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Section 14. Rheology

Effect of long-chain branching on the rheology of 1,4-polyisoprene

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Abstract

The presence of long chain branches in 1,4-polyisoprene (PI) is shown to increase the sensitivity of temperature of the terminal relaxation. The excess activation energy associated with branching increases in proportion to the molecular weight of the branches. In these respects, PI behaves like other branched polymers, which means that the reptation-based interpretation of the temperature-dependence of branched polymers cannot be correct. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

A complete theory of polymer rheology, able to relate quantitatively the low frequency dynamics to the chain structure, is lacking. The most popular approach is the reptation (or tube) model [1,2], which provides a plausible conceptual framework. However, the model's predictions are at odds with experimental data concerning the shape of the relaxation function [2,3], the temperature dependence of relaxation properties (e.g., the divergence of the friction constant in the terminal zone from its high frequency value [4–6]), and the relationship between the zero-shear viscosity and molecular weight [1,2].

A useful means to assess rheological models is by systematic variation of the macromolecular topology; however, such studies provide little support for reptation. For example, both ring polymers [7,8] and microgels [9,10] exhibit rheological behavior very similar to linear chains, even though neither species is capable of reptation. The rheology of randomly branched chains and star polymers has received much attention. The smaller coil size of a branched chain will tend to decrease the viscosity, although branches long enough to entangle produce a broadened terminal zone and larger viscosity. Early on it was recognized that the latter was due to the suppression of longitudinal motions [11–13], and qualitatively such results are in accord with reptation. Since reptation involves the entire molecule, an additional mechanism is needed to allow translation of a branched molecule. It has been proposed that this other mode of motion involves simultaneous retraction of all branches, whereby diffusion can proceed along the chain contour [14–17].

The suppression of reptation by long branches leads to the prediction of an exponential increase in zero-shear viscosity with arm molecular weight [14,16,18]

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^b \exp\left(v\frac{M_a}{M_e}\right), \tag{1}$$

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where M_a and M_e represent the arm and entanglement molecular weights, respectively, and the parameters, b and v, are model-dependent. Experimentally it is found that $1/2 \leqslant b \leqslant 2$, while v is of the order unity or less [19–21].

Interpretation of the effect of branching on the temperature dependence of the rheological properties is problematic. From a model such as reptation, which includes only a single friction constant determined by the local chemical structure, the expectation is that branching has no effect on temperature dependencies [13,15]. Contrarily, many experimental studies demonstrate that branched polymers exhibit viscosities and shift factors more sensitive to affected by temperature than their linear counterparts [22–26]. This increased temperature dependence is accompanied by a breakdown of time-temperature superpositioning. Such results pose an important challenge to reptation.

An explanation for a difference in temperature dependencies for linear and branched was proposed by Graessley [27]. Disentanglement via a putative arm retraction mechanism implies that branched chains assume a transient, compact configuration, involving higher concentrations of gauche ("bent") rotamers. The reduced entropy of this contracted state would increase the free energy. For the case (realized only at high temperature) in which the viscosity of the linear chains is described by an Arrhenius function, the flow activation energy of the branch chains, $E_{a,Br}$, can be expressed as [27]

$$E_{a,Br} = E_{a,lin} + E^{\ddagger}, \tag{2}$$

where $E_{a,\,lin}$ is the activation energy for flow of the corresponding linear polymer and $E^{\ddagger}$ is the transition state energy associated with the compact conformations. If the gauche state has a higher energy than the trans (extended) conformer, there will be an excess activation barrier, and consequently a larger temperature coefficient for terminal relaxation of branched polymers. This arm retraction mechanism would also account for thermorheological complexity in branched polymers [27].

Even when the temperature dependence of the viscosity cannot be described as a thermally activated process (for example, a WLF behavior obtains), the excess energy due to the long branches is expected to remain Arrhenius [27]. The transition energy associated with the retracted state is predicted to be proportional to the length of the branch [24,27]

$$E^{\ddagger} = \Lambda \frac{M_a}{M_e}. \tag{3}$$

The coefficient, Λ, is chemical structure dependent, and (according to the hypothesis) governed by the gauche/trans energy difference. This dependence leads to the prediction of a correspondence between Λ and the temperature coefficient of the chain dimensions, κ, [24,27]

$$\kappa = \frac{\mathrm{d}\ln\langle r^2\rangle}{\mathrm{d}T}, \tag{4}$$

where $\langle r^2\rangle$ is the mean squared size of the chain coil. Specifically, polymers with negative κ (implying gauche conformers are larger in energy than trans, such that the chain dimensions decrease with increasing temperature) should exhibit an enhanced temperature sensitivity when they have long branches.

In Table 1 are displayed results of Graessley and coworkers for various star polymers. Three species, hydrogenated PI (which is essentially ethylene–propylene copolymer), hydrogenated polybutadiene (≈polyethylene), and 1,2-polybutadiene, have large negative κ and substantial magnitudes for Λ. These numbers are qualitatively consistent with the predicted correlation of chain expansivity with temperature dependency [24,27]; however, the relative ordering of these polymers is inconsistent with the theory. For example, hydrogenated polyisoprene has the largest (negative) κ, but its Λ is the smallest among the three polymers.

According to the arm retraction hypothesis, the effect of temperature should be the opposite (branching *reducing* the temperature sensitivity of the rheology) for polymers with positive κ (Eq. (1)). In direct contradiction, however, the results for 1,4-polybutadiene ($\kappa > 0$) reveal Λ to have the same sign and be only slightly smaller in magnitude than Λ for the polymers in Table 1 with large negative κ. Similarly, hydrogenated 1,2-polybutadiene has a positive (albeit small) κ, while its Λ is reputedly zero (see Table 1). Actually, the data for this polymer is a poor test for the

Table 1
Temperature coefficients for star-branched polymers

Polymer	Λ	κ ($\times 10^3$)	f_e/f [b]	M_a/M_e	ΔT (C) [c]
Hydrogenated polyisoprene [a]	0.165	−1.3	–	23–33	85
Hydrogenated 1,4-polybutadiene [a]	0.25	−1.05	−0.30	12–39	175
1,2-polybutadiene [a]	0.17	ca. −1	–	12	125
1,4-polybutadiene [a]	0.11	0.39	0.12	12–13	50
Hydrogenated 1,2-polybutadiene [a]	0	0.5	–	5–6	100
Polyisoprene [d]	0.07 ± 0.02	0.3 [a]	0.17	15–44	120

[a] From [24] and references therein.
[b] Ref. [28].
[c] Temperature range over which temperature dependency was measured.
[d] This work.

effect of branching because of the small arm molecular weights studied, making determination of Λ difficult.

The interpretation of the temperature response of branched polymers focusses on the relative energy of the gauche and trans conformers, as reflected in the parameter, κ. In analyzing the rheology of stars, it has been suggested that for PI [19,21] and 1,4-polybutadiene [21,24,25] the chain dimensions have a negligible dependence on temperature ($\kappa \approx 0$). If the gauche/trans energy difference were indeed negligible, the Graessley hypothesis asserts an equivalence of the temperature coefficients for linear and branched chains.

An alternative measure of this energy difference can be obtained from thermoelasticity data. Classical theories of rubber elasticity assumed freely jointed chains, whose deformation is entirely entropic. The configurations assumed by real networks may not be equal in energy, however, because the various conformers can have different energies. This difference gives rise to an energetic component in the restoring force, the fractional contribution of which can be expressed as [28]

$$f_e/f = T\frac{\mathrm{d}\ln\langle r^2\rangle}{\mathrm{d}T}, \tag{5}$$

where f_e is the energetic component of the total restoring force, f. The quantity f_e/f is proportional to κ, and thus provides a measure of the difference in trans and gauche energies. The values of f_e/f are listed in Table 1 for hydrogenated polybutadiene (or polyethylene), 1,4-polybutadiene, and polyisoprene. For the former, there is agreement with inferences from the magnitude of κ – the trans conformer is smaller in energy than the gauche, and hence branched polyethylene is predicted to be more affected by temperature than linear polyethylene. This difference concurs with experimental results [24,25]. For 1,4-polybutadiene and PI, the f_e/f data indicate larger energy for the trans conformer, consistent with the positive κs in Table 1. The consequent prediction of the arm retraction hypothesis [24,27] is that Λ will be negative. For 1,4-polybutadiene, this prediction is clearly at odds with experiment [24]. The situation for star-branched PI is confused. Early studies suggested equivalent temperature dependencies for branched and linear PI [19,24,29], while studies on larger molecular weight samples reported an enhancement in temperature sensitivity for the former [30,31].

Studies of star-branched polybutadiene [32] and polystyrene combs [33] were limited to relatively short branches ($M_a/M_e \leqslant 5$), making accurate assessment of temperature dependencies difficult (viz. Eq. (3)). Highly entangled polystyrene stars (M_a/M_e as large as 17) were reported to have the same temperature dependence as linear polystyrene [34]; however, the properties of these 4-arm and 6-arm stars was peculiar. Even at molecular weights of over one million, their viscosities were less than that of linear polystyrenes of equal molecular weight. This difference is unexpected, since reptation theory predicts an exponential dependence of the viscosity of entangled, branched polymers on arm molecular weights (Eq. (1)).

Notwithstanding the absence of quantitative support for a connection between Λ and the conformational energies, the notion that the

Table 2
3-Arm star polyisoprenes

	M_w (kg/mol)	M_w/M_n	M_a/M_e	η_0 (MPa s at 60°C)
S284	284	1.09	15	0.28
S342	342	1.10	18	1.8
S749	749	1.14	39	190
S854	854	1.10	44	1700
S1760	1760	1.15	92	(degrades)

temperature dependence of branched polymers' rheology is well described by the arm-retraction hypothesis seems to have taken hold [19,21]. To further clarify this issue, we have undertaken an experimental study of star-branched PI having large M_a/M_e values. This report describes our recent findings.

2. Experimental

The polyisoprenes (Polymer Source, Inc., Quebec, Canada), included those used in previous work [30,31], along with additional 3-arm stars of different molecular weight. Linear PI was anionically polymerized using *sec*-butyl lithium, with subsequent coupling carried out using 2,4,6-triallyloxy-1,3,5-triazine. The star-PI were fractionated using benzene/methanol (as many as twenty times for the larger molecular weight samples) to remove uncoupled chains. Molecular weights and polydispersities, determined by size-exclusion chromatography calibrated for polyisoprene, are listed in Table 2. All samples included a mixture of 0.25 wt% zinc 2-mercaptotoluimidazole and 0.25 wt% octylated diphenylamine as an anti-degradants.

Dynamical mechanical measurements were carried out on a Bohlin rheometer. Torsional creep and recovery were measured with a Plazek constant stress apparatus [35]. A more detailed description of the mechanical measurements can be found elsewhere [30].

3. Results

The viscosities were measured for the star-branched PI by creep experiments. For the larger molecular weights, steady state could not be attained, so the extrapolation method of Ninomiya was employed [36], whereby terminal viscosities are obtained via the extrapolation

$$\eta_0^{-1} = \lim_{1/t \to 0} [mJ(t)/t], \tag{6}$$

where m ($\equiv$ d log $J(t)$/d log t), which equals unity at steady state, attained values of at least 0.7 herein.

For sample S1760, the terminal viscosity could not be determined because the material degraded well before the approach of steady-state. This degradation was unique to the star-branched PI, although, as seen from the GPC of the material before and after shearing (Fig. 1), it does not appear to simply involve detachment of the arms [37].

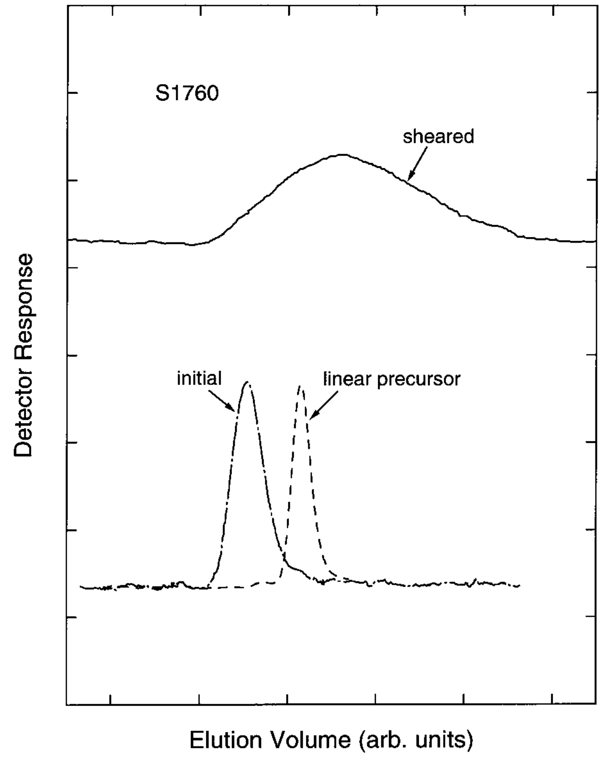

Fig. 1. Size exclusion chromatograms for S1760 initially and after slow shearing overnight at 60°C. Degradation of the PI is evident; however, as seen by comparison to the chromatogram of the linear PI (dashed curve), this reduction in molecular weight does not correspond to arm-detachment from the coupling moiety.

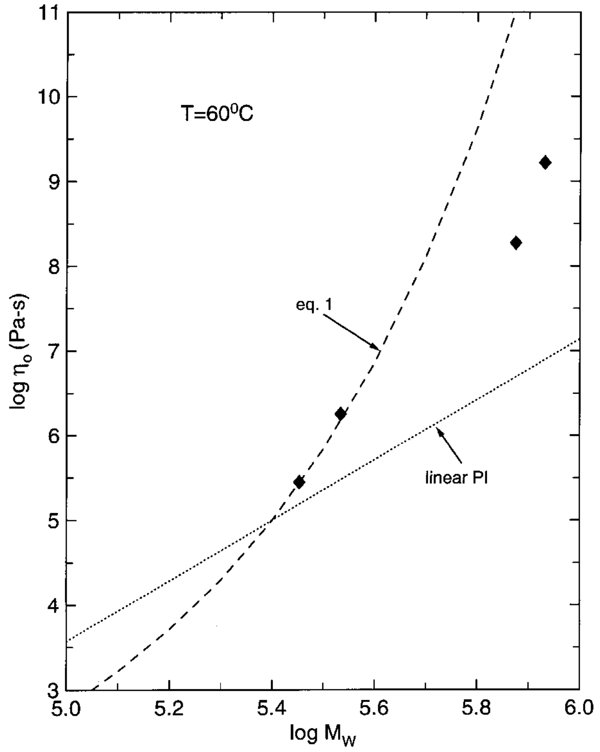

Fig. 2. Viscosity of 3-arm star PI at 60°C (◆). The solid line is Eq. (1) with $b = 3/2$ and $\nu = 0.47$. The dashed line represents the viscosity of linear polyisoprene (taken from Ref. [30]).

The viscosities of the 3-arm star PI are shown in Fig. 2. Since the arms for all samples are well-entangled ($M_e = 6400$ g/mol for PI [38,39]), the viscosities exceed that of linear PI of equivalent molecular weight. The solid curve in the figure corresponds to Eq. (1) using $b = 3/2$ and $\nu = 0.47$, as suggested for star-PI [19]. Note that for the largest molecular weight herein, Eq. (1) predicts a viscosity at least three orders of magnitude too large. Evidently, the increase of PI's viscosity due to branching is less than the exponential dependence expected from suppression of reptation. In this respect, star-PI is similar to branched polystyrene, for which the viscosity of 4-arm stars is less than implied by an exponential dependence on M_a/M_e [20].

The zero-shear viscosity and the terminal relaxation time are directly related

$$\eta_0 \propto \tau G_N^0 \tag{7}$$

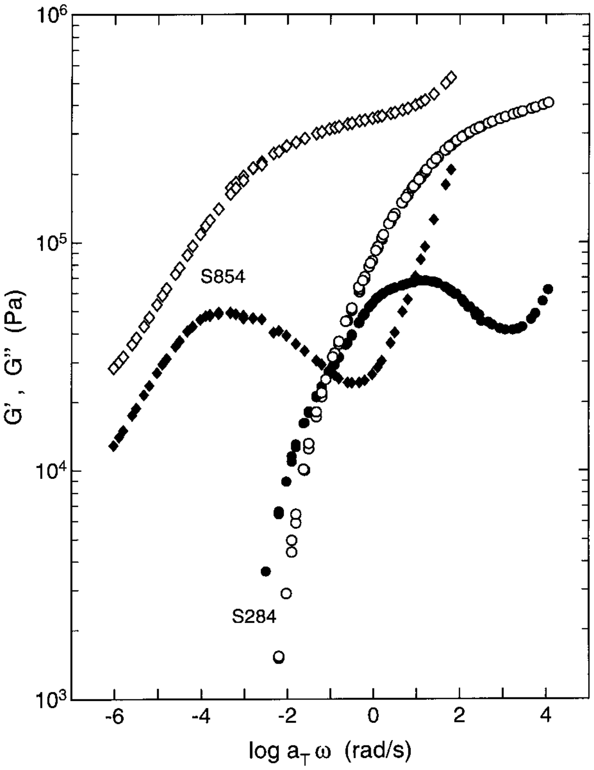

Fig. 3. Dynamic mechanical storage (hollow symbols) and loss (solid symbols) moduli for representative 3-arm star PI. Data was obtained for each sample at three temperatures, and superimposed using a reference temperature of 30°C (S284, circles) and −29°C (S854, diamonds), respectively. Deviations in the terminal zone from thermorheological simplicity are too subtle to be evident in this plot.

and, since the plateau modulus, G_N^0, is not affected by temperature, η_0 and G_N^0 have the same temperature dependence. Thus, we can use the variation of τ with temperature to assess the chain retraction hypothesis for star-branched PI. Representative dynamic mechanical spectra are shown in Fig. 3 for respective star-PI's having relatively short ($M_a = 95\ 000$) and long arms ($M_a = 285\ 000$).

4. Discussion

A relaxation time can be defined as the inverse of the frequency corresponding to the maximum in the loss modulus. These values are plotted in Fig. 4, along with the best-fit to the Vogel–Fulcher equation [40]. Also shown in the figure is the curve

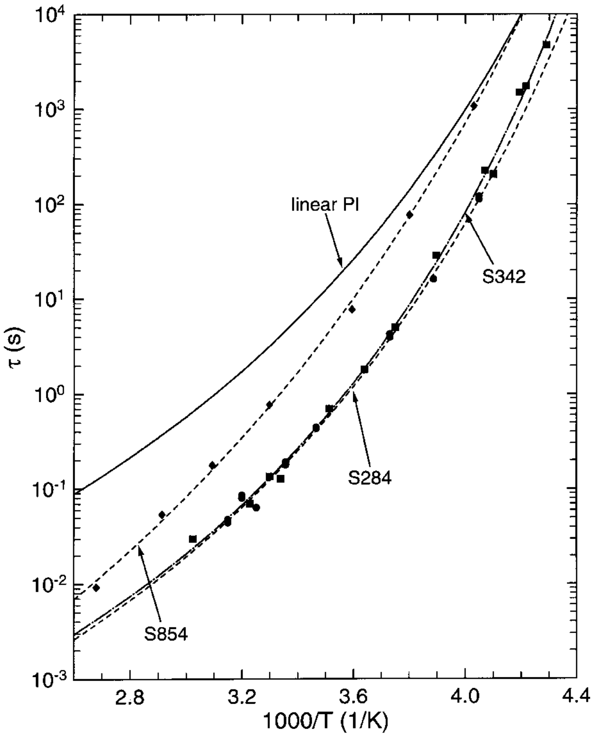

Fig. 4. Reciprocal of the frequency of the maximum in the loss modulus for linear from [30] and 3-arm star PI (S284 •••; S342 ■■■; S854 ♦♦♦). The lines represent fits to the Vogel–Fulcher equation.

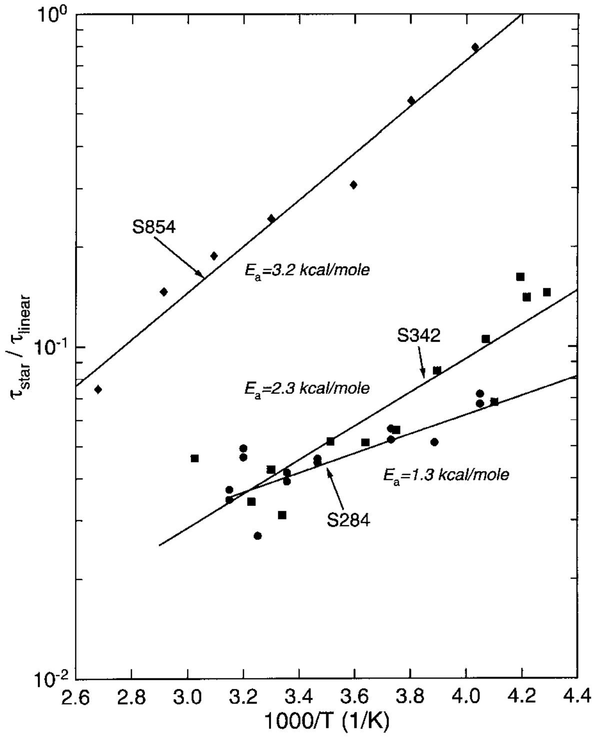

Fig. 5. The data of Fig. 5 normalized by the terminal relaxation time of linear PI. The slopes increase with the molecular weight of the 3-arm star.

for linear PI [30]. Although all the data in Fig. 4 are non-Arrhenius, such that no activation energy can be defined, it is obvious that linear and branched PI have different temperature dependencies. For example, the change in the relaxation time for the largest molecular weight star exceeds that for linear PI by more than a factor of ten over the measured range of temperatures. Note that this difference is not due to any difference in the local friction coefficient, as evidenced by the equivalence of the glass transition temperatures at these molecular weights [30].

To quantify this behavior, we replot the data of Fig. 4 in the form suggested by the Graessley analysis [24,27]; that is, the relaxation times for the stars are normalized by that of linear PI. The resulting curves (Fig. 5) have slopes increasing with increase in M_a/M_e. This increase is consistent with Eq. (3), which predicts that the excess activation energy, $E^{\ddagger}$, increases in proportion to the arm length.

In Fig. 6 we plot the slopes from Fig. 5 versus M_a/M_e. Notwithstanding the scatter in the data, we estimate that $A \sim 0.1$ kcal/mole, which falls on the lower end of the range of activation coefficients determined for star-branched polymers of various chemical structure [21,24]. However, as seen in Table 1, there is no correlation of A with either κ or f_e/f. In fact, for PI $E^{\ddagger}$ has the wrong sign. Clearly, a prediction of temperature dependencies for star-branched PI based on reptation and arm retraction ideas is at odds with experimental results.

5. Conclusion

The intuitive appeal of reptation undoubtedly contributes to its popularity; however, single chain theories are inherently limited in their ability to describe the complex, cooperative dynamics in a dense phase. Consequently, despite more than

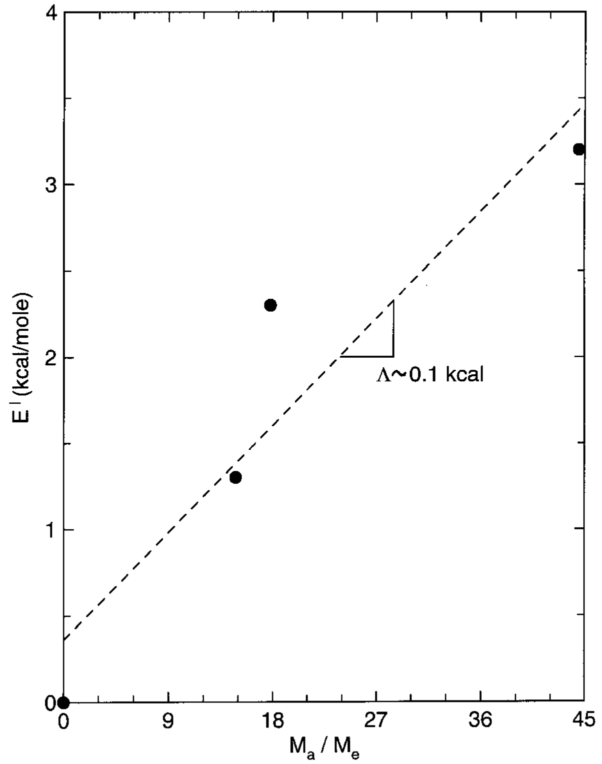

Fig. 6. The excess activation energy (from the slopes in Fig. 6) versus the number of entanglements per arm for star-PI, yielding an estimate for $\Lambda \approx 0.1$ kcal/mole (see Eq. (3)).

two decades of research, fundamental issues concerning the rheology of entangled polymers remain to be satisfactorily addressed. These include the shape of the terminal relaxation function [2,3], the molecular weight dependence of the zero-shear viscosity [1,2], the breakdown of the time-temperature superposition principle in the glass transition zone [4–6], and the "reptation-like" rheology of ring polymers [7,8] and microgels [9,10]. Herein we have shown that another problem, the effect long chain branching has on the temperature dependence of the terminal relaxation, is also without explanation.

Acknowledgements

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References

[1] P.G. de Gennes, J. Chem. Phys. 55 (1971) 572.
[2] M. Doi, S.F. Edwards, The Theory of Polymer Dynamics, Oxford University, Oxford, 1986.
[3] M. Rubenstein, R. Colby, J. Chem. Phys. 89 (1988) 5291.
[4] D.J. Plazek, I.-C. Chay, K.L. Ngai, C.M. Roland, Macromolecules 28 (1995) 6432.
[5] P.G. Santangelo, K.L. Ngai, C.M. Roland, Macromolecules 29 (1996) 3651.
[6] K.L. Ngai, D.J. Plazek, Rub. Chem. Technol. 68 (1995) 376.
[7] G.B. McKenna, B.J. Hostetter, N. Hadjichristidis, L.J. Fetters, D.J. Plazek, Macromolecules 22 (1982) 1834.
[8] S.F. Tead, E.J. Kramer, G. Hadziioannou, M. Antonietti, H. Sillescu, P. Lutz, C. Strazielle, Macromolecules 25 (1992) 3942.
[9] M. Antonietti, T. Pakula, W. Bremser, Macromolecules 28 (1995) 4227.
[10] C.M. Roland, C.A. Bero, K.L. Ngai, M. Antonietti, Mater. Res. Soc. Proc. Series 411 (1996) 367.
[11] V.C. Long, G.C. Berry, L.M. Hobbs, Polymer 5 (1964) 517.
[12] G. Kraus, J.T. Gruver, J. Polym. Sci. A 3 (1965) 105.
[13] G.C. Berry, T.G. Fox, Adv. Polym. Sci. 5 (1968) 261.
[14] P. de Gennes, J. Phys. (Paris) 36 (1975) 1199.
[15] W.W. Graessley, Accnts. Chem. Res. 10 (1979) 332.
[16] M. Doi, N.Y. Kuzuu, J. Polym. Sci. Lett. Ed. 18 (1980) 775.
[17] J. Klein, Macromolecules 19 (1986) 105.
[18] D.S. Pearson, E. Helfand, Macromolecules 17 (1984) 888.
[19] L.J. Fetters, A.D. Kiss, D.S. Pearson, G.F. Quack, F.J. Vitus, Macromolecules 26 (1993) 647.
[20] J. Roovers, Polymer 26 (1985) 1091.
[21] G.S. Grest, L.J. Fetters, J.S. Huang, D. Richter, Adv. Chem. Phys. 94 (1996) 67.
[22] R.S. Porter, J.P. Knox, J.F. Johnson, Trans. Soc. Rheol. 12 (1968) 409.
[23] R.A. Mendelson, W.A. Bowles, F.L. Finger, J. Polym. Sci. Poly. Phys. Ed. 8 (1970) 105.
[24] J.M. Carella, J.T. Gotro, W.W. Graessley, Macromolecules 19 (1986) 659.
[25] V.R. Raju, H. Rachapudy, W.W. Graessley, J. Polym. Sci. Polym. Phys. Ed. 17 (1989) 1223.
[26] C.B. Gell, W.W. Graessley, V. Efstratiadis, M. Pitsikalis, N. Hadjichristidis, J. Polym. Sci. Poly. Phys. Ed. 35 (1997) 1943.
[27] W.W. Graessley, Macromolecules 15 (1982) 1164.
[28] B. Erman, J.E. Mark, Structures and Properties of Rubberlike Networks, Oxford University, Oxford, 1997.
[29] D. Boese, F. Kremer, L.J. Fetters, Macromolecules 23 (1990) 1826.
[30] C.A. Bero, C.M. Roland, Macromolecules 29 (1996) 1562.
[31] C.M. Roland, C.A. Bero, Macromolecules 23 (1996) 7521.
[32] J. Roovers, Macromolecules 24 (1991) 5895.
[33] J. Roovers, W.W. Graessley, Macromolecules 14 (1981) 766.

[34] W.W. Graessley, J. Roovers, Macromolecules 12 (1979) 959.
[35] D.J. Plazek, J. Polym. Sci., Part A-2 6 (1968) 621.
[36] K. Ninomiya, J. Chem. Phys. 67 (1963) 1152.
[37] Anecdotally, branched PI is reputed to be less stable than the linear polymer, even in the absence of deformation (S.K. Varshney, personal communication).
[38] J.T. Gotro, W.W. Graessley, Macromolecules 17 (1984) 2767.
[39] C.M. Roland, Macromolecules 25 (1992) 7031.
[40] J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1980.