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# The coupling model approach to the terminal relaxation

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Various predictions of the coupling model (CM) are known to be in agreement with observations of relaxation phenomena in polymers. However, as shown herein, when applied to the terminal relaxation, the model deviates from experimental data for monodisperse polymers; to wit the shape of the terminal relaxation spectrum does not conform to the CM equation. Nevertheless, the main premise of the model—that the dynamics transition from intermolecularly uncorrelated to entanglement-coupled relaxation at a temperature-independent crossover time—is supported by the data. Specifically, it is shown that the continuity condition of the model, relating the magnitudes of the non-cooperative and cooperative relaxation times, can be determined numerically to yield predictions for the molecular weight and temperature dependencies of the terminal viscosity in agreement with experiment. Previously the derivation of this continuity relation relied on the assumption of a specific form for the relaxation function's shape.

The discrepancy concerning the shape of the relaxation function is apparently due to alleviation of the entanglement constraints, with consequent time-dependence of the coupling parameter. Previously, the coupling parameter has been regarded as strictly constant; however, at times approaching and longer than the terminal relaxation time, mitigation of the lateral constraints causes a decrease in the degree of intermolecular cooperativity, and hence in the coupling strength. The deviation of experimental spectra from the model's prediction is likely due to the neglect of this fluctuation in the severity of entanglements. Published by Elsevier Science Ltd.

**(Keywords: coupling; terminal relaxation; polymer)**

## INTRODUCTION

Tobolsky and coworkers[1] used the empirical Kohlrausch equation[2]

$$G(t) = G_N^0 \exp\left[-\left(\frac{t}{\tau^*}\right)^{\beta}\right] \tag{1}$$

to describe the terminal relaxation behaviour of polymers. In this relation, also known as the stretched-exponential function, $G_N^0$ is the rubbery plateau modulus and $\tau^*$ is the relaxation time. Tobolsky found that the shape parameter $\beta$ varied with molecular weight, attributing it to molecular weight polydispersity[1].

While Tobolsky's approach was purely empirical, there is a theoretical description of relaxation, the coupling model (CM), which can lead to equation (1). According to the CM[3,4], which focuses on the consequences of intermolecular cooperativity, at short times the dynamics are unaffected by intermolecular constraints; however, at some temperature insensitive crossover time, $t_c$, the chain motions (e.g. Rouse modes[5]) become mutually inhibited through entanglement interactions. By describing the effect of the entanglement constraints in a particular fashion, the form of equation (1) is obtained for the relaxation function[3] (with $\beta$ replaced by $1 - n$, where $n$ is the coupling parameter). The coupling parameter is a measure of the strength of the intermolecular interactions; larger $n$ indicates stronger constraints on the chain motions. Since the nature of the entanglements constraint is largely independent of chemical structure[6], the coupling parameter for terminal relaxation should be essentially the same for all polymers[3].

The CM is based on general physical principles[3,4] and as such is also applicable to the local segmental dynamics. In this case there is a direct connection between local chemical structure and the strength of the intermolecular cooperativity[7], as reflected in the magnitude of $n$. For local segmental motion, the ideas underlying the CM are directly supported by quasielastic neutron scattering experiments[6,7]. These neutron experiments[8,9], as well as molecular dynamics simulation data[9,10], indicate $t_c$ to have a magnitude of a few picoseconds for local segmental relaxation. Since the terminal relaxation involves motion over longer length scales, we expect $t_c$ to be larger than the value associated with segmental relaxation.

The relaxation time, $\tau^*$, depends both on the local friction and on the coupling parameter. As a consequence of continuity of the relaxation functions (intermolecularly non-cooperative for $t < t_c$ and entanglement constrained for $t > t_c$) at $t = t_c$, the terminal relaxation time can be expressed as[3,4]

$$\tau^* = (t_c^{-n} \tau_0)^{1/(1-n)} \tag{2}$$

where $\tau_0$ is the relaxation time for the longest Rouse mode. This form for the continuity condition assumes the non-cooperative relaxation ($t < t_c$) proceeds via exponential decay. Even when this is not the case, an exponential function is often adequate to over a few decades of time[11]. Note that while various relaxation models invoke equation (1)[12], equation (2) is unique to the coupling model. All previous applications of the coupling model to the terminal relaxation

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have assumed equation (1); this assumption will be tested herein. However, the essence of the coupling model, the continuity condition [one form of which is equation (2)], is by no means contingent on the validity of equation (1).

This relationship between $\tau^*$ and $\tau_0$, together with equation (1), have been used to address various long time ($t \gg t_c$) properties, including: (i) the correlation between the temperature dependence of $\tau^*$ and the shape of the relaxation spectrum[4,7,13]; (ii) the correlation of the shape of the spectrum with chemical structure[14–17]; (iii) the anomalous plasticization of mixtures; (iv) the breakdown of time–temperature superpositioning in the softening zone[18]; (v) differences in activation energies for self-diffusion and viscosity[4]; and (vi) the difference in temperature dependencies of branched and linear polymers[19,20]. The latter three phenomena involve application of the CM to terminal relaxation behaviour.

The low frequency dynamics of unentangled polymers are well described by the Rouse model[5]. The coupling model assumes that the Rouse model remains valid even for high molecular weight polymers when $t < t_c$, since entanglements have not yet begun to interfere with the chain motion. Thus, the non-cooperative relaxation times of the coupling model are just the Rouse relaxation times

$$\tau_{0,p} \propto \frac{M_W^2 \zeta_0}{p^2 kT} \quad (p = 1, 2, 3 \ldots) \tag{3}$$

where $\zeta_0$ is the monomeric friction coefficient and $M_W$ the molecular weight.

At longer times, entanglements exert their influence, whereby the $\tau_{0,p}$ become the longer relaxation times given by equation (2). In application of the CM, only the longest ($p = 1$) Rouse relaxation time is considered, based on the idea that the slowest mode makes the dominant contribution to the terminal behaviour[21]. Substituting the longest Rouse relaxation time into equation (1), the terminal viscosity is calculated as

$$\eta_0 = \int_0^\infty G(t)\,\mathrm{d}t = \frac{G_N^0 \tau^* \Gamma[1/(1-n)]}{(1-n)} \tag{4}$$

where $\Gamma$ denotes the gamma function (we omit the subscript on $\tau^*$, noting that it is the relaxation time associated with the $p = 1$ Rouse mode). Similarly, the steady-state shear compliance is given by

$$J_e^0 = \frac{\Gamma[2/(1-n)]}{G_N^0 \Gamma^2[(1/(1-n)]} \tag{5}$$

These relationships for $\eta_0$ and $J_e^0$, which do not rely on equation (2), were previously derived by Tobolsky[1]. From equations (2) and (3), the CM's prediction for the molecular weight dependence of the terminal viscosity is

$$\eta_0 \propto \tau^* \propto M^{2/(1-n)} \tag{6}$$

If the viscosity exhibits an Arrhenius temperature dependence with an activation energy $E_a^*$ then

$$E_a^* = \frac{E_a}{(1-n)} \tag{7}$$

where $E_a$ is a primitive (unaffected by intermolecular interaction) activation energy. In utilizing equations (4)–(7), the value of the coupling parameter is invariably determined by fitting the loss modulus

$$G''(\omega) = \omega \int_0^\infty G(t)\cos(\omega t)\,\mathrm{d}t \tag{8}$$

with $G(t)$ given by equation (1). Efficient algorithms for transforming the Kohlrausch equation into the frequency domain have been published[22].

## EXPERIMENTAL

Linear polystyrene (lot no. 50124) was obtained from the Pressure Chemical Co. The weight average molecular weight of the polymer was 233 000 with a polydispersity of 1.06. Dynamic mechanical data were obtained with a Bohlin VOR rheometer using a parallel plate geometry. Sample radii and gaps were typically 13.5 and 2 mm, respectively. The dynamic shear modulus was usually measured from 40 Hz down to as low as $1.5 \times 10^{-4}$ Hz. Values of the terminal viscosity, $\eta_0$, and the steady-state shear compliance, $J_e^0$, were obtained as[5]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{9}$$

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} \tag{10}$$

## RESULTS AND DISCUSSION

### *Polybutadiene*

Rendell *et al.*[23] interpreted the terminal relaxation data of Colby *et al.*[24] for 1,4-polybutadiene (PBD) in terms of the coupling model, deducing $n$ to be in the range of 0.40–0.43. More recently, terminal relaxation data for another PBD series was similarly analysed by Palade *et al.*[25] who obtained $n = 0.41$. In both these studies, the values reported for the coupling parameter were guided by the expectation that equation (6) of the CM should agree with the known molecular weight dependence of the terminal viscosity. In order to satisfy the $M_W^{3.4}$ dependence

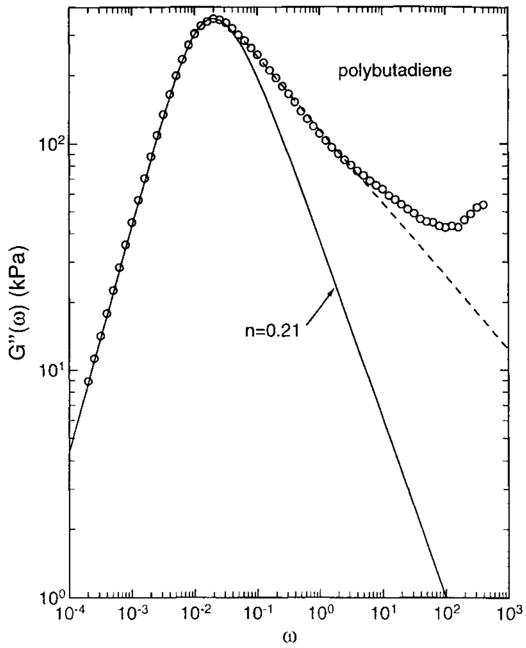

**Figure 1** Terminal loss modulus for PBD of $M_W = 925\,000$ (○)[29]. The solid line is the fit of equations (1) and (8), which yields $n$ ( = 1 − $\beta$) = 0.21. The dashed line towards higher frequency is a power-law extrapolation [equation (12)] of the terminal dispersion

established experimentally for polybutadiene[26], $n$ must equal 0.41.

Displayed in *Figure 1* is the dynamic mechanical data of Colby *et al.*[24] for PBD of $M_W = 925\,000$. Higher in molecular weight than the PBD's analysed previously[23,25], this polymer's terminal relaxation should be better resolved (longer rubbery plateau) from any interfering contributions from higher frequency motions. This is in keeping with Graessley and coworkers's suggestion[24,27] of a 'limiting case' at sufficiently high molecular weight, whereby the terminal dispersion becomes invariant in shape.

The dispersion in *Figure 1* does not conform well to the stretched exponential function on the high frequency side of the peak. To the extent that equation (1) does not provide an accurate description of the terminal relaxation function, the determination of $n$ is somewhat arbitrary. We focus on lower frequencies, assuming that contributions other than the terminal relaxation might be responsible for the discrepancies at higher frequency, and obtain a best-fit $n = 0.21$. This is much less than the value necessary to give the molecular weight dependence of $\eta_0$ determined by experiment. Although equations (1) and (8) with $n = 0.21$ ($\beta = 0.79$) significantly underestimate the intensity of the peak on the high frequency side, no better fit to the experimental data can be achieved using larger values for the coupling parameter. We obtain the same result (not shown) from an analysis of Roover's data for 760 000 molecular weight PBD[28]; the best fit to the loss modulus dispersion yields a value of 0.21 for the coupling parameter.

If it is assumed that equation (1) describes the terminal dispersion, then equations (4) and (5) can be used to calculate the terminal viscosity and steady-state shear compliance, respectively. In the past, agreement of calculated values with experimental determinations of these quantities has been taken as corroboration of the CM. In *Table 1* we list the plateau modulus, terminal viscosity and steady-state compliance reported by Colby *et al.*[24] for the polybutadiene of *Figure 1*. We calculate the plateau modulus by integration of the fitted Kohlrausch function[5]

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega)\, \mathrm{d}\ln\omega \qquad (11)$$

which yields $G_N^0 = 0.86$ MPa. Using this value, we calculate from equations (4) and (5) values for $\eta_0$ and $J_e$ which are consistent with the experimental results (*Table 1*). Such agreement ostensibly confirms the adequacy of equations (1) and (8) for describing the terminal relaxation. In reality, any relaxation function having an $\omega^{-1}$ dependence for $G''$ at low frequencies will yield correct values for $\eta_0$ and $J_e^0$. The shape of the fitting function at frequencies higher than the maximum in the dispersion has negligible effect on these quantities.

To demonstrate this point, we carry out the same calculation, but substitute the following power law at high frequencies [i.e. beyond the peak in $G''(\omega)$]:

$$G''(\omega) \propto \omega^{-0.345}, \quad \omega > 3\omega_{\max} \qquad (12)$$

where $\omega_{\max}$ is the frequency of the maximum in the loss modulus. Such an extrapolation of the terminal dispersion has been recommended by Graessley and coworkers[24,27]. As shown in *Figure 1*, this power law describes the data well from the peak in $G''(\omega)$, althrough about two decades past the maximum. As seen in *Table 1*, when equation (12) is used for high frequencies, the values calculated for $\eta_0$ [equation (4)] and $J_e^0$ [equation (5)] are essentially equal to the results obtained using equations (1) and (8) to describe the entire terminal dispersion. Any equation accurate for $G''(\omega)$ at lower frequencies will provide acceptable values for the terminal viscosity and compliance. Thus, neither equation (4) nor equation (5) offers a test of the validity of the stretched exponential form for the terminal relaxation function.

**Table 1** Polybutadiene results

| | Experimental | Calculated [equations (4), (5), and (13)] | |
|---|---|---|---|
| | | Kohlrausch | Power law[a] |
| $G_N^0$ (kPa) | 1.15 | 0.86 | 1.16 |
| $\eta_0$ (Pa-s) | $4.5 \times 10^7$ | $4.3 \times 10^7$ | $4.2 \times 10^7$ |
| $J_e^0$ (kPa$^{-1}$) | 1.6 | 1.53 | 1.54 |

[a] Using equation (12) to extrapolate dispersion on the high frequency side

Equation (7) from the CM can be used to account for the breakdown of time–temperature superpositioning in the softening zone. Such thermorheological complexity has been observed for many polymers, including, for example, polystyrene[29], polyisobutylene[30] and atactic polypropylene[31]. Recently, Zorn *et al.*[32] interpreted their rheological data on PBD in terms of the CM, specifically addressing the breakdown of time–temperature superpositioning. However, in this work[32] the coupling parameter for the terminal relaxation was not determined; a value of 0.425 was assumed based on the literature. As is clear from *Figure 1*, such a value for $n$ is problematic, notwithstanding any apparent utility in reconciling properties such as the breakdown in time–temperature superpositioning.

### *Polystyrene*

Ngai and Rendell[33] analysed published[34] dynamic mechanical data on monodisperse polystyrene, determining that $n = 0.425$ for the terminal loss peak. In *Figure 2* is shown dynamic mechanical data for a higher molecular weight polystyrene ($M_W = 233\,000$) measured at 433K. The

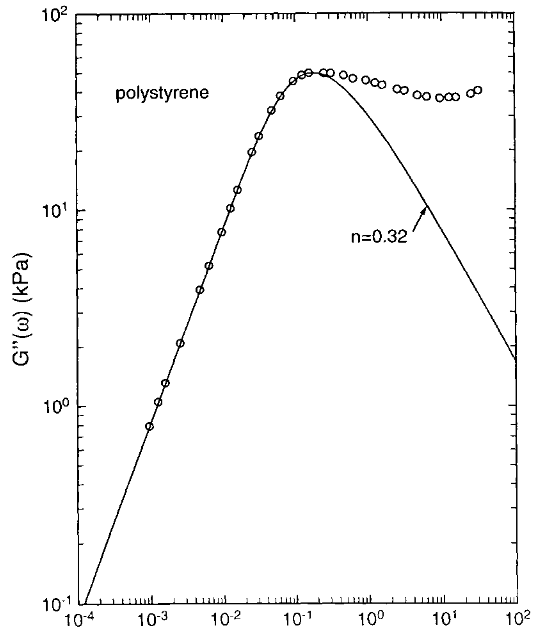

**Figure 2** Terminal loss modulus for polysytrene ($M_W = 233\,000$), along with the fit to equations (1), and (8) ($n = 0.32$)

best fit to equations (1) and (8), which only describes the low frequency side well, yields 0.32 for the coupling parameter. This $n$ is smaller than necessary to give the correct molecular weight dependence of viscosity ($\eta_0 \propto M_{\mathrm{W}}^{3.4}$ [35]).

Using $n = 0.32$, we obtain from equations (4) and (5) $\eta_0 = 8.3 \times 10^2$ Pa-s and $J_e^0 = 12$ MPa$^{-1}$, respectively. We measure using equations (9) and (10) $\eta_0 = 8.2 \times 10^5$ Pa-s and $J_e^0 = 12$ MPa, respectively, at $T = 433$K. As discussed for PBD, the agreement simply reflects the fact that these quantities are governed by the magnitude of $G''(\omega)$ at low frequencies; it does not corroborate the Kohlrausch form for the terminal relaxation function.

From equation (7), relating the apparent activation energy for the terminal viscosity to a non-cooperative, 'primitive' activation energy, the CM makes a prediction concerning the relative temperature dependencies of the terminal and segmental relaxations. However, this prediction is based on the value of the coupling parameter. Using the putative value of $n = 0.425$ for PS's terminal relaxation, Ngai and Plazek[36] were able to give a quantitative accounting for the temperature dependence of PS's segmental relaxation. A smaller coupling parameter, however, opens this rationale to question. In fact, a coupling parameter for the terminal relaxation equal to 0.32 would shift the segmental relaxation temperature dependency predicted by the CM outside the range of the experimental data[36].

Tobolsky *et al.*[1] fitted equation (1) to the terminal relaxation modulus for polystyrenes of varying molecular weights, reporting $\beta$ to be in the range 0.495–0.650, which corresponds to $0.350 < n < 0.505$. In *Figure 3* we display his data for two molecular weights, $M_{\mathrm{W}} = 242\,000$ and 450 000, along with equation (1) using both his reported coupling parameters, and significantly different values for $n$. It can be seen that the PS spectra can be described at least as well using coupling parameters that are outside the range required by the CM analysis. In general it is difficult to uniquely describe time-domain relaxation functions; the problem is exacerbated when, as herein, the data only poorly conform to the fitting function.

### *Polyisoprene*

The viscoelastic properties of monodisperse polyisoprenes in the terminal region were recently measured using both dielectric and mechanical spectroscopies[19,20]. Shown in *Figure 4* are the loss modulus and the dielectric normal mode peak for linear PI of $M_{\mathrm{W}} = 357\,000$, along with the fits to equations (1) and (8). These results are similar to those for PBD and PS—there is excellent agreement at low frequencies, but the function underestimates both experimental dispersions on the high frequency side. This deviation is much larger for the mechanical data than for the dielectric peak. The narrower breadth of the normal mode is a consequence of the symmetry property of chains having unreversed dipoles[20]. The best-fit $n$ values for the mechanical and dielectric data in *Figure 4* are 0.37 and 0.13, respectively. The latter in particular is too small for equation (6) to be in agreement with the experimentally determined relation $\eta_0 \propto M_{\mathrm{W}}^{3.6}$ [37,38]. Additionally, the CM in its present form does not anticipate a difference in the terminal relaxation spectra measured dielectrically *versus* by mechanical spectroscopy.

### *Hydrogenated polybutadiene*

Previously, Ngai and Plazek[21] used the Kohlrausch equation to fit the terminal loss modulus of hydrogenated polybutadiene (HPB) of $M_{\mathrm{W}} = 177\,000$, reporting $n = 0.42$. Equation (6) of the coupling model then yields $\eta \propto M_{\mathrm{W}}^{3.4}$ for the molecular weight dependence of the terminal viscosity, in agreement with experiment[27,39]. We now analyse the same HPB data[27,39], but include results for all HPB samples, with molecular weights in the range from 95 600 to 350 000. As shown in *Figure 5*, the breadth of the loss peak increases slightly with molecular weight (with the exception of $M_{\mathrm{W}} = 202\,000$, the data for which is spurious). Emphasizing the

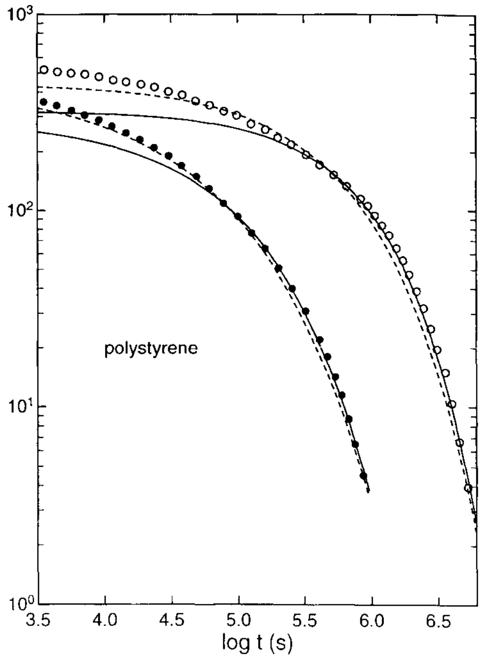

**Figure 3** Relaxation modulus for polystyrene of $M_{\mathrm{W}} = 242\,000$ (solid symbols) and 450 000 (hollow symbols)[1]. The dashed lines are the equation (1) fits reported by Tobolsky[1] ($n = 0.505$ and 0.35 for high and low $M_{\mathrm{W}}$, respectively), while the solid lines correspond to $n = 0.41$ and 0.23, respectively

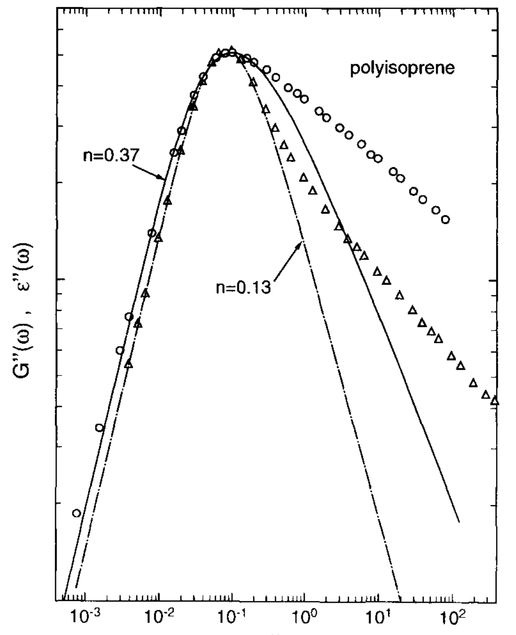

**Figure 4** Normal mode peak (triangles) for PI of $M_{\mathrm{W}} = 357\,000$[24], along with best fit ($n = 0.13$) of equations (1) and (8). Also shown is the loss modulus for the same polymer (circle)[25], along with the fitted curve for $n = 0.37$

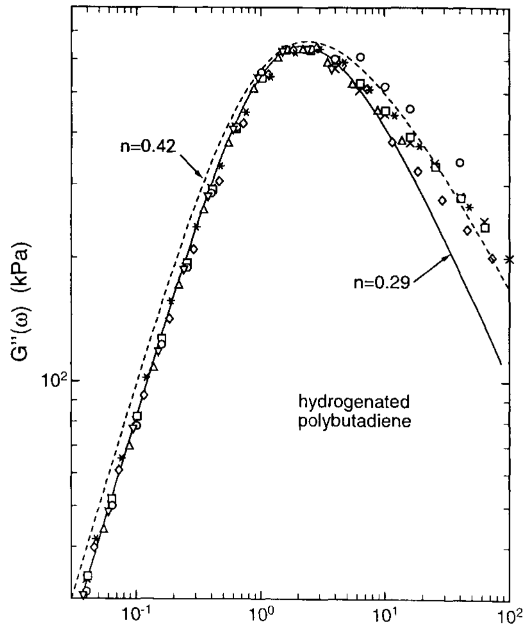

**Figure 5** Terminal loss moduli for HPB of $M_W$ = 95 600 (∇), 150 000 (Δ), 174 000 ( * ), 202 000 (○), 212 000 (□), 359 000 ( × ) and 361 000 (◇)[32,44]; the data have been shifted to superimpose on the curve for $M_W$ = 359 000. The lines correspond to equations (1) and (8) with $n = 0.29$ (——) and $n = 0.42$ (- - -), respectively

low frequencies, the best-fit coupling parameters fall in the range $0.21 < n < 0.29$.

From equation (6), the value of $n = 0.29$ gives for the viscosity a 2.8 power dependence on molecular weight; thus, the CM's prediction for the molecular weight dependence of the viscosity is at odds with experiment. This is in addition to the weak $M_W$-dependence of $n$, and the limited ability of equations (1) and (8) to describe the loss modulus toward higher frequencies. If we improve the fit at higher frequencies using $n = 0.42$ (*Figure 5*), the intensity is overestimated on the low frequency side of the peak.

In addition to the molecular weight dependence of the viscosity, the CM makes a prediction concerning the temperature sensitivity of $\eta_0$ relative to that of self-diffusion[40]. Specifically, the larger activation energy for the viscosity is ascribed to a larger coupling parameter. Although this explanation requires only that $n_\eta > n_{\text{diffusion}}$ the quantitative prediction[40] rely on $n_\eta = 0.42$, a doubtful proposition in light of *Figure 5*.

### *Continuity condition*

The results above make clear that the CM approach goes awry when equation (1) is used to describe the terminal relaxation. However, the premise of the CM—that the relaxation transitions from uncorrelated to intermolecularly cooperative dynamics at a temperature insensitive time—may still be correct, notwithstanding the deficiency of the Kohlrausch fitting function. This transition in relaxation behaviour underlies equation (2), the continuity condition. Virtually all the success of the CM, for example in describing and predicting segmental relaxation properties[4,8-10,13-18,41-45], arises from the application of equation (2). Thus, if the validity of the continuity condition for the terminal relaxation can be demonstrated, the failings apparent in *Figures 1–5* become less important. Departure of the terminal relaxation from stretched exponential decay could be due simply to interference from other relaxation modes. In fact, this is exactly the situation found for segmental relaxation in random copolymers[15,31,46,47], semicrystalline polymers[13,48], polymer blends[49-54] and networks[55]—the segmental dispersion deviates from equation (1) due to inhomogeneous line broadening. However, for all these cases, equation (2) remains valid.

The continuity equation expresses the relationship between of the microscopic relaxation time prevailing at short times and the macroscopic relaxation time actually observed in most experiments. Equation (2) assumes stretched exponential decay for $t > t_c$, an incorrect assumption as evidenced by the preceding results. Thus, if the continuity condition is valid, it will have a different form than equation (2). We can numerically evaluate the continuity relation from experimental data. To do this we note that at $t_c$, the non-cooperative relaxation time is given by [cf. equation (2)]

$$\tau_0 = \frac{t_c}{\ln(G_N^0/G(t))} \qquad (13)$$

and evaluate how $G(t)$ shifts in time for a change in $\tau_0$. If $G(t)$ were given by equation (1), this shift, of course, corresponds to the variation in $\tau^*$. Thus, the shift factor, defined as the ratio, $t_c/t$, necessary to satisfy equation (13) for given $\tau_0$, is determined, with its dependence on $\tau_0$ defining the continuity condition. Since $\tau^*$ has a power-law dependence on $\tau_0$ [equation (2)], we assume the same functionality; hence, a double logarithmic plot of $t_c/t$ *versus* $\tau_0$ will have a slope equal to $1/1 - n$. This provides a determination of the coupling parameter based only on the fundamental premise of the model regarding the onset of intermolecular cooperativity effects at a temperature insensitive time. Any problem deviation of the terminal relaxation function from the form of equation (1) is circumvented.

To carry out the calculation, we first transform the $G''(\omega)$ data in *Figure 5* for HPB ($M_W$ = 361 000) into the time

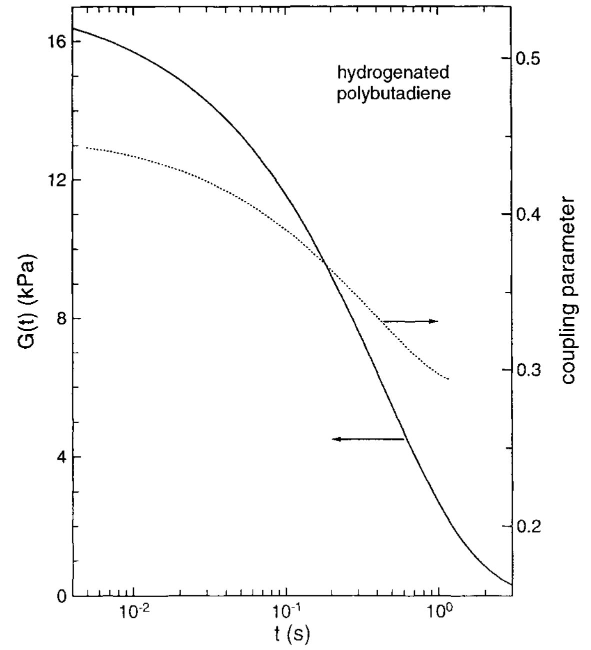

**Figure 6** Relaxation modulus calculated from the $G''(\omega)$ data for HPB ($M_W$ = 361 000) in *Figure 5*. The dotted line is the coupling parameter determined from the continuity condition [equation (13)] assuming a power law dependence of the macroscopic relaxation time on $\tau_0$

domain [see equation (8)]. This is conveniently done by first calculating the relaxation spectrum[5]. The result is shown in *Figure 6*. Also displayed in *Figure 6* is the coupling parameter, determined from the quantity $\mathrm{dlog}(t_c/t)/\mathrm{dlog}(\tau_0)$, evaluated at each time of the $G(t)$ plot. We have assumed $t_c = 1$ ps, consistent with neutron scattering[8,9] and simulation data[10,41]. A fundamental assumption of the coupling model is that the intermolecular coupling and hence $n$, are constants in time for $t > t_c$. In fact, however, the evaluation of the coupling parameter from the shape of the HPB relaxation modulus indicates that $n$ decreases with time.

The magnitude of the coupling parameter in *Figure 6* is consistent with previous work[19] which, however, had assumed a time-invariant $n$. The value of $n$ associated with the onset of the terminal relaxation is $\approx 0.43$, which yields the correct molecular weight and temperature dependencies [equations (6) and (7)] for the terminal viscosity. The same conclusion is reached from similar analyses of the data for PBD, PS and PI.

## DISCUSSION

Previously, application of the coupling model to the terminal relaxation relied on equation (1); this is oversimplified, yielding an inadequate description of the terminal dispersion. We believe the problem lies in the neglect of the fact that the constraints associated with the terminal relaxation in polymers are principally lateral (transverse) to the chain contour. This feature, which causes each chain to behave as if confined in a tube, is the basis for the reptation model[56], commonly used to interpret the rheology of polymer melts. Similar to the failing seen herein for the CM, reptation theory does not accurately predict the shape of experimental relaxation functions. Modifications have been proposed to account for this discrepancy[55–59].

Evidently any theory of low frequency chain dynamics must take into account the lateral constraints restricting the Rouse motion of a chain. The CM's assumption that these constraints are permanent means that the coupling parameter remains constant for times longer than $t_c$. Consistent with the results in *Figure 6*, mitigation of the lateral constraints by motion of neighbouring chains will effect a decrease in $n$ with time. The correlation function resulting from a time-dependent $n$ would still follow the $G(t)$ of equation (1) until $t$ is of the order of or larger than the lateral constraint lifetime ( $\approx \tau^*$), after which its decay will accelerate. Notwithstanding the inadequacy of equation (1), the predictions of the CM concerning the molecular weight and temperature dependencies of the terminal relaxation remain valid, as demonstrated herein through a numerical evaluation of the continuity condition [cf. equation (2)]. To demonstrate that the failing of equation (1) is indeed related to the phenonmenon of constraint mitigation, an extension of the model is required. Some preliminary efforts along these lines, addressing the dielectric normal mode relaxation in polymers, have been made[60].

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