~0.25 arc s, in agreement with our result when all data from 1925 are used.

The Brown University Observatory is still used by the Skyscrapers, an organization of amateur astronomers, and its accurate position, scaled from the detailed US Geological Survey map of the area, has been provided by John Cardillo Jr. Jeannie Behnke discovered the unpublished reports of the lighthouses and docked Coast Guard cutters in the US Naval Observatory Archives.

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Diffusional behaviour of entangled star polymers

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The dynamic properties of concentrated solutions and melts of linear polymers are reasonably well understood in terms of the reptation concept, whereby molecules are constrained to curvilinear motion within 'tubes' formed by entanglements with their neighbours[1–3]. Understanding of dynamics of entangled nonlinear polymers, however, is still rather limited. Reptation in such cases is expected to be strongly suppressed, but there is little direct evidence for this, and conflicting models have been proposed[4–6]. We report here a critical study of the diffusion coefficient D of a series of model linear and three-arm star-branched polymers, diffusing in an entangled linear polymer melt matrix, designed to elucidate dynamic mechanisms for the entangled stars. Measuring D as a function of diffusant degree of polymerization N we find, for the linear molecules, $D \propto N^{-2}$, as expected for purely reptative motion[1,7–9]. For the case of moderately short stars, however, D falls considerably faster than an inverse square power law, and is well fitted by an exponential type relation $D \propto e^{-\alpha N}$. There is evidence that for the longest stars used in the present study it is the release of entanglements by reptation of the linear matrix molecules which dominates the dynamics. This is the first direct indication of such 'tube-renewal' effects in a system of entangled polymers[8].

The experimental technique and sample-preparation procedure have been described previously[9,10]; the approach involves monitoring, by IR microdensitometry, the diffusion broadening of an originally step-like concentration profile, of the deuterium labelled diffusant molecules, within the polymer matrix. The matrix used is a highly entangled linear polyethylene (HDPE1); the linear and three-arm star-branched polyethylene-like diffusant molecules were prepared by deuteration of the corresponding monodispersed 1,4-polybutadiene polymers[11]. Molecular characteristics are given in Table 1.

Figure 1 shows $D(N)$ as a function of the degree of polymerization N of diffusants, in an HDPE1 melt at 176 °C. For the linear polymer a best-fit power relation (solid line, a)

$$D(N) = D_0 N^{-1.95\pm0.1}$$

is indicated. This is in good agreement with the inverse square law ($D \propto N^{-2}$) expected for pure reptation, and also compares well with the results obtained previously[9] for deuterated polyethylene diffusing in the same conditions. For the three-arm star polymers the variation of D with N is initially considerably more rapid than a power law. A good (least squares) fit to the first five points (17 experiments) is obtained by the exponential relation

$$D(N) = D_s e^{-\alpha N} \quad (1)$$

(curve b, Fig. 1).

This exponential suppression of D is consistent with the mechanism proposed by de Gennes[4], whereby the reptation of the star-branched polymer entangled in a fixed network is hindered by the branching point. In order that translational diffusion of the star occurs, it is necessary that some retraction (rather than reptation) of an arm down its own 'tube' towards the centre monomer takes place; this leads to a relation of the type $D \sim F(N) e^{-\alpha' N}$, where $F(N)$ is a power function of N (typically N^{-2}). Such a power-exponential relation is also consistent with the data. The crucial point, however, is the essentially exponential decay of D with N for the stars, for $N \lesssim 1{,}500$.

For the longer stars ($N \gtrsim 1{,}500$) we note a strong deviation from the exponential relation (curve b, Fig. 1). This may be attributed to the fact that the linear melt matrix is not strictly

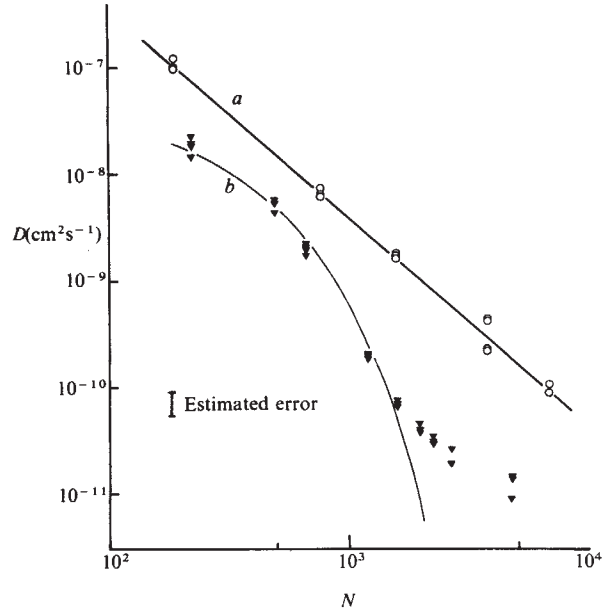

Fig. 1 The variation of D with degree of polymerization N for linear (○) and three-arm star-branched (▼) deuterated polybutadiene molecules diffusing in a linear polyethylene melt (HDPE1, $M_w = 1.6\times10^5$, $M_w/M_n \simeq 15$) at 176 ± 0.5 °C. Each point represents a separate experiment run over differing lengths of time (varying by a factor of up to ~4 within sets of points), and is the mean of ~10 independent concentration profile measurements[9]. Curve a is a regression analysis best-fit ($r^2 = 0.99$) to the data for the linear diffusants (15 experiments), $D = D_0 N^{-1.95\pm0.1}$, where $D_0 = (2.8\pm0.4)\times10^{-3}$ cm^2 s^{-1}. Curve b is the best exponential fit (regression analysis, $r^2 = 0.99$) to the data for the five shortest stars (17 experiments), $D = D_s e^{-\alpha N}$, where $D_s = (4\pm1)\times10^{-8}$ cm^2 s^{-1}, $\alpha = 4.2\times10^{-3}$.

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Table 1 Molecular characteristics of linear and three-arm star-branched polybutadiene (PBD) samples

	Sample	$(M_w/10^3)$	(M_w/M_n)	N
Linear	CDS-B-3	2.6	1.04	190
	LF-1	10.8	1.02	770
	LF-2	22	1.04	1,570
	LF-3	53	1.03	3,750
	LF-4	96	1.06	6,830
Three-arm star-branched	JK-8A	3.1	1.07	220
	JK-5A	6.8	1.07	490
	JK-6A	9.3	1.04	660
	WG-2A	16.8	1.04	1,200
	WG-1A	21.9	1.06	1,560
	JK-4A	27.6	1.04	1,960
	JK-3A	31.2	1.04	2,220
	JK-2A	37.2	1.05	2,650
	JK-1A	66.3	1.05	4,720

The molecular weights of the precursor PBD polymers (92% 1,4-PDB; 8% 1,2-PBD) were determined using osmometry and size-exclusion chromatography. The PBD samples, monomer structure $+CH_2-CH=CH-CH_2+$, were deuterated at high pressures[11] (to yield the polyethylene-like monomer structure $+CH_2-CHD-CHD-CH_2+$) and then used as the diffusant molecules in the present study. The N values given are the numbers of main-chain CH_2/CHD units in the diffusants. M_w and polydispersities for the stars are obtained from the corresponding values for the linear precursors; independent measurements on the stars indicated a degree of branching $f = 3.0 \pm 0.1$. Control measurements following deuteration showed essentially complete saturation of the PBD, and negligible degradation.

speaking a fixed network. When D for the stars becomes sufficiently low, the motion of the linear melt molecules themselves leads to a relaxation of entanglements about the star polymers; this results in a more rapid diffusive motion than the exponentially slow arm-retraction mechanism. Such 'constraint-relaxation' or 'tube-renewal' effects are a natural consequence of the movement of the linear melt molecules[8], and have been predicted[12], but not hitherto observed, for entangled systems where reptation is suppressed.

The present study shows that, for three-arm star-branched molecules diffusing in a highly entangled linear matrix, the diffusion coefficient initially decreases exponentially with star molecular weight. This provides direct support for the notion that reptation of such stars in a fixed network is suppressed, and suggests that translational diffusion (and hence the longest relaxations) must take place by retraction of the star-arms within their 'tubes' of entanglements. For sufficiently long star molecules diffusing in the linear melt matrix, the results indicate that such a retraction mechanism gives way to one dominated by constraint release, due to the motion of the matrix molecules themselves.

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Mixing basaltic and dacitic magmas by forced convection

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Although magma mixing is an old concept which has been applied to many magma types, recent petrographic studies have revived interest in the theory by suggesting that it may account for the origin of calk-alkaline magma[1–6] and mid-ocean ridge basalt[7–9]. There has been no previous experimental investigation into how two magmas with different properties can mix to form a homogeneous magma of andesitic composition or to produce textures such as observed in banded dacite. We present here the results of experiments demonstrating that basaltic and dacitic magmas can be easily mixed by forced convection to form both banded dacite and homogeneous andesite in less than a few hours.

An olivine tholeiite, 1921 lava of Kilauea[10] and a dacite, of Moriyoshi volcano, northern Japan[11], were powdered then sintered to prepare two rods of separate compositions. The sintered rods were fixed to the upper and the lower shafts and melted in an IR radiation image convergence furnace[12]. When the ends of both rods were melted (around 1,250 °C), both were connected and rotated in opposite directions so that the two melts were mixed by forced convection. The run products were investigated under a polarizing microscope and chemically analysed using an energy-dispersive type electron probe micro-analyser, based on the method of Fujimaki and Aoki[13]. A series of experiments were performed by changing the duration of the run, rotation rate and the positions of the two rods.

Figures 1 and 2 show photography and chemistry, respectively, of a series of products obtained with a constant rotation rate (48 r.p.m.) but different run durations. It is apparent that basaltic and dacitic magmas are easily mixed in <2 h to form: (1) an homogeneous magma of andesitic composition in the basaltic part and (2) a banded texture in the dacitic part. The texture and chemical composition formed by mixing were found to vary systematically as a function of run duration. Similar results were obtained when rotation rates were changed with a duration of the run kept constant. When the positions of the upper and lower rods were reversed, essentially similar results were obtained except for a reverse of the positions of homogeneous magma and banded texture.

Basaltic drops are trapped in the dacite melt to form streaks, whereas dacite drops are torn and rise into the basalt melt (Fig. 1). After 2 h, the melt in the basalt side becomes almost homogeneous, whereas in the dacite side, a banded texture develops, which has a similar appearance to naturally observed banded pumice[14].

No change in composition is noted after 5 min (Fig. 2*a*), but after 1 h (Fig. 2*b*) the composition near the interface between the two melts starts to change. After 2 h (Fig. 2*c*), the basalt has changed completely to an andesitic composition (SiO_2 = 56%) even near the unmelted part. The compositions of the drops trapped in the melts of the opposite sides show a more drastic change than does the composition of the bulks. The volume of dacite melt decreases whereas that of andesite melt increases as the run duration or rotation rate increases.

The observations can be summarized as follows: (1) the chemical composition of basalt changes significantly to andesite as mixing proceeds, whereas that of the dacite melt remains unchanged, (2) the gradient of compositional change away from the interface with the unmelted part is rather gentle on the

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