detailed investigation of this matter will be published in a full account.

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References and Notes

(1) For a definition of ladder polymers, see: Overberger, C. G.; Moore, J. A. *Adv. Polym. Sci.* **1970**, *7*, 113.

(2) Blatter, K.; Schlüter, A.-D.; Wegner, G. *J. Org. Chem.* **1989**, *54*, 2396. Vogel, T.; Blatter, K.; Schlüter, A.-D. *Makromol. Chem., Rapid Commun.*, in press.

(3) Blatter, K.; Schlüter, A.-D. *Chem. Ber.* **1989**, *122*, 1351.

(4) For the decreasing stability of more and more extended π-systems, see: Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.

(5) Majunsz, J.; Catala, J. M.; Lenz, R. W. *Eur. Polym. J.* **1983**, *19*, 1043. Heitz, W. *Chem.-Ztg.* **1986**, *110*, 385. Ballauff, M.; Schmidt, G. F. *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 163. Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1054, 1060. Opitz, K.; Schlüter, A.-D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 456.

(6) For the nomenclature of angular annulated polycyclic ring systems, see: Balaban, A. T.; Harary, F. *Tetrahedron* **1968**, *24*, 2505. Balaban, A. T. *Pure Appl. Chem.* **1982**, *54*, 1075.

(7) The rational name of polymer **4** is poly[1,7,11,16-tetrahexyl-9,9a,10,12,13,14,15,17,17a,18-decahydro-9,18-dioxo-10,17:12,15-diepoxyphenanthro[1,2-*a*]pentacene-13,14:3,4-tetrayl-3,4-dicarbonyl].

(8) A suspension of **5** (1.0 mmol; **a**, 1.15 g; **b**, 1.32 g) and **2** (1.0 mmol; **a**, 0.55 g; **b**, 0.73 g) in 10 mL of tetralin is heated under nitrogen to 180 °C until the evolution of carbon monoxide ceases (10 min). Then the solvent is removed in vacuo, the residue is dissolved in chloroform (**a**, 300 mL; **b**, 100 mL), and polymer **4** is precipitated from this solution with methanol. After a second dissolution/precipitation cycle pure **4** (**a**, 0.55 g (63%); **b**, 0.95 g (78%)) is obtained as slightly yellow powder. The analytical and spectroscopical data are given for polymer **4b** only. IR: ν 1680 (s), 1645 (m) cm^{-1}; UV (chloroform): λ_{max} (ϵ) = 320 (40700), 390 (7900). ^1H NMR (300 MHz, CD_2Cl_2; all lines are very broad and unstructured): δ 0.4–2.3 (92 H), 2.4–3.9 (12 H), 5.7–6.5 (4 H), 7.6–8.5 (6 H). ^{13}C NMR (75 MHz, $CDCl_3$): see Figure 1. Elem anal. Calcd for $(C_{84}H_{114}O_6)_n$ (MW 1219.8): C, 82.71; H, 9.42; O, 7.87. Found: C, 81.26; H, 8.87; O, 7.59.

(9) TOSS pulse sequence; spinning frequency 2.955 kHz; neat; 20 °C; standard, TMS external.

(10) From the ^{13}C NMR spectrum of **3b**, it cannot be deduced whether all possible isomers are formed. The existence of a complex mixture of isomers certainly helps the objective to obtain soluble material.

(11) The incoming monomer **2** has two choices of orientation (cisoid/transoid) relative to the growing chain, if all isomers caused by the stereochemistry of the epoxy bridges are neglected.

(12) From a VPO measurement (toluene, room temperature) a lower limit for $\bar{P}_n$ is obtained: $\bar{M}_n$ = 8050 ($\bar{P}_n$ = 7).

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Dynamic Behavior in Ternary Homopolymer Solutions Using Dynamic Light Scattering

A recent communication[1] described dynamic light scattering (DLS) experiments on the homopolymeric polyisobutylene system PIB_1/PIB_2/chloroform, in which one polymer was present at semidilute concentration. The purpose was to explore the consequences of the recent thermodynamic theory of Benmouna et al.[2–4] for diffusion in ternary polymer solutions. Their result follows a line of development from the earlier studies of Phillies[5,6] and subsequently Pusey et al.[7] on dilute solutions of hard spheres of different sizes who had also demonstrated the possibility of simultaneously isolating the collective diffusion coefficient and the self-diffusion coefficient, although different arguments were used.

It was shown that if the respective diffusion coefficients differ sufficiently, two relaxation processes, arising from the modulation of the signal for the one polymer due to the presence of the second, should be observable. Benmouna et al. found that one obtains the collective diffusion coefficient (D_c) of the matrix (semidilute) polymer on the one hand and the interdiffusion coefficient (D_I) of the other and gave explicit expressions for these quantities as a function of concentration. It is important that by using a trace amount of the probe chain its self-diffusion coefficient may be measured. The following experiments reveal the potential of this approach, which forms a useful complement to existing techniques for determining polymer self-diffusion coefficients in semidilute solutions, viz., pulsed-field-gradient NMR (PFG NMR) and forced Rayleigh scattering (FRS).

We have used a broad-band autocorrelator (an ALV multibit, multi-τ, model employing 23 simultaneous sampling times and 191 exponentially spaced channels) together with a newly developed method for Laplace inversion to give the decay time spectrum covering wide spans in delay time, typically 6–8 decades. It was found possible to determine the self-diffusion coefficient for the trace component with good precision for a wide range of relative molecular weights of probe and matrix chains when using a concentration of the probe chain of less than 1% w/v since in this concentration range D_{probe} has a negligible dependence on its own concentration.[1] There will, of course, always be a (in fact, narrow) range of relative molecular weight where the components cannot be separated owing to the noise inherent in the data.

We have used a new constrained regularization calculation REPES[8] to obtain the decay time distributions. The algorithm differs from CONTIN[9] in that the program directly minimizes the sum of the squared differences between the experimental and calculated $g^{(2)}(t)$ function using nonlinear programming. We selected the a priori chosen parameter P ("probability to reject") = 0.5. In each solution the moments of the peaks are given in the output, yielding the relative amplitude and frequency of each resolved component. The distributions were observed to be closely similar to those obtained using CONTIN with a similar degree of smoothing and the maximum entropy method, MAXENT.[10,11]

Examples of the decay time distributions have been given in ref 1. Peak assignments were confirmed[1] using PFG NMR to independently determine the probe and matrix self-diffusion coefficients in the binary systems.

In the DLS experiments, two extreme cases were examined and are described below:

(1) the self-diffusion of large ($M = 4.9 \times 10^6$) probe chains in semidilute solutions of low MW polymers as a function of the concentration of the latter;

(2) the self-diffusion of small chains in semidilute solutions of the high MW matrix chains with the added criterion that the radius of gyration of the probe exceed the correlation length of the matrix polymer in the semidilute range.

In the experiments under (1), diffusion was approximately described by the Stokes–Einstein (S–E) equation; i.e., the product $D\eta$ was almost independent of the con-

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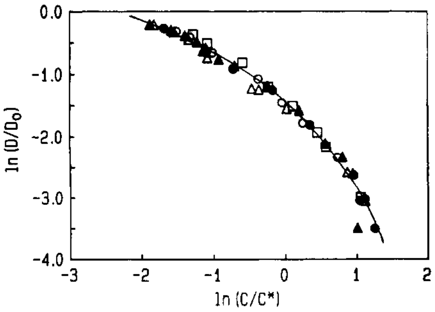

Figure 1. Logarithmic diagram (natural logarithms) of D/D_0 versus the matrix concentration reduced by the overlap concentration C^*. The data are for the probe $M = 4.9 \times 10^6$ in various matrix molecular weights: 8.04×10^4 (△), 1.82×10^5 (▲), 2.47×10^5 (●), 6.1×10^5 (○), 1.1×10^6 (□).

centration (C) of the low MW matrix polymer over wide ranges of C, where η is the bulk viscosity of the solutions. Furthermore, a log–log plot of D/D_0 versus C for the high MW probe chain was found to superimpose on the same plot for hard spheres (large stearic acid coated SiO_2 spheres) diffusing in the same polymer matrix.[1] Also, a master curve was found for diffusion of the probe in a wide range of molecular weights of the matrix when its reduced concentration (C/C^*) is used, and this is illustrated in Figure 1.

In experiments under (2), on the other hand, $D\eta$ increased strongly with concentration above the overlap concentration for the high MW matrix (C^* was almost identical with the critical entanglement concentration C_E). This behavior has been interpreted by Martin[12] as demonstrating that a different mechanism (reptation) is valid when the probe is smaller than the matrix chain. This conclusion would at first sight appear to be confirmed since the present data also fit reasonably well with the predictions of scaling theory[13] for self-diffusion in semidilute solutions; i.e., over a limited range of C, we find that the data follow the good-solvent scaling equation

$$D_s \sim C^{-1.75}M^{-2} \qquad (1)$$

where C is the matrix concentration and M is the probe MW.[1]

The measurements were extended to higher concentrations than those under (1) to examine trends in the exponents. At the highest concentrations it was observed that the exponent may increase from −1.75 toward a limiting slope of −3 as earlier suggested.[14] Above C^*, the MW dependence of D_s approximates −2. That the predicted exponents are found means that the measurements indeed typify the semidilute regime for the matrix polymer at the higher concentrations. On the above evidence, the results would appear to support current theory and this broadly agrees with the findings of other groups using, for example, FRS[14] and PFG NMR.[15,16]

The influence of the matrix MW is pronounced. When the matrix concentration is multiplied by its MW (which is equivalent to normalizing with the entanglement concentration), the data superimpose as shown in Figure 2 and correspond to $D_{\mathrm{probe}} \sim M_{\mathrm{matrix}}^{-1}$. This is contrary to reptation theory, which is predicated on independence of matrix MW. These observations mean, on the one hand, that we are in a concentration region where the exponents predicted by scaling for self-diffusion are found but, on the other, a strong dependence on matrix MW is noted. This is instead in line with the conclusions of Skolnick et al. for diffusion in congested systems. Skolnick et al.[18] and Pakula and Geyler[19] have described comprehensive simulation experiments on congested polymer systems. They were able to verify the experimentally observed $D_s \sim M^{-2}$ relationship as well as that between the viscosity and MW ($\eta \sim M^{3.4}$) but were not able to find any evidence for the "tube", which is the fundamental postulate of the reptation model. The arguments were recently extended to the homogeneous melt and a phenomenological derivation of the $D_s \sim M^{-2}$ relationship was given.[18b] Extension to bidisperse melts led to the prediction: $D_{\mathrm{probe}} \sim M_{\mathrm{matrix}}^{-1}$.

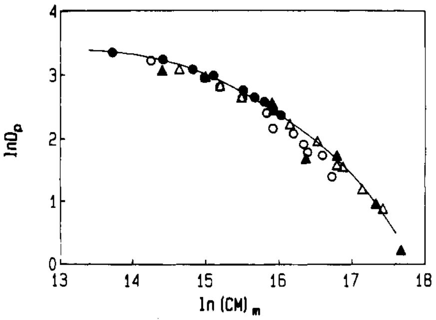

Figure 2. Plots of ln (D/D_0) versus ln (CM) for self-diffusion of PIB probe ($M = 2.47 \times 10^5$) in matrix chains of MW: 2.47×10^5 (●) (NMR data); 1.1×10^6 (○); 1.9×10^6 (△); 4.9×10^6 (▲), where C and M refer to the concentration and molecular weight of the matrix chains.

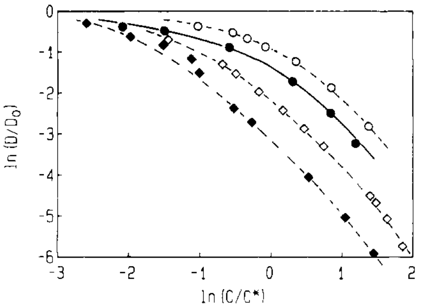

Figure 3. Logarithmic plots of (D/D_0) versus (C/C^*) for PIB: 1.82×10^5 (○); 2.47×10^5 (●); 6.1×10^5 (◇); and 8.56×10^5 (◆) (probes) in PIB 4.9×10^6 (matrix). The continuous line corresponds to the universal curve of Figure 1 and represents Stokes–Einstein behavior.

The above conclusions are reinforced by the data shown in Figure 3 depicting results using various low MW probes in a fixed matrix. Note that the continuous line is taken from the universal curve in Figure 1 for a large probe chain in various low MW matrix solutions and which typifies systems showing S–E behavior; i.e., $D\eta$ is approximately independent of C.[1] At a given concentration, D_{probe} is of the same magnitude as for S–E diffusion although may be either greater or smaller, depending on the relative size of the probe chain and the correlation length of the matrix. There is no indication that different self-diffusion mechanisms operate for probe chains much greater or much smaller than those constituting the matrix. The continuous line, which is a common curve for the data of 4.9×10^6 in 2.47×10^5 as matrix as well as for 2.47×10^5 in 4.9×10^6 as matrix, emphasizes this point.

Figure 4 shows the diffusion data in Figure 3 multiplied by M^2. In the semidilute range, the curves coincide, confirming the M^2 dependence above C^*. A line of slope −1.75 has also been included for comparison, although it is clear that over the whole concentration range a smooth curve would adequately represent the data.

The above data fall nicely in line with the expectations for self-diffusion in congested systems without resort to the sophisticated reptation model. (This is not to say, of course, that in other concentration or MW ranges or in the melt reptation does not occur.) It may be argued that, at even higher concentrations, where the chains become more

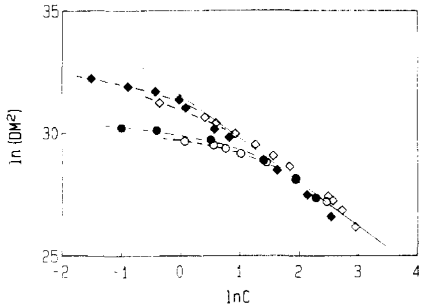

Figure 4. Data from Figure 3 logarithmically plotted as DM^2 (probe) versus concentration of the matrix (4.9×10^6). The line has been given a slope of −1.75 for comparison purposes.

entangled, reptation will be valid. Thus, Lodge and Wheeler[20] argue that reptation will prevail only at concentrations where the probe chain has become well-entangled with those of the matrix.

There has been an increasing discussion concerning the validity of the reptation model in polymer solutions. Phillies[17] was the first to present a large body of experimental self-diffusion data in a unified manner using the stretched exponential form

$$D_s \sim D_s^\circ \exp(-\alpha C^\nu) \qquad (2)$$

where D_s° is the infinite dilution value of D_s and α and ν are scaling parameters.

It may be noted that the present data sets only lie on a common line if the reduced concentration (C/C^*) is used in eq 2 and the exponent is then $\nu = 0.8$.

Subsequently, an alternative mechanism for diffusion in congested systems was presented by Phillies[17] on the basis of hydrodynamic arguments without resorting to reptation or descriptions of hydrodynamic screening.

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References and Notes

(1) Brown, W.; Zhou, P. *Macromolecules*, in press.
(2) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, Z. *Macromolecules* **1987**, *20*, 1107.
(3) Borsali, R.; Duval, M.; Benoit, H.; Benmouna, M. *Macromolecules* **1987**, *20*, 1112.
(4) Borsali, R.; Duval, M.; Benmouna, M. *Macromolecules* **1989**, *22*, 816.
(5) Phillies, G. D. J. *J. Chem. Phys.* **1974**, *60*, 983.
(6) Phillies, G. D. J. *J. Chem. Phys.* **1983**, *79*, 2325.
(7) Pusey, P. N.; Fijnaut, H. M.; Vrij, A. *J. Chem. Phys.* **1982**, *77*, 4270.
(8) Jakeš, J., to be submitted for publication.
(9) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(10) Livesey, A. K.; Licinio, P.; Delaye, M. *J. Chem. Phys.* **1986**, *84*, 5102.
(11) Licinio, P.; Delaye, M.; Livesey, A. K.; Lêger, L. *J. Phys. (Paris)* **1987**, *48*, 1217.
(12) Martin, J. E. *Macromolecules* **1986**, *19*, 922.
(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(14) (a) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782. (b) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.
(15) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431; **1981**, *14*, 1334.
(16) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260.
(17) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367; **1987**, *20*, 558.
(18) (a) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 1567; **1987**, *86*, 7164; **1987**, *86*, 7174. (b) Skolnick, J.; Yaris, R.; Kolinski, A. *J. Chem. Phys.* **1988**, *88*, 1407. (c) Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1988**, *88*, 1418.
(19) Pakula, T.; Geyler, S. *Macromolecules* **1987**, *20*, 2909.
(20) Lodge, T. P.; Wheeler, L. M. *Macromolecules* **1986**, *19*, 2983.

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