Diffusion in Polyethylene Blends: Constraint Release and Entanglement Dilution

Ernst D. von Meerwall,*,†,‡ Nazan Dirama,‡ and Wayne L. Mattice†

Maurice Morton Institute of Polymer Science and Physics Department, The University of Akron, Akron, Ohio 44325-3909

Received February 8, 2007; Revised Manuscript Received March 26, 2007

ABSTRACT: We have used the ^{1}H pulsed-gradient NMR method to augment our earlier diffusion measurements in *n*-alkane and polyethylene (PE) melts and blends with measurements in 12 additional melts and in three series of blends at $T = 150$ °C across the full concentration (c) range. Blends were based on $M = 33$ kDa PE and contained either *n*-C50 alkane, $M = 1.8$ kDa PE, or $M = 6.7$ kDa PE. The results again agree with our theoretical synthesis involving a smooth transition from Rouse to reptational behavior including constraint release and free volume host effects which depend on T, M, and c. Tube dilation is assumed contained in the constraint-release mechanism; contour length fluctuations are not considered to affect center-of-mass diffusion. The generalized constraint-release term not only reproduces the c and M dependences of both D in fully entangled blends but also mimics or supplants entanglement dilution in blends of PE with (unentangled) *n*-alkanes *n*-C50 and *n*-C12. This approach provides a superior alternative in the interpretation of constraint release by shifting from static entanglements spatially diluted by unentangled species to undiluted entanglements whose release rate is accelerated by diffusing diluent. This interpretation is now consistent with fully entangled blends in homologous blends at all M. These results are in semiquantitative agreement with earlier work in polybutadienes.

I. Introduction

The nature of entangled motion in polymer chains has attracted a great deal of experimental and theoretical attention.[1,2] There is general agreement that whereas solutions of macromolecules in small-molecule solvents pose particular conceptual and interpretive difficulties, the case of melts and blends of monodisperse homologous linear chains is thought to be nearing consensus.[3,4] Still, an undisputed comprehensive theory for the emergence of entangled motion remains elusive. In particular, the roles of constraint release[5] and contour-length fluctuation[6] during the transition are not yet fully understood.[7]

Below the molecular weight M_c characterizing the onset to entangled motion, the Rouse theory[8] tends to hold sway even if the conditions for its applicability are not fully met.[9] For the case of self-diffusion in that regime, the molecular weight (M) dependence of the diffusion coefficient D scales as M^{-1}. Well above M_c, strict reptation theory[10,11] demands $D \sim M^{-2}$. Experimental difficulties have until recently prevented the latter asymptote from being confidently established.[7,12] In melts and blends additional effects must be incorporated in any interpretive theory. Substantial host effects, related to the strongly M-dependent viscosity, are usually treated using the free volume theories.[13−16] Just as these host effects asymptotically recede as M increases, the release of constraints by diffusing host chains[17,18] in the wider vicinity of M_c, and dilution of entanglements in the presence of diluent or short-chain homologous species, begin to cause upward departures from the strict reptation prediction applicable to single diffusing chains in a fixed network. The role of contour length fluctuation,[6] while well established for bulk mechanical and transport properties, seems less well understood for the case of self-diffusion.[7]

Pulsed-gradient spin-echo NMR (PGSE) diffusion measurements[19] have played a substantial role in the elucidation of the nature of the entanglement transition. The experiment is undemanding chemically and comes close to a first-principles determination of equilibrium Brownian motion. The alkane−polyethylene series,[14,20−24] and blends based on it,[16] have been explored in considerable detail; the related hydrogenated polybutadienes,[25] as well as polybutadiene[26,27] and polyisoprene melts and blends,[15] have also been examined with a view to the application of appropriate theories.

Recently, molecular dynamics (MD)[28−30] and dynamic Monte Carlo (MC)[31−33] simulations have paralleled certain experimental investigations of diffusion. While some of this effort was undertaken to establish the validity of the simulations, the most recent work has provided valuable insights into the kinetics and dynamics of chains, and their motional segments, diffusing in the constraining vicinity of its neighbors.

The present work was undertaken with the aim of extending both the experimental work and the applicable theoretical models of diffusion in the vicinity of M_c. It involves the following components: (1) performing PGSE measurements of self-diffusion in 12 additional polyethylene (PE) melts with molecular weights between $0.5M_c$ and $20M_c$, where little previous data were available, and measuring two-component self-diffusion in liquid binary blends of PE with PE (two series) and with *n*-C50 as a function of concentration; (2) combining the results with those of single-component self-diffusion previously obtained for liquid *n*-alkane melts with carbon numbers from 8 to 60; (3) using a synthesis of current concepts of polymer dynamics to characterize the transition from unentangled to entangled diffusion (Rouse, free volume with chain-end and density terms, reptation with constraint release); and (4) dedicating particular attention to the expected effects of entanglement dilution and constraint release and their potential overlap and competition on both sides of the entanglement transition, comparing the results with those obtained for polybutadiene blends. Preliminary oral reports of portions of this work have been given.[34,35]

---

* Corresponding author. E-mail: evonmee@uakron.edu.
† Maurice Morton Institute of Polymer Science.
‡ Physics Department.

10.1021/ma070342q CCC: $37.00

Table 1. New *n*-Alkane and Polyethylene Samples

sample	M_n	M_w/M_n	supplier (date)
$C_{50}H_{102}$	702	1.00	Fluka Chemicals (1998)
PE 0.81K	808	1.18	Polymer Source (2002)
PE 1.11K	1110	1.11	Fluka (2002)
PE 1.79K	1790	1.12	Fluka (2002)
PE 1.80K	1800	1.10	Polymer Source (2002)
PE 3.38K	3280	1.05	Polymer Source (2002)
PE 4.65K	4650	1.05	Polymer Source (2002)
PE 6.7K	6700	1.06	Polymer Source (2002)
PE 10.4K	10400	1.04	Polymer Source (2002)
PE 12.5K	12500	1.05	Polymer Source (2002)
PE 18.5K	18500	1.04	Polymer Source (2002)
PE 22.5K	22500	1.05	Polymer Source (2002)
PE 33.0K	33000	1.05	Polymer Source (2002)

II. Experiment

A. Samples. The *n*-alkane chosen for this study was *n*-pentacontane, $C_{50}H_{102}$ (Fluka Chemical Corp.), and was used as supplied. The nominal purity of this preparation was given as puriss. (99%).

The polyethylene host materials were obtained either from Polymer Source, Inc. (Dorval, PQ, Canada), or from Fluka Chemical Corp. The selection emphasized an intermediate range of molecular weights near and above M_c where few previous diffusion measurements had been reported. The suppliers' characterizations are shown in Table 1. In our diffusion experiments the neat PE samples' modest *D* distribution in each case was consistent with a log−normal *M* profile having the known polydispersity.

NMR and mass spectrometric analyses were performed on two specimens: the 1.79 kDa Fluka sample and the 1.8 kDa Polymer Source specimen. Whereas the former was shown to be nearly pure linear polyethylene, the latter was found to contain occasional side groups: some 5% of the main-chain carbons have side groups of less than four carbons, and 0.2% have side chains of four or more carbons. Some scatter in the diffusion data (see below) is the likely consequence of such irregularities, presumed to exist in the Polymer Source preparations.

Binary blends were prepared by weighing requisite aliquots of the ingredients, mixing these in powdered form where possible, inserting into 7 mm o.d. NMR sample tubes in amounts totaling between 200 and 300 mg, and compacting mechanically. Sample tubes were flushed and filled with dry nitrogen and hermetically sealed. Concentration equilibration and elimination of bubbles required overnight heating to 150 °C. There was no evidence of thermal degradation.

B. Diffusion Experiment. Experimental results for *n*-alkane melts, two PE melts, and two alkane-PE blend series were available from earlier detailed investigations by this laboratory.[14,16] These data were used to extend the *M* range available for comparison with theory. For the present work, new pulsed-gradient spin-echo (PGSE) diffusion measurements were made at 33 MHz in our highly modified wide-line spectrometer at 150.5 °C. We measured 12 polyethylene melts of molecular weights *M* from 0.81 to 33 kDa and of three series of blends: *n*-pentacontane and two PE specimens, of $M = 1.8$ and 6.7 kDa, each dissolved in a polyethylene of $M = 33$ kDa PE at concentrations spanning the full range.

Our methods of making nonspectroscopic spin-echo diffusion measurements and interpreting the resulting data have been described in detail elsewhere.[36] Briefly, the three-pulse stimulated echo radio-frequency sequence was coordinated with a matched pair of pulsed magnetic field gradients of magnitude *G* and duration δ, separated by time Δ. Radio-frequency phase-sensitive detection of the echo signal recorded 3 kHz off-resonance was followed by Hamming-windowed magnitude Fourier transformation, integrating the peak area, and performing rms baseline correction. As a consequence of the gradient pulses the spin echo in a diffusing substance is attenuated; here the amplitude was recorded as a function of pulse duration δ incorporated in a gradient parameter *X* (see eq 1). In this investigation, the parameter settings for all data to be shown below were fixed values of $\Delta = 70$ ms, $G = 231$ G/cm, and a small steady gradient $G_0 = 0.3$ G/cm, with δ varied in 15−30 steps until the echo signal was attenuated to the background noise level or until 10 ms was reached. Echo height measurements were signal-averaged over 6−12 passes.

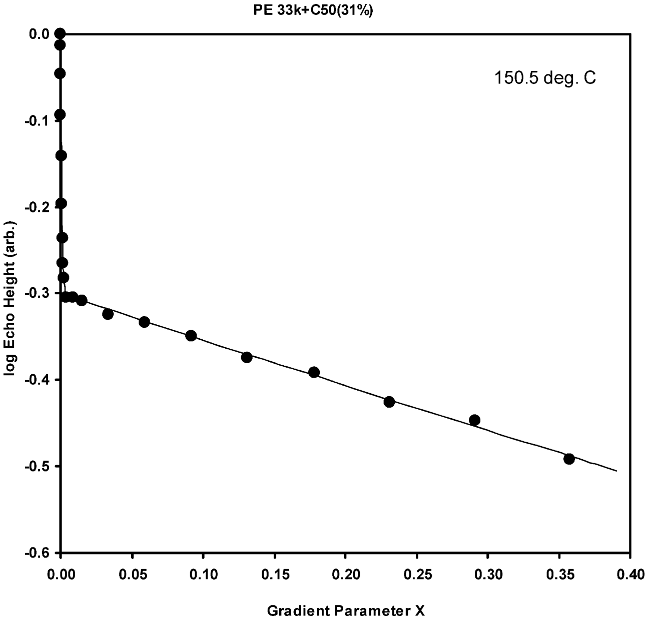

Figure 1. Diffusional echo attenuation at 150 °C in a sample of 31 wt % *n*-pentacontane in 33 kDa polyethylene. Fit of eq 1 to the data is consistent with a monodisperse fast component plus a slow component whose *D* distribution is derived from the known polydispersity of the PE.

The diffusional echo attenuation was analyzed off-line by the current version of the Fortran code DIFUS5.[37] The echo amplitude *A* was adequately reproduced by a two-component model of the form

$$\frac{A(X)}{A(0)} = f_1 \exp[-\gamma^2 D_1 X] + (1 - f_1) \exp[-\gamma^2 D_2 X] \qquad (1)$$

where γ is the proton gyromagnetic ratio and

$$X = \delta^2 G^2 (\Delta - \delta/3) + \text{small correction terms in } GG_0$$

This model has three adjustable parameters: the two diffusion coefficients D_1 and D_2 and the relative echo amplitude f_1. While the quality of the fit of this two-component model was in all cases at least marginally satisfactory, a slight improvement of the agreement with echo attenuation data was usually possible by taking into account the host polymer's molecular weight distribution. This involved replacing the single slow component 2 by a disperse ensemble of rate components mapped onto the known *M* distribution using reptational scaling;[38] thus, D_2 was supplanted by $D(M_n)$, the reference diffusion coefficient of molecules of number-average mass. (A separate measurement in the three neat PE samples confirmed this analysis of the slow component in the blends.) In the case of melts, f_1 was set either to zero or to unity, depending on the need to deal with polydispersity ($f_1 = 1.0$ for pentacontane). Two sample echo attenuation plots with fits of the modified two-component, three-parameter version of eq 1 are shown in Figures 1 and 2. Accurate modeling of the echo attenuation of the slow component, especially in the initial overlap region, is a prerequisite for the reliable extraction of results (D_1 and f_1) of the fast-diffusing component.

To check for possible departures from Fickian diffusion, the 33 kDa specimen and two blends of this material, with 15% *n*-pentacontane and with 45% 1.8 kDa PE, were examined over a range of diffusion times Δ between 8 and 275 ms. These limits are imposed by practical considerations related to signal-to-noise ratio

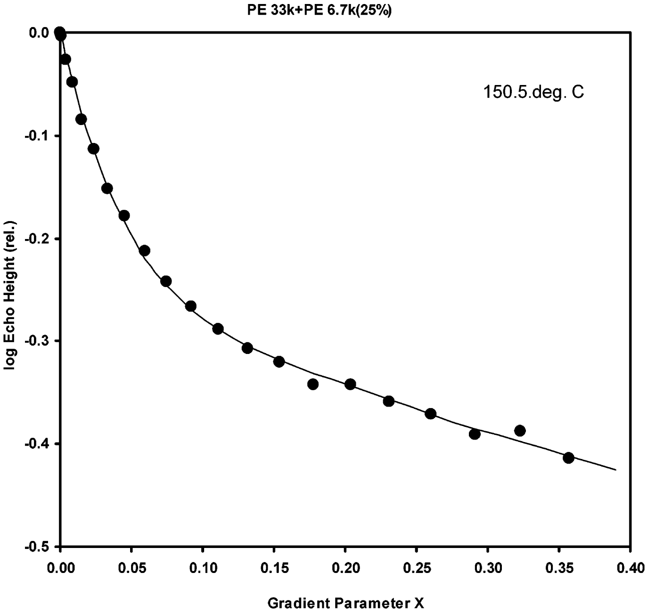

Figure 2. Echo attenuation in a blend of 25 wt % of 6.7 kDa PE in 33 kDa PE. Fit to the data of eq 1 is consistent with a fast-diffusing component plus a slow component whose D distribution is consistent with the known polydispersity of the PE.

and hence to attainable precision in the extracted diffusion coefficient(s). Any explicit time dependence of the (apparent) diffusion coefficients could arise from inhomogeneities, particularly in the blends. A lower limit for the length scale of such inhomogeneities, if detected, is given by Fick's second law; for the D values obtained in this work, this length ranges between 0.5 μm and over 2 μm. Since this length greatly exceeds the coiled dimensions of our molecular chains, segmental motions are inaccessible here; true macroscopic inhomogeneities of this dimension or larger are thought to be unlikely in our fully liquid blends. In fact, within experimental error no time dependence of any D was observed, and the single value of Δ used in the bulk of the work was chosen to minimize the uncertainties of the extracted diffusion coefficients.

III. Theory: Diffusion in Melts and Blends

In unentangled *n*-alkane/polyethylene melts and blends, D_i of species $i = 1, 2$ had been found[14,16] in previous work to adhere to an expression depending on temperature T, molecular weights M_i, and volume fraction υ_1, as follows:

$$D(T,M_1,M_2,\upsilon_1) = \frac{A}{M_\mathrm{i}} \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \exp\left[-\frac{B_\mathrm{d}}{f(T,M_1,M_2,\upsilon_1)}\right] \tag{2}$$

in terms of a constant A, an intrinsic thermal activation energy E_a, a free volume overlap factor B_d, and fractional free volume f. In blends of homologous ingredients, as here, f must account for the chain-end free volume[13] V_e in addition to a segmental contribution $f_\infty = f(T, M \rightarrow \infty)$ present at all M:

$$f(T,M_\mathrm{i},\upsilon_\mathrm{i}) = f(T,\infty) + 2V_\mathrm{e}(T)\, \rho(T,M^*(\upsilon_\mathrm{i}))/M^*(\upsilon_\mathrm{i}) \tag{3}$$

where

$$\frac{1}{M^*} = \frac{\upsilon_1}{M_1} + \frac{1-\upsilon_1}{M_2}$$

The original application of this synthesis, to *cis*-polyisoprenes, was successful in reproducing experimental data[15] without the need to consider variations in the density. But in *n*-alkanes and PE the density ρ is a pronounced function of M and T, an effect which was accurately modeled on the basis of the same free volume parameters. Detailed molecular dynamics simulations have also been successfully analyzed using these expressions, with parameters in good agreement with those derived from experiment.[28,29]

If the heavier species 2 begins to approach the entanglement ("ent") onset molecular weight M_c^0 in the melt, it was shown[25] that eq 2 was to be modified to account for reptation ("rep"), including constraint release ("CR")

$$D_i\,(\text{all } M_1, M_2) = \left[\frac{1}{D_\mathrm{Rouse}} + \frac{1}{D_\mathrm{ent}}\right]^{-1} \tag{4}$$

where

$$D_\mathrm{ent} = D_\mathrm{rep} + D_\mathrm{CR} \tag{5}$$

and

$$D_\mathrm{CR} = \alpha D_\mathrm{rep}\left[\frac{M_\mathrm{c}}{M_2}\right]^2 \quad \text{with } \alpha \approx 15 \tag{6}$$

Well-known substitutions are $D_\mathrm{Rouse} \sim M^{-1}$ (included in eq 2) and $D_\mathrm{rep} \sim M^{-2}$; other terms in eq 2 are retained. The fit of theory to data for PE was found to be relatively insensitive to the value of α; the value chosen lies near the midpoint of the range.

A recent report[39] has suggested that at least for the shorter alkanes the unentangled diffusional Rouse M dependence M^{-1} should be replaced by $M^{-\nu}$, with $\nu = 0.7$, to account for hydrodynamic interactions and chain stiffness. A reexamination of the results of the earlier work of this laboratory[14,16] using a correspondingly altered version of the theory shows that all of the melt and blend data can be equally well reproduced as with the strict Rouse exponent, provided modest adjustments are permitted to three parameters, A, E_a, and the temperature dependence of f_∞. In no case are the results and conclusions of the present work, dealing mainly with effects near and above M_c, significantly affected. It should be noted that trace diffusion of *n*-alkanes (8−36 carbons) in two high-M rubbery polymer melts were reported[40] to exhibit M exponents of -1.02 ± 0.02 and -0.85 ± 0.08, suggesting that alkane chain stiffness effects are likely to be modest.

The dilution of the entanglements of the heavy species by the lighter one is accounted for[41,42] by using an expression originally applied to long-chain polymers diluted by small-molecule solvents:

$$M_\mathrm{c} = M_\mathrm{c}^0/(1-\upsilon_1)^n, \quad 1 < n < 1.2 \tag{7}$$

This expression, used only when $M_\mathrm{c}^0 < M_2$, is substituted into eq 6. A further, approximate, refinement was necessary[16] since as $\upsilon_1 \rightarrow 1$, the binary blend approaches a dilute solution of M_2 in solvent M_1; in such cases D_2 exhibits an M_2 exponent near −0.6 to −0.8.

For the "fully entangled" case $M_2 > M_1 > M_\mathrm{c}^0$, analytical theories for D_i in blends are not available; expressions reported for D_CR apply only to melts or to trace concentrations.[17,18,43] In an attempt to extend these to the full concentration domain, previous work by this laboratory[27] had resulted in the suggestion of the following adaptation of eq 5 of ref 17. It is intended as a replacement for eq 7 with its substitution of eq 6 and may be referred to as generalized constraint release:

$$D_\mathrm{CR}(i) = \alpha D_\mathrm{rep}(i,M_\mathrm{c}^0)[(M_\mathrm{c}^0)^{1.5} M_i/M_\mathrm{host}{}^{2.5}] \tag{8}$$

We postulate the existence of an effective host, with molecular weight approximated as a simple average based on the weight fractions w_i of the two species:[27]

$$M_{\mathrm{host}} = w_1 M_1 + (1 - w_1) M_2 \qquad (9)$$

This approach ensures that in fully entangled blends the theory will generate a nonnegligible concentration dependence of both diffusion coefficients, as observed experimentally. Without a concentration-dependent M_{host}, the only concentration dependences of D_1 and D_2 (i.e., $D(M_n)$) would be small remnants of the chain-end free volume effect, which becomes increasingly insignificant at high M_1 and M_2 (see eq 3). Still, this approach may well be too simplistic to capture the subtleties of the dynamic behavior and evolution of the tube constraining either of the diffusing species, although basic lateral tube dilation should yield to treatment in the context of D_{CR}. More importantly, the effects of contour length fluctuations,[6] known to be significant at least in bulk dynamic and transport properties near and above the entanglement transition, have not yet yielded to reliable quantitative analysis in self-diffusion in blends and are not included here.

It is tempting to apply the generalized constraint-release mechanism of eqs 8 and 9 to the additional case $M_2 > M_c^0 > M_1$, where entanglement dilution of species 2 by the lighter component 1 is traditionally described by eq 7. It will be seen below that this attempt is quite successful, provided that entanglement dilution is not also invoked. In other words, entanglement dilution and generalized constraint release are effectively alternatives, either of which alone satisfactorily reproduces the data in this regime. We regard the implications of this choice as significant; they will be discussed in the next section.

In fact, there is no apparent reason not to apply generalized constraint release at all values of M_1 and M_2 and at all concentrations, including fully unentangled melts and blends. The addition of Rouse and entangled friction coefficients postulated by eq 4 ensures that D_{CR}, whatever its form, will rapidly become insignificant as M_1 and M_2 fall below M_c^0. (Its increasing irrelevance above M_c is directly evident from eq 6 or eq 8.) Comparisons with earlier data in *n*-alkane melts and binary blends amply confirm this conclusion. The salutary effect of applying eqs 8 and 9 in all cases is that doing so is conceptually consistent, fully in the spirit of eq 4 and its substitutions. That approach envisions a single recipe to describe diffusion at all molecular weights without breaks or discontinuities at M_c in any of its algorithmic components. The latter parameter serves as a reference for the very gradual development of lateral restraints to chain motion, in keeping with observation.

IV. Results and Discussion

A. Melts. Figure 3 shows all diffusion data at 150.5 °C collected by this laboratory in *n*-alkanes and polyethylene melts. Of these, alkane data are taken from ref 14, one measurement in an alkane (C_{50}) and two measurements in PE melts (6.2 and 13.9 kDa) are taken from ref 16, and 12 new measurements in PE represent the present work. (Data previously published are shown as open symbols in Figure 3.) The theory of eqs 2−9 was evaluated with the set of parameters provided by the earlier studies; no further adjustment of parameters was performed.

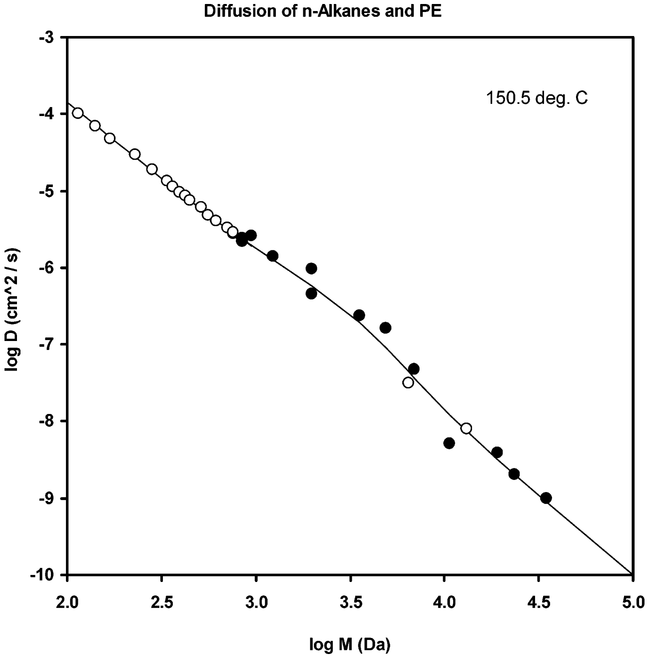

Figure 3. Molecular weight dependence of diffusion in melts. Open symbols show data from previous work: *n*-alkanes from ref 14 and alkane C_{50} and PE melts 6.2 and 13.9 kDa from ref 16. Closed symbols represent present work in PE. Line shows evaluation of the theory of eqs 2−9.

It is seen that the theory, quantitatively calibrated for alkanes and extended to apply over the full range of molecular weights, reproduces the data in the entangled regime at least semiquantitatively. Some scatter among the PE data exceeds that expected on the basis of the experimental uncertainties of individual measurements. This effect is attributed to irregularities in the microstructure of the PE chains (see above).

It may be of preliminary interest to examine the observed power-law exponents (slopes of log D vs log M) in the asymptotic regions of Figure 3. In the alkane region up to and including C_{60}, the slope of data as well as theory at 150.5 °C is -1.97 ± 0.02. In the PE region above 3 kDa, scatter in the data prevents a usefully precise determination, but examination of the theory shows that the slope flattens from a value of -2.59 centered on $M = 4$ kDa to -2.01 near $M = 40$ kDa. Thus, the predictions of pure reptation theory are asymptotically approached near $M > 20M_c$.

The transition from unentangled to entangled behavior is barely discernible in Figure 3 as a small bulge in the vicinity of $M_c \approx 1750$, generated by eq 4 and only slightly augmented by eq 8 with $M_{\mathrm{host}} = M$. In fact, at this level of precision a single straight line, with a slope close to -2.0, is only slightly inferior in the quality of fit to all data of Figure 3. (This phenomenon is, however, confined to temperatures near 150 °C; the power-law slopes of the *n*-alkane diffusion data are strongly dependent on temperature.[14]) It is clear that the transition from unentangled to entangled diffusion is quite subtle and is further obscured by chain-end free volume effects which augment alkane diffusion increasingly at low M, simulating a power-law slope well steeper than the -1 expected as Rouse behavior. This observation confirms those of earlier work,[16,21,25] including that in polybutadienes.[26,27] Greater clarity about this transition is available through the elimination of differential chain-end effects, e.g., either through a conventional constant free volume correction or preferably via studies of trace diffusion in a common homologous host. Such a study, augmented by dynamic Monte Carlo simulations, has recently been performed in this laboratory.[44]

B. Entangled PE Blends. In binary blends both of whose components are entangled in their own melts it has been observed (e.g., in polybutadienes) that the two self-diffusion

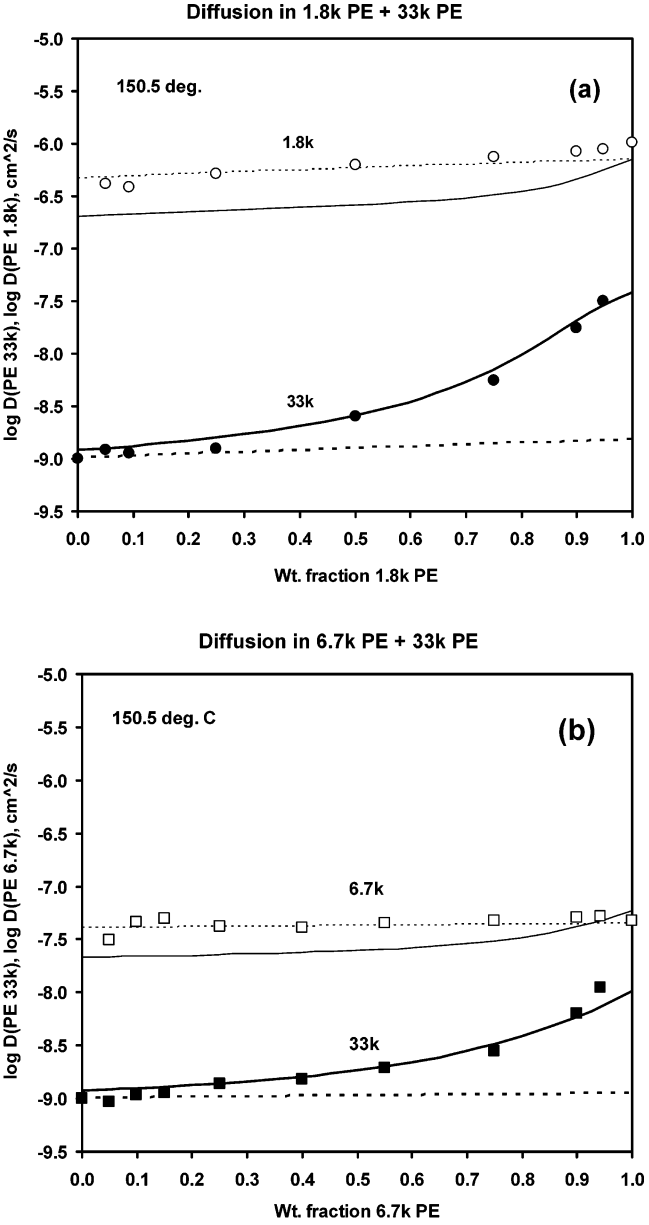

Figure 4. Concentration dependence of diffusion of both ingredients in a blend of (a) 1.8 kDa PE or (b) 6.7 kDa PE with 33 kDa PE. Dashed lines represent model of eqs 6 and 7 assuming full entanglement of both species but no variation of host molecular weight; solid lines postulate a concentration dependence of host M according to eqs 8 and 9.

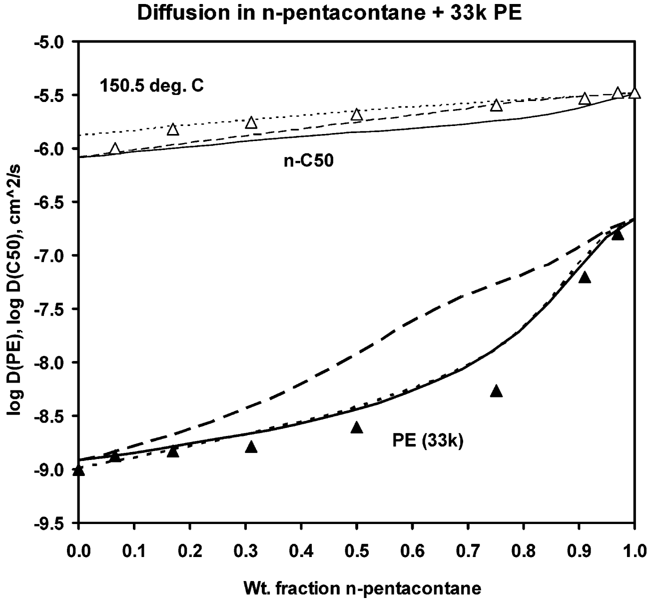

Figure 5. Concentration dependence of both ingredients in a blend of *n*-pentacontane with 33 kDa PE. Theory (not fitted) assumes PE to be entangled in its own neat melt. Dotted lines postulate entanglement dilution by lighter component (eqs 6 and 7); solid lines assume generalized constraint release (eqs 8 and 9), and dashed lines postulate both of these effects combined.

coefficients are notably concentration-dependent. This observation would not be expected on the basis of strict reptation theory, which generates only the pronounced differences in D, presumably independently of the proportion of the components. Standard constraint-release theory suggests a mechanism for these observations, but a useful quantitative theory applicable across the full composition range currently depends on adaptations of the kind provided by eqs 8 and 9.

Figure 4a,b shows measurements of D_1 and D_2 in two entangled PE blends, one in which $M_1 \approx M_c^0$ and the other with $M_1 \approx 4M_c^0$; in both cases $M_2 \approx 19M_c^0$. Three observations are in order. First, use of the generalized constraint release formalism in the context of the complete theory of eqs 2−5 generates a composition dependence of both D_1 and D_2 appropriate in form and magnitude; second, the concentration dependence of D_2 is, as required, larger than that of D_1; and third, the concentration dependences of both D_1 and D_2 are smaller as M_1 increases and constraint release becomes less important. All three experimentally observed trends thus are at least semi-quantitatively reproduced by the theory of eqs 8 and 9, with the caveat that the new CR theory somewhat underpredicts observation for D_1 for reasons not entirely clear.

These results have been achieved based on assumptions whose validity is not assured. The form of eq 9 is likely to be simplistic in view of its inability to reflect the segmentally local distributions of entanglements in a blend. Also, the absence from the theory of effects arising from contour-length fluctuations may be questioned. These effects on diffusion are thought likely to be smaller than on bulk properties such as relaxation and viscosity, but this matter still awaits both experimental and theoretical explication. The present results suggest that ignoring contour length fluctuations has at most minor effects on the present cases. That this interpretive scheme is not applicable merely to the alkane−PE system is attested to by recent work in polybutadiene blends,[27] in which similar, but less quantitative, conclusions were drawn.

C. Alkane−PE Blends. Inspection of the generalized constraint release algorithm suggests that its effects must gradually vanish as M_1 and M_2 fall below M_c^0. Indeed, reanalyzing the alkane blend data of ref 16 (*n*-dodecane/*n*-hexatriacontane) shows theoretical traces indistinguishable from those without the reptation and constraint release terms.

Of more critical interest are cases in which an unentangled alkane is blended with a polyethylene with $M > M_c^0$. The composition dependence of both D_1 and, especially, D_2 should reveal the manner in which the initially entangled behavior of the heavier species returns to an unentangled state as light component is added. In previous work[16] using a blend of *n*-dodecane with a 13.9 kDa PE, application of eqs 6 and 7 was found to reproduce the measured diffusion rates satisfactorily across the full concentration range.

Figure 5 shows data and theories for present work on a blend of *n*-pentacontane and 33 kDa PE. Once again, the original constraint release formula coupled with entanglement dilution is found to be satisfactory. However, replacement of this

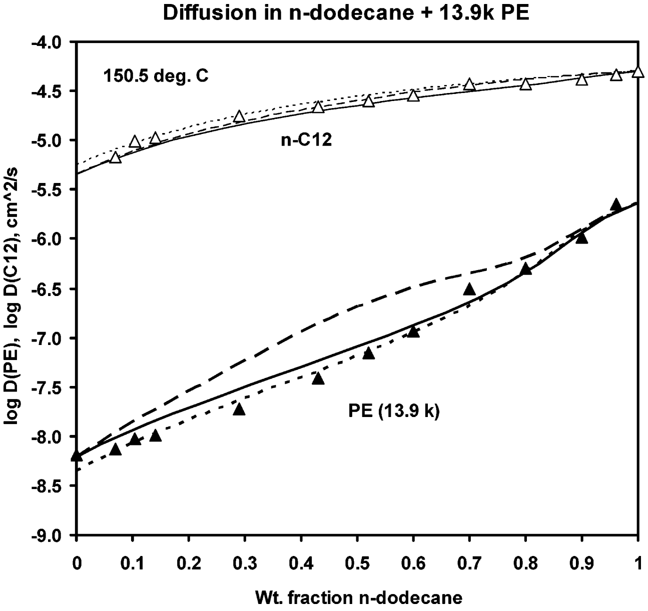

Figure 6. Concentration dependence of both ingredients in a blend of *n*-dodecane with 13.9 kDa PE (data taken from ref 16). Lines describe theories as given in caption to Figure 5.

formulation with the generalized constraint release formulation, eqs 8 and 9, is nearly indistinguishable in form and hence in the quality of agreement with the data. But the agreement is destroyed when entanglement dilution is invoked in addition to generalized constraint release.

Figure 6 reproduces data from the previous work.[16] The reanalysis has very similar results, but the disagreement with the data from invoking both entanglement dilution and generalized constraint release is less pronounced as a consequence of the smaller M_1 and M_2. Indeed, a similar reanalysis of data for blends of *n*-decane with a 6.2 kDa PE (not shown here[16]) shows an even smaller disagreement, and the effects of constraint release on *n*-alkane blends (*n*-dodecane/*n*-hexacontane; not shown here[16]) are nearly absent; hence, any distinction between formulations vanishes as well.

The success and operational equivalence of entanglement dilution and the more generalized constraint release, coupled with the failure of an approach invoking their combination, lead to the conclusion that there is an interpretive choice: as homologous diluent is added, one may regard entanglements either as increasingly widely spaced or else as maintaining their original spacing but increasingly transient and irrelevant on the slower time scale of segmental motions.

The choice is, thus, between a spatial and a temporal view of entanglement constraints. It is unlikely that diffusion experiments alone will be able to decide which of these approaches has more merit. It would, of course, be difficult to abandon the spatial view for originally entangled polymer chains diluted by, and perhaps dissolved in, small-molecule solvents, but the situation in homologous blends seems less clear. It may be suggested that preference should be given to the temporal view on grounds of consistency, perhaps esthetics: only generalized constraint release is fully consistent with the already successful approach[25] of eq 4, postulating a seamless and smooth transition between unentangled and fully entangled diffusion. In that approach, use of any theoretical components sharply separated at $M = M_c^0$ (e.g., eq 7) would be inappropriate.

V. Summary and Conclusions

The results and conclusions of this work may be summarized as follows:

(1) We augmented our previous PGSE diffusion measurements in liquid *n*-alkanes by measuring 12 PE liquid melts in the range $0.5M_c < M < 20M_c$ and binary blends of a 33 kDa PE with *n*-alkane C_{50} and two other PE species (1.8 and 6.7 kDa), over the full concentration range.

(2) We extended our earlier model of the diffusion of melts, and of both components in blends, which invokes using thermal activation, monomeric friction, Cohen−Turnbull free volume concepts with a Bueche chain-end free volume term based on correct density information, and the model of Pearson et al. making a smooth transition to entangled behavior, by including a more general approach to the effects of constraint release.

(3) The extension of the constraint-release concept accounted for the variation of the effective host molecular weight over the full concentration range in entangled blends, based on our recent work with polybutadiene blends. Using this enhanced theoretical synthesis, we semiquantitatively reproduced all our melt and blend data. Possible contour length fluctuation effects were not observed or included. Of course, detailed quantitative agreement with data cannot reasonably be expected of the theory in its current state, not because its parameters are at fault but because certain underlying assumptions and the form incorporating these are sure to be oversimplified.

(4) We found that in our *n*-alkane−PE blends acceleration of temporal constraint release through the addition of the lighter component is indistinguishable from spatial entanglement dilution but that the temporal approach, generalized constraint release, may be preferable from a conceptual standpoint.

Work currently in progress in this laboratory concentrates on systems for which dynamic Monte Carlo simulations, compared with equivalent experiment, permit further insight into the segmental kinetics in the vicinity of the entanglement transition. Work on polypropylenes of various stereochemical compositions is nearing completion.[45]

Acknowledgment. This work is in part distilled from the MS Thesis of Nazan Dirama (Physics, University of Akron, 2004, unpublished). Mass spectrometric characterization of two specimens was provided by Dr. K. Wollyung and Prof. C. Wesdemiotis; ^{1}H and ^{13}C NMR analysis was performed by Dr. D. Savant and Prof. P. Rinaldi. The authors thank Prof. Shi-Qing Wang and Dr. Shanfeng Wang for several enlightening discussions about segmental dynamics of entangled blends and Dr. Numan Waheed for his critical reading of the manuscript and several helpful suggestions. We gratefully acknowledge support of this work by NSF under Grants DMR 00 98321 and DMR 04 55117.

References and Notes

(1) This subject is extensively reviewed in: McLeish, T. C. B. *Adv. Phys.* **2002**, *51*, 1379.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 68.
(3) Lodge, T. P.; Rotstein, N. A.; Prager, S. *Adv. Chem. Phys.* **1990**, *LXXIX*, 2.
(4) Lodge, T. P. *Phys. Rev. Lett.* **1999**, *83*, 3218.
(5) Green, P. F.; Mills, P. J.; Palmstrom, C. J.; Meyer, J. W.; Kramer, E. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(6) Frischknecht, A. L.; Milner, S. T. *Macromolecules* **2000**, *33*, 5273.
(7) Tao, H.; Lodge, T. P.; von Meerwall, E. D. *Macromolecules* **2000**, *33*, 1747.
(8) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(9) Lin, H.; Mattice, W. L.; von Meerwall, E. D. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2556.
(10) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572. *Macromolecules* **1976**, *9*, 587, 594.
(11) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818; *75*, 38.
(12) Wang, S. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1589.

(13) Bueche, F.; Kelley, F. N. *J. Polym. Sci.* **1960**, *45*, 267.

(14) von Meerwall, E.; Beckman, S.; Jang, J.; Mattice, W. L. *J. Chem. Phys.* **1998**, *108*, 4299.

(15) von Meerwall, E.; Grigsby, J.; Tomich, D.; Van Antwerp, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1037.

(16) von Meerwall, E.; Feick, E. J.; Ozisik, R.; Mattice, W. L. *J. Chem. Phys.* **1999**, *111*, 750.

(17) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.

(18) Viovy, J. L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 3587.

(19) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.

(20) Fleischer, G. *Colloid Polym. Sci.* **1986**, *264*, 1.

(21) Pearson, D. S.; Ver Strate, G.; von Meerwall, E.; Schilling, F. C. *Macromolecules* **1987**, *20*, 1133.

(22) Fleischer, G.; Appel, M. *Macromolecules* **1995**, *28*, 7281.

(23) Fleischer, G. *Colloid Polym. Sci.* **1987**, *165*, 89.

(24) Appel, M.; Fleischer, G. *Macromolecules* **1993**, *26*, 5520.

(25) Pearson, D. S.; Fetters, L. J.; Graessley, W. W.; Strate, G. V.; von Meerwall, E. *Macromolecules* **1994**, *27*, 711.

(26) Wang, S.; von Meerwall, E.; Wang, S.-Q.; Halasa, A.; Hsu, W. L.; Zhu, J. P.; Quirk, R. P. *Macromolecules* **2004**, *37*, 1641.

(27) von Meerwall, E.; Wang, S.; Wang, S.-Q. *Polym. Prepr.* **2003**, *44*, 287.

(28) Harmandaris, V. A.; Doxastakis, M.; Mavrantzas, V. G.; Theodorou, D. N. *J. Chem. Phys.* **2002**, *116*, 436.

(29) Harmandaris, V. A.; Angelopoulou, D.; Mavrantzas, V. G.; Theodorou, D. N. *J. Chem. Phys.* **2002**, *116*, 7656.

(30) Harmandaris, V. A.; Mavrantzas, V. G.; Theodorou, D. N.; Kröger, M.; Ramirez, J.; Öttinger, H. C.; Vlassopoulos, D. *Macromolecules* **2003**, *36*, 1376.

(31) Rapold, R. F.; Mattice, W. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2435.

(32) Doruker, P.; Mattice, W. L. *Macromolecules* **1998**, *31*, 1418.

(33) Cho, J.; Mattice, W. L. *Macromolecules* **1997**, *30*, 637.

(34) Dirama, N.; Mattice, W. L.; von Meerwall, E. *Bull. Am. Phys. Soc.* **2003**, *48*, 7.

(35) Dirama, N.; Mattice, W. L.; von Meerwall, E. *Bull. Am. Phys. Soc.* **2004**, *49*, 960.

(36) Evolving and current practices of this laboratory are described in: Iannacchione, G.; von Meerwall, E. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1991**, *29*, 659. Pacanovsky, J.; Kelley, F. N.; von Meerwall, E. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1994**, *32*, 1339. Oh, J. S.; Isayev, A. I.; von Meerwall, E. *Rubber Chem. Technol.* **2004**, *77*, 745.

(37) von Meerwall, E. D.; Ferguson, R. D. *Comput. Phys. Commun.* **1981**, *21*, 421.

(38) von Meerwall, E.; Palunas, P. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1439.

(39) Freed, D. E.; Burcaw, L.; Song, Y.-Q. *Phys. Rev. Lett.* **2005**, *94*, 067602.

(40) von Meerwall, E.; Ferguson, R. D. *J. Appl. Polym. Sci.* **1979**, *23*, 3657.

(41) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1967**, *5*, 261.

(42) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1668.

(43) Tead, S. F.; Kramer, E. J. *Macromolecules* **1988**, *21*, 1513.

(44) von Meerwall, E. D.; Lin, H.; Mattice, W. L. *Macromolecules* **2007**, *40*, 2002.

(45) Waheed, N.; Mattice, W. L.; von Meerwall, E. *Macromolecules* **2007**, *40*, 1504.

MA070342Q