathbf{k}_\mu$ or $\mathbf{k}_r$ we have

$$\tilde{P}_r(\mathbf{k}_r) = 1 - k_r^2\langle r^2\rangle/6; \qquad \tilde{P}_\mu(\mathbf{k}_\mu) = 1 - k_\mu^2\langle\mu^2\rangle/6 \quad (22)$$

and expanding eq 21 to second order yields eq 3, as derived by Doi. Since we can also write

$$\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r) = 1 - \mathbf{k}_r^2\langle r^2\rangle/6 - k_\mu^2\langle\mu^2\rangle/6 - \mathbf{k}_\mu\cdot\mathbf{k}_r\langle\boldsymbol{\mu}\cdot\mathbf{r}\rangle/3 \quad (23)$$

eq 20 permits us to derive

$$\langle\boldsymbol{\mu}\cdot\mathbf{r}\rangle/\langle r^2\rangle = \langle\boldsymbol{\mu}\cdot\mathbf{r}\rangle_0/\langle r^2\rangle_0 \quad (24)$$

These results are very general. Nowhere in the derivation did we make use of the form of Q. Q can be any function of the internal coordinates and includes, therefore, three-body interactions etc. The above expressions for $\langle\boldsymbol{\mu}\cdot\mathbf{r}\rangle$ and $\langle\mu^2\rangle$ in terms of $\langle r^2\rangle$ are valid for any sort of perturbation dependent only on the internal chain structure as long as the chains are long enough for the Gaussian approximation, eq 15, to apply.

3. Average Dipole Moment at Fixed End-to-End Vector

In this section we derive, for later use, the average dipole moment over an ensemble for which the end-to-end vector is fixed. Denote this $\langle\boldsymbol{\mu}\rangle_{\mathbf{r}}$. Of course, we may write

$$P_r(\mathbf{r})\langle\boldsymbol{\mu}\rangle_{\mathbf{r}} = \int \mathrm{d}\boldsymbol{\mu}\ \boldsymbol{\mu}P_{\mu r}(\boldsymbol{\mu},\mathbf{r}) \quad (25)$$

Direct differentiation of the Fourier integral for $\tilde{P}_{\mu r}$ yields

$$[\nabla_{k_\mu}\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r)]_{\mathbf{k}_\mu=0} = i\int \mathrm{d}\boldsymbol{\mu}\int \mathrm{d}\mathbf{r}\ P_{\mu r}(\boldsymbol{\mu},\mathbf{r})\exp[i\mathbf{k}_r\cdot\mathbf{r}]\boldsymbol{\mu} \quad (26)$$

But then inverse Fourier transformation of eq 26 yields

$$\int \mathrm{d}\boldsymbol{\mu}\ P_{\mu r}(\boldsymbol{\mu},\mathbf{r})\boldsymbol{\mu} = -i(2\pi)^{-3}\int \mathrm{d}\mathbf{k}_r\exp[-i\mathbf{k}_r\cdot\mathbf{r}][\nabla_{k_\mu}\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r)]_{\mathbf{k}_\mu=0} \quad (27)$$

Differentiation of the scaling law, eq 20, yields

$$[\nabla_{k_\mu}\tilde{P}_{\mu r}(\mathbf{k}_\mu,\mathbf{k}_r)]_{\mathbf{k}_\mu=0} = (C_{r\mu}/C_{rr})\nabla_{k_r}\tilde{P}_r(\mathbf{k}_r) \quad (28)$$

Inserting this into eq 27 and integrating by parts yield

$$\int \mathrm{d}\boldsymbol{\mu}\ P_{\mu r}(\boldsymbol{\mu},\mathbf{r})\boldsymbol{\mu} = (C_{r\mu}/C_{rr})\mathbf{r}P_r(\mathbf{r}) \quad (29)$$

Comparing this with eq 25 yields

$$\langle\boldsymbol{\mu}\rangle_{\mathbf{r}} = (C_{r\mu}/C_{rr})\mathbf{r} = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0\langle r^2\rangle_0^{-1}\mathbf{r} = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle\langle r^2\rangle^{-1}\mathbf{r} \quad (30)$$

The last equality in eq 30 follows from eq 24.

4. Intermediate Value of the Dipole–Dipole Correlation Function

The dielectric dispersion of any system is controlled by the dipole–dipole correlation function:[6]

$$C(t) = \langle\mu^2\rangle^{-1}\langle\boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle \quad (31)$$

We point out in the Introduction the empirical fact that $C(t)$ for polymer solutions relaxes over two separate time scales. Let τ_1 and τ_2 represent the relaxation times for these two separate relaxations. In this section, we calculate the value of $C(t)$ at intermediate times $\tau_1 \ll t \ll \tau_2$. The value of $C(t)$ at intermediate times is equal, of course, to the relative strength of the low-frequency relaxation. We assume that at any times $t \ll \tau_2$, the end-to-end vector of the chain changes imperceptibly, while at any times in the interval $\tau_1 \ll t \ll \tau_2$, the dipole moment has had time to relax to equilibrium within the ensemble of fixed $\mathbf{r}$, which is to say that it is distributed according to $P_{\mu r}(\boldsymbol{\mu},\mathbf{r})$ for $\mathbf{r}$ fixed at its initial value. Suppose we begin at time $t = 0$ with the polymer in some particular initial configuration and that the end-to-end vector and dipole moment of the chain in this configuration are $\mathbf{r}_i$ and $\boldsymbol{\mu}_i$, respectively. At times t in the interval $\tau_1 \ll t \ll \tau_2$ the dipole moment has taken on the value $\boldsymbol{\mu}_f$ while the end-to-end vector still equal $\mathbf{r}_i$. The average of $\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_f$ at time t may be written

$$\boldsymbol{\mu}_i\cdot\langle\boldsymbol{\mu}_f\rangle_{\mathbf{r}_i} = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle\langle r^2\rangle^{-1}\boldsymbol{\mu}_i\cdot\mathbf{r}_i \quad (32)$$

which follows from eq 30. All that remains to generate $C(t)$ is to average eq 32 over initial conditions and then divide by $\langle\mu^2\rangle$. Therefore, we obtain

$$C(t) = \Gamma, \qquad \text{when } \tau_1 \ll t \ll \tau_2 \quad (33)$$

where Γ is the ratio defined in eq 1. This result follows immediately from eq 30 and from the assumption that the molecular weight is large enough that the two dispersions are well separated.

Equations 24 and 3 permit us to predict the excluded-volume behavior of Γ. We obtain

$$\Gamma = [\alpha_r^2/\alpha_\mu^2]\Gamma_0 = \frac{\alpha_r^2(\alpha_\mu^2 - 1)}{\alpha_\mu^2(\alpha_r^2 - 1)} \quad (34)$$

Note that $\Gamma \rightarrow 1$ with increasing excluded-volume interaction. We conclude that the excluded-volume effect increases the strength of the low-frequency dispersion.

5. Summary

In this paper we have shown that the relative strength of the low-frequency, molecular-weight-dependent dielectric dispersion is given by the ratio Γ, defined in eq 1. This result is very general. It depends on an assumption of large molecular weight, sufficiently large that the unperturbed chain obeys Gaussian statistics and that the two dielectric dispersions are well separated in time or frequency domains. In particular it is valid for chains with arbitrary excluded-volume interactions including three-body and higher terms.

This result is consistent with what one would expect. Any chain for which $\langle \boldsymbol{\mu}\cdot\mathbf{r}\rangle$ is zero will yield $\Gamma = 0$. Such chains are indeed expected[1-3] to exhibit only a single, relatively fast, molecular-weight-independent dielectric dispersion in dilute solution. On the other hand, chains for which the total dipole moment can be represented as due to two opposite and equal charges at opposite ends of the chain have $\Gamma = 1$. Such chains also exhibit a single dispersion, but one which is, in this case, slower and dependent on the molecular weight.[1-3] Chains with intermediate values of Γ display both dispersions. Note that Γ, by its definition, is limited to the range $0 \leq \Gamma \leq 1$.[4]

In addition, we predict, in eq 34, the excluded-volume behavior of Γ and observe that Γ increases with increasing excluded volume. Excluded volume acts to increase the strength of the low-frequency dispersion.

The experimental verification of theoretical predictions of the excluded-volume effect has always been rather difficult. This is because the quantity which is easiest to calculate, $\langle r^2\rangle$, unlike R_g or $[\eta]$, has evaded direct experimental measurement. We note here, however, that the Nagai–Ishikawa–Doi formula relates $\langle r^2\rangle$ directly to the measurable quantity $\langle \mu^2\rangle$.

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Dispersion and Polydispersity Effects in the Transport of Xanthan in Porous Media

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ABSTRACT: Recent experimental work on the flow of xanthan through nonadsorbing porous media has demonstrated a clear surface exclusion effect in which larger molecular weight species propagate faster than smaller fractions through the pore structure. Effluent measurements in these experiments include an assay for total polymer concentration and intrinsic viscosity of the produced solutions. Assuming zero hydrodynamic dispersion, these results may be analyzed using simple surface exclusion models to obtain the original molecular weight distribution (MWD) of the native polymer. In this paper, we model the transport of polymer through porous media using a multicomponent representation of the MWD, including the effects of hydrodynamic dispersion and surface exclusion. These calculations indicate that the data in such experiments are more difficult to interpret than the simple surface exclusion models alone would suggest. As a result of our calculations, supplementary experiments, necessary to clarify the interpretation, are suggested.

1. Introduction

Polymer transport in porous media is very important in a wide range of applications including polymer flooding in enhanced oil recovery (EOR), flow through membranes, and chromatographic columns. In describing the flow of polymers mathematically using macroscopic transport equations, a number of effects may have to be included in the formulation such as polymer dispersion, adsorption, excluded volume effects, chemical reactions, and viscous instabilities. In previous work on the modeling of polymer transport in porous media as it applies to EOR, the polymer has invariably been considered as a single-component species transported in the aqueous phase.[1-4] However, most polymers are polydisperse, and it is not expected that the transport properties of the lower and higher molecular weight species should be the same. Recently, experiments have been conducted by Lecourtier and Chauveteau[5,6] on the flow of xanthan through silicon carbide columns, which show that the single-component assumption is not adequate to describe polymer transport under all circumstances. In this work, Lecourtier and Chauveteau[5,6] showed that, in nonadsorbing porous media, the larger molecular weight species have a higher average pore velocity than smaller molecular fragments or tracer particles. They interpreted this as being due to entropic exclusion of the semirigid xanthan molecules from the walls of the pores,[5-8] with the larger molecules showing a stronger surface exclusion effect. They used these observations as the basis to obtain the molecular weight distribution (MWD) of the original polymer.

In this work, we investigate the transport modeling of polymer flow in porous media using a multicomponent

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