Self-entanglement effects on the Rouse dynamics of a polymer

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The dynamics of flexible chains in good solvents have become relatively well understood for all cases where the monomer–solvent interaction is dominant compared either with the friction between different chains or with internal barrier effects inside one chain: hydrodynamic interactions play an essential role for long chains and excluded volume effects renormalize the elastic restoring forces[1]. The fact that the chain cannot intersect itself ('topological interaction') is a more subtle effect, which is important for polymers in theta solvents[2], concentrated polymer solutions[1] and polymer melts[1,3–6].

In this communication we discuss the effect of topological interactions on a single chain in a theta solvent. To focus our attention only to this effect we neglect hydrodynamic[2] and van der Waals interactions[7]. (The latter only renormalize at the theta point some non-universal prefactors.) As a model we consider a single chain consisting of N rigid links of length $l=1$ freely jointed together in three dimensions. In order to simulate the effect of entanglements we use a 'dynamic kink-jump' method for Monte Carlo simulation[7] including an intersection prohibition[6] (i.e. segmental motions where chain intersections appear, are rejected). We are interested in the diffusion constant of the chain

$$D=\lim_{t\to\infty}\frac{g_{CG}(t)}{6t\,l^2},\quad g_{CG}(t)=\langle[\vec{R}_{CG}(t)-\vec{R}_{CG}(0)]^2\rangle \tag{1}$$

where $\vec{R}_{CG}(t)=\frac{1}{N+1}\sum_{i=1}^{N+1}\vec{r}_i(t)$ is the time-dependent centre of gravity, $\vec{r}_i(t)$ denotes the position of bead i, and in the time-dependent mean square displacement of a monomer

$$g_r(t)=\langle[(\vec{r}_n(0)-\vec{R}_{CG}(0))-(\vec{r}_n(t)-\vec{R}_{CG}(t))]^2\rangle \tag{2}$$

where $n\simeq N/2$ in order to avoid end effects. In the absence of topological interactions our model exhibits the Rouse dynamics [8,9] with $D_0=B_0/N$ and $g_r^0=l^2\sqrt{t/\tau_0}$ where $1/\tau_0=(12/\pi)B_0$ [9] and $g_r^0(t)\simeq N/4$ for times larger than the relaxation time of the chain which is of the order of N^2. $g_r^0(t)$ and $g_{CG}^0(t)$ are shown in *Figure 1* for $N=160$ as a typical example. The corresponding curves where topological interactions have been included, are denoted by $g_r(t)$ and $g_{CG}(t)$ respectively. Obviously entanglement effects do not change qualitatively the dynamics of a single free draining polymer. But the mobility B changes significantly. Estimates of D and τ are listed together with their standard deviations in *Table 1*. The slightly larger errors for τ_0 and related quantities at small N compared with the values at larger N reflect the fact that $g_r(t)$ and $g_r^0(t)$ exhibit $\sim\sqrt{t}$ the more pronounced the larger the relaxation time of the chain which is $\propto N^2$.

In agreement with previous calculations[8,9] $B_0=D_0N\propto 1/\tau_0$ are constant for $N\gg 1$ and $ND_0\tau_0=\pi/12$ which is close to our estimate. In contrast the interpretation of the N dependence of D and τ is not sufficiently conclusive as to be seen in *Table 1*. The estimates of D/D_0 are well fitted by $0.954/N^{0.05}$, but we do not think that this has a deep meaning and presumably results from finite size effects, so that $D/D_0\to$constant for $N\to\infty$. This statement is in contrast to some previous suggestions[2] where one expects a stronger effect under theta conditions than that reported above. These suggestions are mainly based on the assumption that the number of nearest neighbour contacts P in the coil, ($P\propto N^{1/2}$ under theta conditions) is proportional to the average number of entanglement

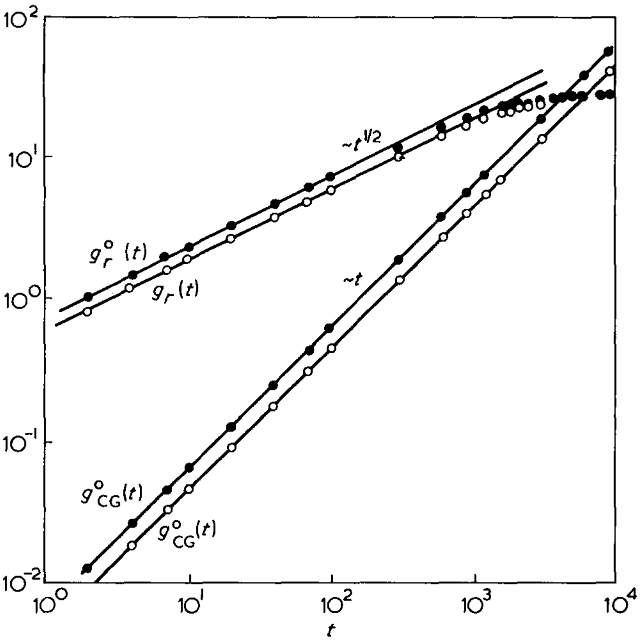

Figure 1 Log–log plot of the correlation functions $g_r(t)$, $g_r^0(t)$, $g_{CG}(t)$, $g_{CG}^0(t)$ for N = 160

Table 1 D and τ estimates and standard deviations

N	D_0N	$1/\tau_0$	$ND_0\tau_0$	D/D_0	τ_0/τ	$ND\tau$	N_e/N
20	0.158(1)	0.44(2)	0.36(2)	0.82(1)	0.77(3)	0.38(2)	0.120(1)
40	0.1645(9)	0.49(1)	0.336(9)	0.79(1)	0.72(3)	0.368(9)	0.152(1)
80	0.164(2)	0.570(8)	0.286(9)	0.77(1)	0.68(1)	0.324(9)	0.1806(5)
160	0.165(3)	0.587(6)	0.283(8)	0.74(1)	0.646(8)	0.324(8)	0.1998(3)

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points $N_e \propto P \propto N^{1/2}$ which should be responsible for topological restrictions (i.e. possible self-intersections of the chain). This is in contrast to our estimates which give $N_e/N \simeq 0.24 - \theta(1/N)$ (*Table 1*). The reason for this discrepancy is presumably: Using the definition for the total number of direct contacts (see equation (I.4) in ref. 2), which is the sum of over all probabilities of binary contact between two monomers of positions (n) and (m) along the chemical sequence, gives $P \propto \sum_{m=1}^{N} \sum_{n=1}^{m} |n-m|^{-3/2} \sim N$ in contrast to their own phenomenological estimate $P \propto N^{1/2}$ (see equation (I.3) in ref. 2).

In summary, although the number of effective entanglement points in theta solvents, is far larger than expected, the characteristic correlation functions $g_r(t)$ and $g_{CG}(t)$ do not change qualitatively compared to the free draining limit. The diffusion constant of the centre of gravity is reduced by about 25%.

However, it is not clear how far topological interactions dominate the dynamics of dilute polymer solution in theta solvent compared to hydrodynamic interactions. In polymer melts where hydrodynamics are usually assumed to be negligible, our results indicate that at least for times where $g_{CG}(t) < 1$ (i.e. reptation dynamics is negligible) the dynamics should be of a Rouse type with topological interactions[6].

References

1 de Gennes, P. G. *Macromolecules* 1976, **9**, 587, 594
2 Brochard, F. and de Gennes, P. G. *Macromolecules* 1977, **10**, 1157
3 Edwards, S. F. and Grant, J. M. V. *J. Phys.* 1973, **A6**, 1169, 1186
4 Doi, M. and Edwards, S. F. *Faraday Trans. II* 1978, **74**, 1789, 1818
5 de Gennes, *J. Chem. Phys.* 1980, **72**, 4756
6 Baumgärtner, A. and Binder, K. *J. Chem. Phys.* (in press)
7 Baumgärtner, A. *J. Chem. Phys.* 1980, **72**, 871
8 Rouse, P. E. *J. Chem. Phys.* 1953, **21**, 1272
9 de Gennes, P. G. *Physics* 1967, **3**, 37

A new and convenient fluorescence molecule for probing molecular motions in bulk polymers: 10, 10'-Diphenyl-bis-9-anthrylmethyloxide (Diphant)

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Fluorescence emission is a sensitive technique used to characterize the physical properties of molecular assemblies[1]. Non-conjugated bichromophores which can emit excimer and monomer (locally excited) fluorescence are used as probes: intramolecular excimer fluorescence formation requires conformational mobility of the linking chain, within the monomer lifetime, to allow the two chromophores to reach a binding distance[2]. Generally, the ratio of excimer to monomer fluorescence intensity (I_D/I_M) reflects the microscopic properties of the medium; inter alia bibenzylether[3] bisnaphthylmethylether[4] and bispyrenes[5] have recently been used to study the microviscosity of micelles or phospholipid membranes.

Excimer fluorescence of guest aromatic vinyl polymers dissolved at low concentration in a polymer host matrix have been investigated by Frank[6] in order to observe the relaxation process near the glass transition. The author shows that in a rigid medium, excimer sampling arises from an activated exciton migration to preformed excimer sites. As analysis of fluorescence spectra of polymers in a polymer matrix is complex, one way of simplifying the problem is to examine intramolecular excimer formation in a small molecule for which singlet exciton migration is not possible. The method of dispersing small molecules in a rigid medium has already been used to restrict the molecular motions and not as a means of investigating the effects of structure and morphology of the polymer on the rotational process of the probe.

The object of this work was to study the influence of the polymer matrix on the probe mobility by means of excimer fluorescence. Various reasons make Diphant a convenient probe and these are as follows:

A high quantum yield allows the use of Diphant in very small concentrations. Fluorescence quantum yields of Diphant in methylcyclohexane at 20°C are respectively $\Phi_M = 0.21$ and $\Phi_D = 0.34$ [7].

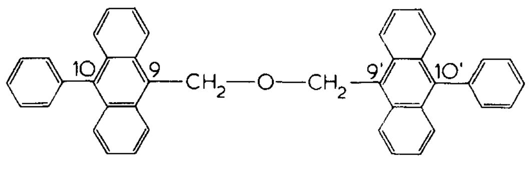
The excimer and monomer emission bands are well separated so that overlap between them is not important.

A good excimer stability allowing a study over a wide range of temperature.

A long wavelength of fluorescence excitation (365 nm) making possible the use of host polymers absorbing in the u.v.

In this communication, we report preliminary investigations concerning intramolecular excimer formation in Diphant dispersed in two elastomers, polyisoprene (PI) and polybutadiene (PB).

Experimental



Diphant (see formula) was prepared according to published procedure[7]; it is in the form of yellow crystals whose melting point is 203°–204°C. It is chemically stable

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