From these results, it is apparent that the exponent *a* for poly(*o*-TFMPA) is smaller than that for poly(CPA), which implies that the polymer chain of poly(*o*-TFMPA) is less rigid than that of poly(CPA).

Acknowledgment. We thank Sanyo Chemical Industries, Ltd., for donating poly(CPA) and Dr. K. Okuhara for donating *m*-TFMPA, *p*-TFMPA, and *p*-FPA.

Registry No. $W(CO)_6$, 14040-11-0; *o*-TFMPA (homopolymer), 96504-22-2; *p*-TFMPA (homopolymer), 96504-19-7; *p*-FPA (homopolymer), 96504-20-0; *m*-TFMPA (homopolymer), 96504-21-1.

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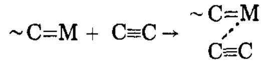
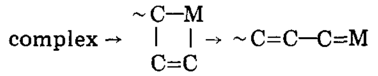
first stage (coordination)



$$\sim C{=}M + C{\equiv}C \rightarrow \begin{array}{c}\sim C{=}M\\ \vdots\\ C{\equiv}C\end{array}$$

complex

second stage (cycloaddition, ring scission)



$$\text{complex} \rightarrow \begin{array}{cc}\sim C & M\\ | & |\\ C & C\end{array} \rightarrow \sim C{=}C{-}C{=}M$$

They stated that the coordination ability of the acetylenic monomers is governed mainly by the steric factor. Since our results show the effect of the electronegativity of the CF_3 group in monomers on the polymerizability, the propagation seems to be controlled at the second stage in the present polymerizations.

Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 5. Comparison with Three Alternative Models

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Over the past several years, to examine local relaxation processes in polymers we have developed a damped orientational diffusion model[1–4] of polymer local main-chain motion. In this model[1] the main-chain orientational motion is treated in the context of a continuum damped diffusion equation where the discrete nature of local polymer motion is recognized by introducing a short-wavelength cutoff that corresponds (roughly) to the smallest motional unit and where the interaction of the diffusing mode with the solvent is modeled by a damping constant. The resulting damped diffusion model (DD) can be analytically solved for the normalized orientational autocorrelation function

$$\Phi_{DD}(t) = \tfrac{1}{2}e^{-\beta t}(\pi/\delta t)^{1/2}\,\mathrm{erf}\,[(\delta t)^{1/2}] \qquad (1)$$

$\Phi_{DD}(t)$ depends on two adjustable parameters: β, the damping constant, and δ, an effective small-scale jump rate ($=Dk_m^2$, where D is the diffusion constant or jump probability, and k_m is the wave vector cutoff corresponding to the minimum allowed motional unit). More recently, we have extended this model to include the effects of chain–chain interactions by using a complex damping constant[3] and to include the effect of side chains on local main-chain motions.[4] For a regular repeating array of side chains, it has been shown that side chains merely modify the main-chain damping constant. We have demonstrated[2] that NMR and local dielectric relaxation processes can be adequately described by this model.

Recently, Viovy, Monnerie, and Brochon presented a very detailed study of the fluorescence depolarization of polystyrene in dilute solution and showed that the damped diffusion model fits their measured autocorrelation function very well and that the parameters of the model were insensitive to the size of the fitting window about zero time.[5] Actually, they used an earlier version of the model[6] which employed a hard rather than a soft long-wavelength cutoff to represent the effect of the damping. However we have shown[2] that the two versions of the model lead numerically to the same correlation function. Since the physical interpretation of the damping is more apparent with the soft rather than with the hard cutoff, we shall refer to the latter damped diffusion version of the model.

Another model that has been used to fit local relaxation processes in polymers is the Hall–Helfand model[7] (HH). In this model, two processes are considered, an individual reorientation process which leads to an exponential decay, and a cooperative process where the correlation diffuses down the chain. This leads to an autocorrelation function of the form

$$\Phi_{HH}(t) = e^{-\kappa_0 t}e^{-\kappa_1 t}I_0(\kappa_1 t) \qquad (2)$$

where I_0 is a modified Bessel function. Here κ_0 corresponds to the individual reorientation relaxation constant and the terms containing κ_1 correspond to the cooperative motion.

Recently, Weber and Helfand[8] calculated orientational autocorrelation functions using a Brownian dynamics simulation and were not able to fit the calculated orientational correlation function with the Hall–Helfand functional form. They argued that there are also slower decaying processes and hence used a modified Hall–Helfand (MHH) correlation function

$$\Phi_{MHH}(t) = (1-\alpha)\Phi_{HH}(t) + \alpha e^{-\mu t} \qquad (3)$$

where μ is a decay constant modeling the slow decay processes and α is a mixing coefficient. The modified Hall–Helfand correlation function contains four parameters and fits the computer simulation very well.

Following the assumption of Weber and Helfand,[8] if in addition to the local reorientation processes embodied in $\Phi_{DD}(t)$, the autocorrelation function of interest is sensitive to long-wavelength, slowly decaying modes, it is natural to consider the modified damped diffusion autocorrelation function (MDD)

$$\Phi_{MDD}(t) = (1-f)\Phi_{DD}(t) + fe^{-\xi t} \qquad (4)$$

Here f and ξ are the DD analogues of α and μ. In both the MHH and MDD cases the long-wavelength parameters by definition must be insensitive to local details and are thus "hydrodynamic" in nature.

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The purpose of this Note is to compare the damped diffusion correlation function with and without modification to the Hall–Helfand and modified Hall–Helfand functions. Before presenting the results of numerical comparison between the two functions, we first present some analytic results. The damped diffusion correlation function can be written in terms of a series in the modified Bessel functions of the first kind as

$$\Phi_{\mathrm{DD}}(t) = e^{-\beta t}e^{-\delta t/2}\left[I_0(\delta t/2) - \frac{1}{2}\sum_{k=1}^{\infty} \frac{-1^k}{k^2 - {}^1\!/_4} I_k(\delta t/2) \right] \quad (5)$$

Notice that the leading term on the right-hand side of eq 5 is the Hall–Helfand correlation function, eq 2, if we identify $\beta \rightleftarrows \kappa_0$ and $\delta/2 \rightleftarrows \kappa_1$, with the rest of the series providing the difference between the two correlation functions. A truncated form of the series in eq 5, designated a generalized diffusion and loss expression, was suggested by Viovy, Monnerie, and Brochon[5] except that the coefficients of the terms in the sum were viewed as fitting parameters rather than fixed quantities. Following Hall and Helfand,[7] the term in the series containing I_j represents the cross-correlation function for two bonds separated by j intervening bonds. Viovy, Monnerie, and Brochon fit the first two terms of the series with a coefficient of unity instead of $^2/_3$ for the I_1 term. This two-term expression fits the data considerably better than the Hall–Helfand correlation function (it should be noted that the experimental precision was inadequate to fit the full four-parameter modified Hall–Helfand expression significantly). The resultant fit is about the same as for the damped diffusion model. This conclusion together with eq 5 suggests that an alternative interpretation of the damped orientation diffusion model is that it is an approximate resummation of the generalized diffusion and loss approach.

From eq 5 it is seen that the damped diffusion and the Hall–Helfand correlation function agree in the limit that $t \rightarrow 0$ (since $I_k(0) = 0$, $k > 0$) if $\beta = \kappa_0$ and $\delta = 3\kappa_1$. In the $t \rightarrow \infty$ limit, both correlation functions decay like an exponential times $t^{-1/2}$ and will agree in this limit if $\beta = \kappa_0$ and $\delta = \pi^2\kappa_1/2$. Hence if the two functions agree at short times, the Hall–Helfand correlation function decays faster than the damped diffusion correlation function at long times. This is consistent with the need of Weber and Helfand[8] to add a slower decaying term to the HH expression in order to agree with their computer simulation.

Weber and Helfand calculated four different vector autocorrelation functions at three different temperatures. The correlation functions they calculated are (1) a bond autocorrelation function calculated from the unit vector along a backbone bond i, (2) a chord autocorrelation function where the unit chord vector connects the midpoint of two adjacent bonds, (3) an out-of-plane autocorrelation function where the out-of-plane vector is the unit vector perpendicular to the plane defined by two adjacent bond vectors, and (4) a bisector autocorrelation function where the bisector vector is a unit vector in the plane of two adjacent bond vectors which bisects the angle between them.

We fit the modified damped diffusion autocorrelation function, eq 4, to the modified Hall–Helfand autocorrelation function employing the parameters given by Weber and Helfand[8] (these parameters are given in Table I for the reader's convenience) for each of the correlation functions at the specified temperatures. Weber and Helfand state that the parameterized modified Hall–Helfand expression is a good representation of the various autocorrelation functions obtained from their simulation.

Table I
Vector Autocorrelation Function (Acf) Fitting Parameters for the Modified Hall–Helfand (MHH) and Damped Diffusion (DD and MDD) Models

		temp, K		
model	parameter	330	373	425
		Bond Acf		
MHH[a]	κ_0	0.7715	1.1236	1.8646
	κ_1	8.6133	13.3690	20.7900
	α	0.1741	0.1694	0.1678
	μ	0.1415	0.1263	0.3932
MDD[b]	β	1.611	1.830	2.850
	δ	28.00	45.24	70.96
	f	0.2086	0.1842	0.1803
	ξ	0.1806	0.1465	0.4151
	SD[c]	2.48×10^{-3}	2.43×10^{-3}	1.90×10^{-3}
		Chord Acf		
MHH[a]	κ_0	0.6617	0.9336	1.5780
	κ_1	5.4201	7.9051	12.2249
	α	0.2718	0.2555	0.2566
	μ	0.1537	0.1299	0.4051
MDD[b]	β	1.477	1.616	2.531
	δ	16.50	25.29	39.35
	f	0.3155	0.2766	0.2736
	ξ	0.1837	0.1479	0.4246
	SD[c]	1.85×10^{-3}	2.03×10^{-3}	1.66×10^{-3}
		Bisector Acf		
MHH[a]	κ_0	3.0157	4.5331	7.2046
	κ_1	14.0252	23.3100	35.2113
DD[d]	β	4.253	6.000	8.984
	δ	40.55	71.35	111.1
	SD[c]	2.93×10^{-3}	4.53×10^{-3}	4.90×10^{-3}
		Out-of-Plane Acf		
MHH[a]	κ_0	3.0321	4.0917	7.5415
	κ_1	11.8765	21.1864	30.8642
	α	0.0018	0.0006	0.0000
DD[d]	β	4.145	5.477	9.300
	δ	33.72	64.33	95.70
	SD[c]	2.32×10^{-3}	4.35×10^{-3}	4.39×10^{-3}

[a] The parameters for the MHH Acf, eq 3, are taken from Table V of ref 8. The units of κ_0, κ_1, and μ are ns^{-1}. [b] The parameters for the MDD Acf are obtained from a 200-point least-squares fit of eq 4 to the MHH Acf with the given parameters (see text). The units of δ, β, and ξ are ns^{-1}. [c] The standard deviation of the 200-point least-squares fit of the DD Acf to the MHH Acf. The values of the Acf over the range of the fitting range from ca. 0.9 to 0.2. [d] The parameters for the DD Acf are obtained from a 200-point least-squares fit of eq 1 to the MHH Acf with the given parameters (see text). The units of δ and β are ns^{-1}.

We used a nonlinear least-squares fitting procedure at 200 equally weighted and equally spaced time points. The points were chosen such that over the fitting window the value of the autocorrelation function varied from ca. 0.9 to ca. 0.2 in each case. The values of the damped diffusion model parameters β, δ, f, and ξ are given in Table I along with the standard deviation obtained from the fitting procedure.

While Weber and Helfand do not give any criterion of goodness for their fit of the MHH correlation function to the computed ones, it appears by examining the figures in their paper that the standard deviations given in Table I are of the same order of magnitude as these obtained by Weber and Helfand. Based on the results of Viovy, Monnerie, and Brochon and those presented here, the damped diffusion model fits polymer local motion relaxation data taken from existing physical or computer experiments as well as the generalized diffusion and loss expression or the modified Hall–Helfand expression. The physical interpretations of the two models are however quite different. The damped diffusion model is a "smoothed out" hydrodynamic description of polymer relaxation. That is, it asserts orientational autocorrelation functions are insensitive to local molecular details. In partial contrast, the modified Hall-Helfand models give a "molecular" explanation of a portion of the local relaxation, embodied in the parameters κ_0 and κ_1, and a "hydrodynamic" description of the long-wavelength relaxation process embodied in the parameters α and μ; thus the MHH expression is a hybrid description of the system. On the other hand, as pointed out above, the "hydrodynamic" explanation given by the damped diffusion model can also be viewed as an approximate resummation of the "molecular" explanation given by a generalized diffusion and loss model.

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Molecular Weight Dependence of the Second Virial Coefficient for Linear Flexible Polymers in Good Solvents

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It is well established experimentally that the second virial coefficient A_2 for a linear flexible polymer in a good solvent decreases with an increase in the polymer's molecular weight M. This decrease is usually represented on a log-log graph by a straight line; i.e.

$$\log A_2 = K - b \log M \qquad (1)$$

where K and b are constants. Reported values of b are in the range 0.2-0.3. However, in some studies[1-4] where A_2 was determined over a very wide range of M, it was found that plots of $\log A_2$ against $\log M$ were not linear but followed a convex-downward curve with an asymptotic slope of -0.20, as shown schematically by line A in Figure 1a and by typical data[4] in Figure 1b. Mathematically, the behavior of this curve is expressed by

$$\mathrm{d} \log A_2/\mathrm{d} \log M < 0 \qquad \text{(approaches } -0.2 \text{ as } M \to \infty) \qquad (2)$$

$$\mathrm{d}^2 \log A_2/(\mathrm{d} \log M)^2 > 0 \qquad (3)$$

The penetration function Ψ is defined by[5]

$$\Psi \equiv A_2 M^2/(4\pi^{3/2} N_A \langle S^2\rangle^{3/2}) \qquad (4)$$

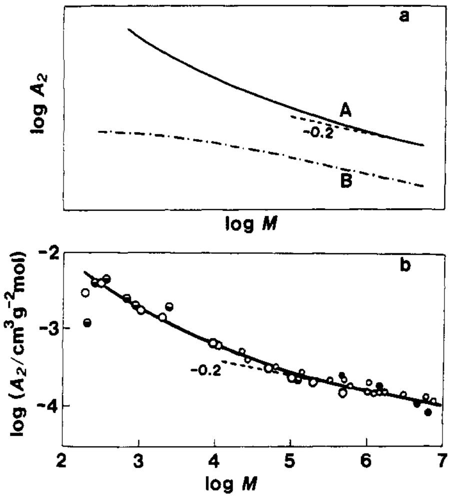

Figure 1. (a) Schematic representation of $\log A_2$ vs. $\log M$ curves for a linear flexible polymer in a good solvent. Line A, experiment; line B, prediction from current theories. (b) Plot of $\log A_2$ vs. $\log M$ for poly(methyl methacrylate) in acetone, a good solvent:[4] (○) Kirste and Wunderlich (*Z. Phys. Chem.* **1968**, *N58*, 133); (●) Cantow and Schulz (*Z. Phys. Chem.* **1954**, *N2*, 117); (o) Schulz and Craubner (*Z. Electrochem.* **1959**, *63*, 301); (◒) Springer et al. (*Z. Electrochem.* **1965**, *69*, 494).

where N_A is the Avogadro constant and $\langle S^2\rangle$ the mean-square radius of gyration of the polymer in the solvent considered. Differentiation of eq 4 with respect to M gives

$$\mathrm{d} \log \Psi/\mathrm{d} \log M = \mathrm{d} \log A_2/\mathrm{d} \log M + 2 - (3/2)\, \mathrm{d} \log \langle S^2\rangle/\mathrm{d} \log M$$

Much experimental evidence is now available for the fact that $\langle S^2\rangle$ of a linear flexible polymer in a good solvent varies in proportion to $M^{1.2}$ at sufficiently high M. Thus, the above relation may be written

$$\mathrm{d} \log \Psi/\mathrm{d} \log M = \mathrm{d} \log A_2/\mathrm{d} \log M + 0.2 \qquad (5)$$

Hence

$$\mathrm{d}^2 \log \Psi/(\mathrm{d} \log M)^2 = \mathrm{d}^2 \log A_2/(\mathrm{d} \log M)^2 \qquad (6)$$

When combined with eq 2 and 3, these relations yield

$$\mathrm{d} \log \Psi/\mathrm{d} \log M < 0 \qquad \text{(approaches zero as } M \to \infty) \qquad (7)$$

$$\mathrm{d}^2 \log \Psi/(\mathrm{d} \log M)^2 > 0 \qquad (8)$$

For $\langle S^2\rangle \propto M^{1.2}$ the radius expansion factor α_S ($\alpha_S^2 \equiv \langle S^2\rangle/\langle S^2\rangle_\Theta$, with $\langle S^2\rangle_\Theta$ the value of $\langle S^2\rangle$ in the unperturbed state) varies in proportion to $M^{0.1}$, since, as is well-known, $\langle S^2\rangle_\Theta$ depends linearly on M. Thus, it can be shown that eq 7 and 8 are equivalent to

$$\mathrm{d}\Psi/\mathrm{d}\alpha_S < 0 \qquad \text{(approaches zero as } \alpha_S \to \infty) \qquad (9)$$

$$\mathrm{d}^2\Psi/(\mathrm{d}\alpha_S)^2 > 0 \qquad (10)$$

provided that α_S is not close to unity.

From eq 9 and 10 it follows that plots of Ψ against α_S for a linear flexible polymer in a good solvent should follow a concave-downward curve as line A′ in Figure 2; i.e., as α_S increases from unity, Ψ should *decrease* monotonically to a certain asymptotic value with a convex-downward curvature. Previous measurements of A_2, which were mostly restricted to relatively small values of α_S, failed to reveal this type of α_S dependence of Ψ, but our recent studies on poly(hydroxybutyrate) in trifluoroethanol[2] and polystyrene in benzene[3] demonstrated it clearly, since they were extended to the values of α_S much larger than those attained before.

The molecular weight dependence of A_2 for linear flexible polymers has been formulated by many authors, previously by two-parameter methods[5] and lately more

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