IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

A solution for the initial-decay-rate puzzle in dynamic light scattering of polymer solutions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys. A: Math. Gen. 24 L579

(http://iopscience.iop.org/0305-4470/24/11/002)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 01/06/2010 at 10:48

Please note that terms and conditions apply.

J. Phys. A: Math. Gen. 24 (1991) L579–L585. Printed in the UK

LETTER TO THE EDITOR

A solution for the initial-decay-rate puzzle in dynamic light scattering of polymer solutions

Yasuhiro Shiwa

Physics Laboratories, Kyushu Institute of Technology, Iizuka, Fukuoka-ken 820, Japan

Received 25 March 1991

Abstract. Previous renormalization-group theories for the initial decay rate of the dynamic structure factor for dilute polymer solutions are critically reviewed, and a possible explanation for the often claimed experimental disagreement with the theoretical predictions is presented.

With the advent of the renormalization group theory in polymer physics, significant progress has been made in recent years to study systematically the static as well as dynamic properties of dilute polymer solutions. In particular, static properties appear to be explained successfully (Oono 1985), though not thoroughly (Fujita 1988, Stockmayer 1988).

As for the dynamical behaviour, a problem of considerable experimental interest is the calculation of the initial decay rate (or the first cumulant) of the dynamic scattering factor. In fact, extensive comparison between theoretical predictions (Lee *et al* 1984, Baldwin 1986) and dynamic light scattering studies (Han and Ackasu 1981, Tsunashima *et al* 1983, 1987a, b, Nemoto *et al* 1984, Wiltzius and Cannell 1986, Bhatt *et al* 1989) have been performed. The prevailing consensus on the part of the experimental study is that the available data could not be interpreted on the basis of the renormalization group theoretical model.

If we study the existing literature carefully, however, we recognize that the reported discrepancies between the experimental data and the renormalization group theoretical prediction cannot be taken without reserve. The purpose of the present letter is to point out this fact and, in so doing, to set the stage for a more complete comparison between theory and experiment.

The initial decay rate is defined as

$$\Omega(k) = -\left[\frac{\mathrm{d}}{\mathrm{d}t}\ln S(k,t)\right]_{t=0} \qquad (1)$$

where $S(k, t)$ is the dynamic structure factor for coherent scattering by isolated linear chain molecules in dilute solutions;

$$S(k,t) = \iint \mathrm{d}\tau\,\mathrm{d}\sigma\langle\exp\{\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{c}(\tau,t)-\boldsymbol{c}(\sigma,0)]\}\rangle. \qquad (2)$$

Here $\boldsymbol{k}$ is the scattering vector, and $\boldsymbol{c}(\tau, t)$ is the position of the chain element, parametrized by the contour variable τ ($0 \leqslant \tau \leqslant N$), at time t.

0305-4470/91/110579+07$03.50 © 1991 IOP Publishing Ltd

The first task of renormalization group theoretical evaluation of the initial decay rate is to set up a model for polymer solution dynamics. Let us recall that the success of modern theories of critical dynamics (Hohenberg and Halperin 1977) stems from the realization that there exists a regime, intermediate between the fully microscopic and the fully macroscopic (hydrodynamic), where a kinetic equation such as the time-dependent Ginzburg–Landau (TDGL) equation is appropriate. We adhere to the same idea in setting up the model for the time evolution of the polymer chains and solvent.

It reads (Oono and Freed 1981, Shiwa 1987) in appropriate units (energy units being chosen such that $k_B T = 1$)

$$\frac{\partial \boldsymbol{c}(\tau, t)}{\partial t} = -\zeta^{-1}\frac{\delta H\{\boldsymbol{c}\}}{\delta \boldsymbol{c}(\tau, t)} + \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{v}(\boldsymbol{r}, t)\delta(\boldsymbol{r} - \boldsymbol{c}(\tau, t)) + \boldsymbol{f}_c(\tau, t) \tag{3}$$

$$\frac{\partial \boldsymbol{v}(\boldsymbol{r}, t)}{\partial t} = \mathbf{T}\cdot\left[\eta_e \nabla^2 \boldsymbol{v}(\boldsymbol{r}, t) - \int \mathrm{d}\tau \frac{\partial H\{\boldsymbol{c}\}}{\partial \boldsymbol{c}(\tau, t)}\delta(\boldsymbol{r} - \boldsymbol{c}(\tau, t)) + \boldsymbol{f}(\boldsymbol{r}, t)\right]. \tag{4}$$

The solvent velocity $\boldsymbol{v}(\boldsymbol{r}, t)$ is assumed to satisfy the incompressibility condition, $\nabla\cdot\boldsymbol{v} = 0$, which explains the appearance of the tensor operator, $\mathbf{T}$; it selects the transverse part of the vector field it is applied to. The parameter ζ denotes the friction coefficient per segment of the chain, and η_e is the solvent viscosity. The Gaussian stochastic noises, $\boldsymbol{f}_c$ and $\boldsymbol{f}$, are assumed to be governed by the autocorrelation functions

$$\langle \boldsymbol{f}_c(\tau, t)\boldsymbol{f}_c(\sigma, t')\rangle = \boldsymbol{I}2\zeta^{-1}\delta(\tau - \sigma)\delta(t - t') \tag{5}$$

$$\langle \boldsymbol{f}(\boldsymbol{r}, t)\boldsymbol{f}(\boldsymbol{r}', t')\rangle = -\boldsymbol{I}\nabla^2 2\eta_e \delta(\boldsymbol{r} - \boldsymbol{r}')\delta(t - t') \tag{6}$$

$\boldsymbol{I}$ being the unit tensor. The dynamical model so defined ensures that the system relaxes to an equilibrium state with the probability distribution $\propto \exp[-H\{\boldsymbol{c}\} - \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\, v^2]$. The free energy functional, $H\{\boldsymbol{c}\}$, associated with the polymer chain configuration $\{\boldsymbol{c}\}$ is chosen to be (Edwards 1965)

$$H\{\boldsymbol{c}\} = \frac{1}{2}\int \mathrm{d}\tau \left[\frac{\mathrm{d}\boldsymbol{c}(\tau)}{\mathrm{d}\tau}\right]^2 + \frac{u}{2}\int\int \mathrm{d}\tau\, \mathrm{d}\sigma\, \delta(\boldsymbol{c}(\tau) - \boldsymbol{c}(\sigma)). \tag{7}$$

Here u represents the strength of the repulsive excluded-volume interaction.

The coupled set of kinetic equations (3)–(6) can be solved for $\boldsymbol{c}(\tau, t)$ perturbatively, the expansion parameter being ζ/η_e. It turns out that, when treated by the renormalization-group technique, it is the expansion in terms of the variable $\varepsilon \equiv 4 - d$, where d is the spatial dimensionality. To order ε, we find (see e.g. Oono 1985) that the time evolution of the configuration of a chain is described by the so-called full-diffusion type of equation

$$\frac{\partial}{\partial t}\mathsf{P}\{c, t\} = \mathsf{L}\mathsf{P}\{c, t\} \tag{8}$$

where $\mathsf{P}\{c, t\}$ is the probability distribution function for the configuration $\{\boldsymbol{c}\}$ at time t. The evolution operator L is given by

$$\mathsf{L} = \int\int \mathrm{d}\tau\, \mathrm{d}\sigma \frac{\delta}{\delta \boldsymbol{c}(\tau)}\cdot \mathsf{D}(\tau, \sigma)\cdot\left[\frac{\delta}{\delta \boldsymbol{c}(\sigma)} + \frac{\delta H\{\boldsymbol{c}\}}{\delta \boldsymbol{c}(\sigma)}\right] \tag{9}$$

with

$$\mathsf{D}(\tau, \sigma) = \frac{1}{\zeta}\left[\delta(\tau - \sigma)\boldsymbol{I} + \frac{\zeta}{\eta_e}\boldsymbol{T}(\boldsymbol{c}(\tau) - \boldsymbol{c}(\sigma))\right] \tag{10}$$

where

$$T(\boldsymbol{r})=(2\pi)^{-d}\int \mathrm{d}^dk\,\frac{1}{k^2}\left(\boldsymbol{I}-\frac{\boldsymbol{kk}}{k^2}\right)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}). \tag{11}$$

At this juncture, we should emphasize that the parameter η_e which appears in our kinetic equation (4) (and accordingly in (10)) is the *local* solvent viscosity *in the neighbourhood of a polymer chain*, and not the *neat* solvent viscosity, say η_s; they can differ as stressed already by Oono and Kohmoto (1983). This may also be inferred easily from the experimental evidence (Morris *et al* 1989, and references cited therein) that the high-frequency limit of the in-phase component of solution viscosity, usually denoted by η'_∞, is not equal to the neat solvent value, η_s. In fact, in the kinetic level of description the bare Onsager coefficients such as η_e are assumed to be determined by the processes taking place on a very short time scale. Therefore, η_e itself depends on the microscopic details of the dynamical solvent–polymer interactions, and to find the relation between η_e and η_s is beyond the scope of our present TDGL model.

Now the renormalization group (ε-expansion) method enables one to obtain the renormalized initial-decay rate. To order ε, it reads

$$\hat{\Omega}(k)\equiv\frac{\eta_e\Omega(k)}{k_BTk^d}=(2\theta)^{-d/2}\frac{\theta}{\xi^*f(\theta)}\exp\left[\frac{u^*}{4\pi^2}\left(1+\frac{g(\theta)}{f(\theta)}\right)+\frac{3\xi^*}{8\pi^2}V(\theta)\right] \tag{12}$$

where we have resummed the energy units explicitly. The wavevector dependence is solely contained in the variable θ, which is closely related to the gyration radius, R_G, through

$$k^2R_G^2=\frac{d}{3}\theta\exp\left(\frac{u^*}{2\pi^2}I\right)\qquad I\equiv-4\left(\frac{31}{96}-\frac{\gamma-\ln 2}{8}\right) \tag{13}$$

where γ is the Euler's constant, $\gamma=0.5772\ldots$. Here u^* and ξ^* are fixed-point values associated with the coupling constants u and ζ/η_e, respectively; they are given by either

$$u^*=\tfrac{1}{2}\pi^2\varepsilon\qquad \xi^*=2\pi^2\varepsilon \tag{14}$$

or

$$u^*=0\qquad \xi=\tfrac{8}{3}\pi^2\varepsilon. \tag{15}$$

These fixed points represent the non-draining cases† in the self-avoiding limit (14) or in the Gaussian chain limit (15). The functions f, g and V in (12) are defined as follows:

$$f(x)=\frac{1}{x}-\frac{1}{x^2}+\frac{e^{-x}}{x^2} \tag{16}$$

$$\begin{aligned}g(x)=2\int_0^1\mathrm{d}t\,&\left\{\frac{e^{-x}}{x^2}A[x-xt(1-t)]+\left(\frac{1}{x}-\frac{1}{x^2}\right)A[-xt(1-t)]-\frac{1-e^{-xt(1-t)}}{x^2t(1-t)}\right\}\\&+\int_0^1\mathrm{d}t\left\{\frac{1}{x(1-t)}+\frac{e^{-xt(1-t)}-1}{x^2t(1-t)^2}\right\}+\frac{e^{-x}}{x}\left[1+A(x)\left(1-\frac{1}{x}\right)\right]\end{aligned} \tag{17}$$

where

$$A(z)\equiv\int_0^z\mathrm{d}t\,\frac{e^t-1}{t} \tag{18}$$

---

† In this connection it is worth remarking that the factor k^d on the left-hand side of equation (12) can be extracted only for these non-draining fixed points.

and

$$V(x)=-\frac{1}{2}\ln x+\frac{1}{4}-\frac{\gamma}{2}-\frac{1}{x}+\frac{1}{2x^2}+\frac{\mathrm{e}^{-x}}{2}\left[\frac{1}{x}-\frac{1}{x^2}-\int_0^\infty \mathrm{d}z\,\mathrm{e}^{-z}\ln\left(1+\frac{z}{x}\right)\right]. \tag{19}$$

As regards the above results, the following remarks are in order. Equations (12) and (13) are essentially the recapitulation of those given by Lee *et al* (1984) and Baldwin (1986). Regrettably, however, those previous calculations contained inadvertent errors. (It is unfortunate that a great number of quantitative comparisons of the published results with experiments have been performed with the errors uncorrected.) Firstly, due to a factor-of-two error in equation (4.10) of Lee *et al*, the value of $\hat{\Omega}(k)$, has been divided by 2 in writing the equation corresponding to (12). Secondly, in their ε-expansion calculation of $\Omega(k)$, Lee *et al* used the so-called cut-off method. Nevertheless, in writing down their final result as a function of kR_{G}, they utilized the expression for R_{G} that has been evaluated by Ohta *et al* (1982) with the so-called dimensional regularization method. It is known that the latter variant of the renormalization group procedure evokes some constant such as 2π in the unnormalized quantities, so that some care should be employed in handling them. The same criticism applies to the result of Baldwin, who evaluated $\Omega(k)$ by the dimensional regularization method while he used the expression for R_{G} calculated by Ohta and Nakanishi (1983) with the cut-off method. Proceeding with a consistent use of the cut-off method throughout the calculation will yield equations (12) and (13).

For references in comparison with experiments, we list the result for the Gaussian chain ($u^*=0$, $\xi^*=8\pi^2\varepsilon/3$) and for the swollen chain limit ($u^*=\pi^2\varepsilon/2$, $\xi^*=2\pi^2\varepsilon$) separately.

(i) Gaussian limit

$$\hat{\Omega}(k)=\frac{3\sqrt{2}}{32\pi^2}\frac{\mathrm{e}^{V(\theta)}}{\sqrt{\theta}f(\theta)} \tag{20}$$

with

$$\theta=k^2R_{\mathrm{G}}^2 \tag{21}$$

and

$$\hat{\Omega}(\infty)=\frac{3\sqrt{2}}{32\pi^2}\exp\left(\frac{1}{4}-\frac{\gamma}{2}\right)\simeq 0.012\,92. \tag{22}$$

(ii) Swollen limit

$$\hat{\Omega}(k)=\frac{\sqrt{2}}{8\pi^2\sqrt{\theta}f(\theta)}\exp\left[\frac{1}{8}\left(1+\frac{g(\theta)}{f(\theta)}\right)+\frac{3}{4}V(\theta)\right] \tag{23}$$

$$\theta=\exp(-I/4)k^2R_{\mathrm{G}}^2 \tag{24}$$

with

$$\hat{\Omega}(\infty)=\frac{\sqrt{2}}{8\pi^2}\exp\left(\frac{11}{16}-\frac{\gamma}{2}\right)\simeq 0.026\,69. \tag{25}$$

In the above we have set $d=3$† and $\varepsilon=1$ in equations (12) and (13).

---

† If one were to put $d=4-\varepsilon$ and ε-expand (12) and (13) naively, one could not obtain the relation $R_{\mathrm{H}}\propto R_{\mathrm{G}}$, where R_{H} is the hydrodynamic radius defined via $R_{\mathrm{H}}^{-1}\equiv\lim_{k\to 0}6\pi\eta_{\mathrm{c}}\Omega(k)/k_{\mathrm{B}}Tk^2$. One should not expand d in ε.

Now that the corrected and refined prediction has been made, there remains experimental assessment of the theoretical prediction. The theory predicts that $\Omega(k)$ should scale as k^3 at large scattering angle, $kR_G \gg 1$. Therefore quite frequently in the light-scattering literature, experimental data are presented by plotting a dimensionless initial-decay rate $\Gamma^*(k)$ against kR_G, where Γ^* is defined as

$$\Gamma^* = \frac{\eta_s \Omega(k)}{k_B T k^3}. \tag{26}$$

If we rewrite equation (26) as

$$\Gamma^*(k) = \lambda_0^2 \hat{\Omega}(k) \qquad \lambda_0^2 \equiv \eta_s/\eta_e \tag{27}$$

we immediately see that the reduced quantity $\Gamma^*(k)$ is not a universal quantity, in contrast to $\hat{\Omega}(k)$; as emphasized before in connection with our kinetic model, η_e (and hence λ_0^2) represents a variety of microscopic modifications of the solvent properties by the addition of polymer. Therefore, $\Gamma^*(k)$ is not a function only of the scaled wavevector kR_G. In particular, different polymer–solvent systems exhibit different values of the asymptote, $\Gamma^*(\infty)$, which can also differ from the universal asymptotic value, $\hat{\Omega}(\infty)$.

In conclusion, we have reanalysed the previous experimental data accumulated by Kurata's group (Tsunashima *et al* 1983, 1987a, b, Nemoto *et al* 1984) for polystyrenes and polyisoprenes in various solvents. The figures show the plot of the reduced decay rate $\hat{\Omega}(k)$ against kR_G in theta solvents (figure 1) and in good solvents (figure 2). As

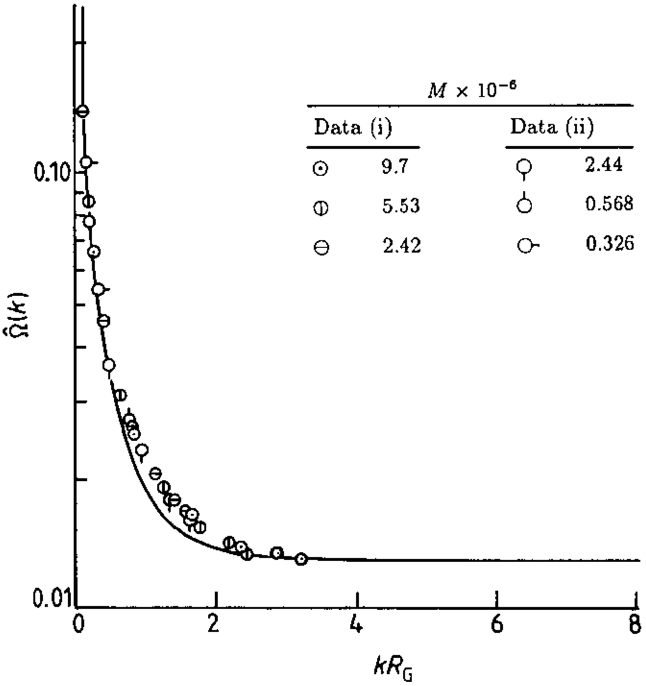

Figure 1. The reduced decay rate $\hat{\Omega}(k)$ as a function of the scaled wavevector kR_G in theta solvents. The full curve represents the renormalization group theoretical prediction in the Gaussian limit. Experimental data shown are due to Tsunashima *et al* (1983, 1987b) for (i) polystyrene in trans-decalin and (ii) polyisoprene in 1,4-dioxane, where M denotes the molecular weight. The unknown non-universal constant λ_0 has been adjusted.

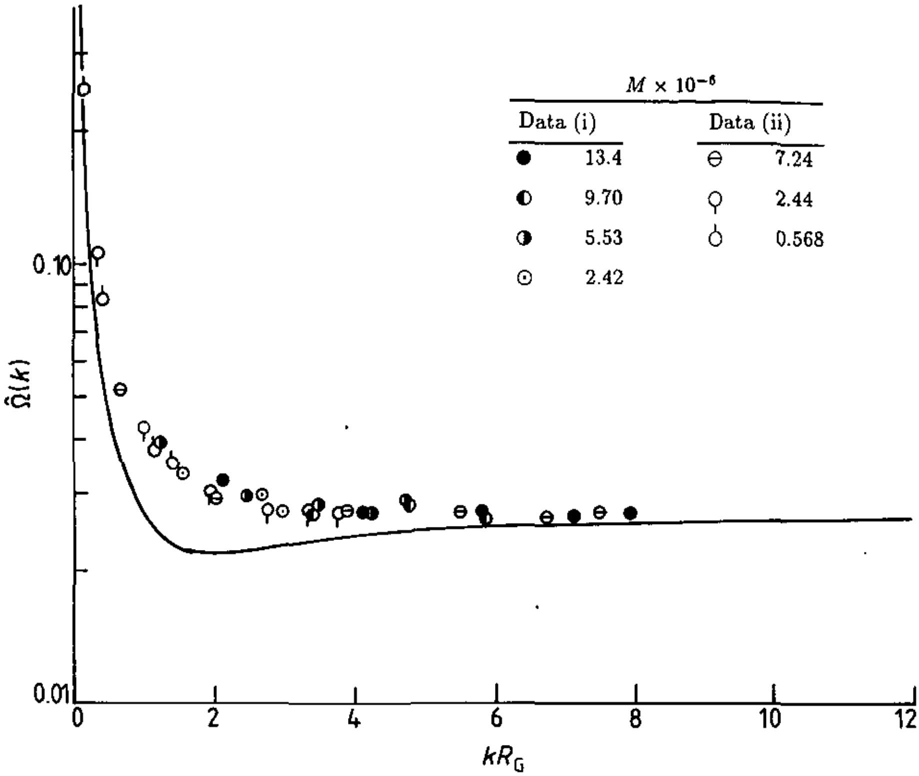

Figure 2. The reduced decay rate $\hat{\Omega}(k)$ against the scaled wavevector kR_G in good solvents. The full curve represents the renormalization group theoretical prediction in the self-avoiding limit. Experimental data shown are due to (i) Nemoto *et al* (1984) for polystyrene in benzene and (ii) Tsunashima *et al* (1987a) for polyisoprene in cyclohexane, where M denotes the molecular weight. The unknown non-universal constant λ_0 has been adjusted.

is seen clearly, different experimental data collapse to a single universal curve in each solvent case†. This finding, in turn, confirms the argument offered in the present letter. Also shown in figures are the theoretical curves calculated by equations (20)–(25). Apart from the non-monotonic behaviour of the theoretical curve for the good solvent system, which may be an artefact due to the lowest-order approximations in the ε-expansion, the theoretical results seem to account for the experimental observations rather well.

Our concern is confined to the initial decay rate in this letter. However, due attention should be paid to the non-universal parameter λ_0 in considering the other dynamic properties of polymer solutions. In fact, a detailed and renewed discussion of the draining effect on various transport properties has been presented elsewhere (Shiwa and Oono 1991) in the light of the presence of this dynamic parameter.

The author is grateful to Professors N Nemoto and Y Tsunashima for kindly providing him with their light-scattering data. He also thanks Professor Y Oono for carefully reading the manuscript and for helpful conversations.

---

† The λ_0-value in each solvent case is found to be as follows: figure 1, (i) 1.87, (ii) 1.93; figure 2, (i) 1.42, (ii) 1.51.

References

Baldwin P R 1986 *Phys. Rev.* A **34** 2234–47

Bhatt M, Jamieson A M and Petschek R G 1989 *Macromolecules* **22** 1374–80

Edwards S F 1965 *Proc. Phys. Soc.* **85** 613–24

Fujita H 1988 *Macromolecules* **27** 179–85

Han C C and Ackasu A Z 1981 *Macromolecules* **14** 1080–4

Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435–79

Lee A, Baldwin P R and Oono Y 1984 *Phys. Rev.* A **30** 968–78

Morris R L, Amelar S and Lodge T P 1988 *J. Chem. Phys.* **89** 6523–37

Nemoto N, Makita Y, Tsunashima Y and Kurata M 1984 *Macromolecules* **17** 425–30

Ohta T and Nakanishi A 1983 *J. Phys. A: Math. Gen.* **16** 4155–70

Ohta T, Oono Y and Freed K F 1982 *Phys. Rev.* A **25** 2801–11

Oono Y 1985 *Adv. Chem. Phys.* **61** 301–437

Oono Y and Freed K F 1981 *J. Chem. Phys.* **75** 1009–15

Oono Y and Kohmoto M 1983 *J. Chem. Phys.* **78** 520–8

Shiwa Y 1987 *Phys. Rev. Lett.* **58** 2102–5

Shiwa Y and Oono Y 1991 *Physica* A in press

Stockmayer W H 1988 *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems* ed M Nagasawa (Amsterdam: Elsevier) pp 1–19

Tsunashima Y, Hirata M, Nemoto N and Kurata M 1987a *Macromolecules* **20** 1992–9

Tsunashima Y, Hirata M, Nemoto N, Kajiwara K and Kurata M 1987b *Macromolecules* **20** 2862–6

Tsunashima Y, Nemoto N and Kurata M 1983 *Macromolecules* **16** 1184–8

Wiltzius P and Cannell D S 1986 *Phys. Rev. Lett.* **56** 61–4