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Dynamics near the Glass Temperature of Low Molecular Weight Cyclic Polystyrene

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ABSTRACT: The segmental relaxation properties of a low molecular weight (4.6 kg/mol), cyclic polystyrene (PS) were characterized. The sample was obtained by fractionation using HPLC at the chromatographic critical condition, which yields a ring uncontaminated by its linear precursor. Both the glass temperature and the temperature dependence of the segmental relaxation times for the ring PS were equivalent to the high molecular weight limiting values for the linear polymer. These results are interpreted by considering the configurational mobility of a polymer lacking chain ends.

Introduction

Much effort has been devoted to studying the effect of molecular architecture on the properties of polymers. In addition to the practical appeal of better performing materials, such work can provide new theoretical insights. Ring polymers are of particular interest, for two reasons: Reptation, the mechanism believed to govern the low-frequency dynamics of long-chain polymers, is unavailable to rings.[1,2] Rings also lack the excess mobility conferred by chains ends to polymers having small molar masses.[3] This is consistent with the fact that, due to intermolecular constraints, cyclic polymers form a very compact, molecular structure.[4,5]

Herein we compare relaxation behavior near the glass temperature, T_g, of a polystyrene ring to that of linear PS. The ring sample was obtained by liquid chromatography at the critical condition (LCCC) and is thus uncontaminated by the precursor linear chains. This work was motivated by previous results showing that the temperature dependence of linear PS's segmental relaxation became weaker (relaxation times changed less with changes in normalized temperature) as the molecular weight decreased.[6] The effect was ascribed to chain ends, which, if correct, implies PS rings of low molar mass will exhibit quite different behavior.

Experimental Section

The polystyrene ring was prepared by anionic polymerization initiated with sodium naphthalenide in THF, followed by cyclization using $(CH_3)_2SiCl_2$.[7] LCCC was used to separate the ring from linear contaminants as well as cyclic dimers.[8] The molecular weight, M_w, was 4.6 kg/mol, as measured by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry.[9] This can be compared to the value $M_w = 4.7$, kg/mol, determined by size exclusion chromatography with light scattering detection. The polydispersity M_w/M_n, measured by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry, was 1.055.

Test specimens were prepared by molding at 135 °C in a vacuum. The calorimetric glass temperature was measured by cooling at 10 deg/min using a Perkin-Elmer DSC-7. Dynamic mechanical measurements for the flow region and in the vicinity of the glass transition were obtained with a Bohlin VOR rheometer using a parallel-plate geometry. Sample radii and gaps were 6.3 and 1.5 mm, respectively. The dynamic shear modulus was measured at angular frequencies in the range from 12 to 6×10^{-5} rad/s temperature at temperatures between 367 and 379 K. Temperature control was ±0.1 deg. Reproducibility was affirmed by replicate measurements after various time periods. For the lowest temperature, measurements were repeated after 4.5 days to ensure the absence of physical aging.

Results

Glass Temperature. The glass temperature of low molecular weight, cyclic polymers is expected to be higher than for the corresponding linear chains, since fewer degrees of freedom need to be frozen out. For the PS ring, we measure $T_g = 373.7 \pm 0.2$ K. This datum is plotted in Figure 1 along with the values for linear PS.[6] The molecular weight dependence of the glass temperature for linear polymers can be described by the Kanig−Ueberreiter equation[10]

$$T_g = \left[\frac{1}{T_g^\infty} + \frac{K}{M_w}\right]^{-1} \tag{1}$$

For PS, $K = 7.8 \times 10^{-4}$ mol/kg and the high molecular weight limiting value $T_g^\infty = 374$ K.[6] Thus, for $M_w = 4.6$ kg/mol, linear PS has a glass temperature 21 deg lower than T_g of the ring. In eq 1, T_g^∞ corresponds to a chain length sufficiently long that the chain end contribution to the configurational freedom becomes negligible. Interestingly, this quantity for linear PS is equal to the glass temperature measured herein for the ring. Since at infinite molecular weight T_g must be the same for rings and linear polymer, the implication is that the

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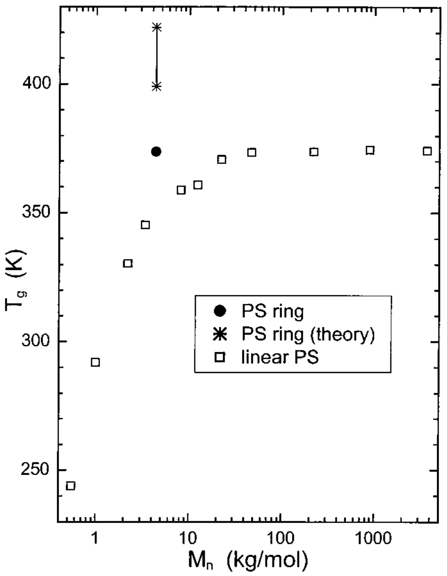

Figure 1. Calorimetric glass temperature of the PS ring measured by cooling at 10 deg/min. (The value obtained by heating at the same rate is 3.5 deg higher.) Also included are data for linear PS of the indicated number-average molecular weight as well as the range of T_g calculated for cyclic PS of $M_n = 4.36$ kg/mol.

current ring is already at its high polymer limiting value. We also note that, prior to the fractionation used herein, the T_g of this ring sample was 3.2 deg lower than T_g^∞,[11] reflecting contamination with the linear precursor.

A T_g for ring PS equal to the high polymer value for linear PS is consistent with the data of Gan et al.[12] Liu et al.[13] also reported glass temperatures for cyclic PS of various molecular weights. Interpolation of their results for $M_w = 4.6$ kg/mol gives a T_g 18 deg lower than measured herein. This difference is too large to be ascribed to contamination of the Liu et al. samples with linear PS. We note, however, that their reported T_g's also exhibit a broad minimum at molecular weights in the range 1−10 kg/mol. There is no physical basis for such a result, which calls into question their data.

Di Marzio and co-workers[3,14] have developed a theory for the T_g of ring polymers. While qualitative agreement with experimental results for rings was achieved, their calculated glass temperatures depend sensitively on the assumed dependence of the number of configurations on molar mass. For PS, the authors considered a range of the parameters, obtaining $T_g = 411 \pm 11$ K for cyclic PS of $M_n = 4.36$ kg/mol.[14] As shown in Figure 1, this is significantly higher than the glass temperature determined herein. Similar results were obtained for other ring polymers—the theory overestimates the effect of cyclization on T_g.

Melt Viscosity. Isothermal dynamic mechanical measurements on the PS ring were carried out at several temperatures. Displayed in Figure 2 is a master curve, which includes only data at the two extremes of the seven measurement temperatures: 367.2 K and the reference temperature 379.2 K (which is 5.2 deg above the calorimetric T_g). The data superpose well in the region toward high frequency where the two data sets overlap. At lower frequencies, thermorheological complexity would be expected.[15]

These data encompass the viscoelastic response from the glassy plateau to the terminal zone. Since the ring has a molar mass more than a factor of 3 smaller than the entanglement molecular weight of linear PS, $M_e = 15.9 \pm 2.9$ kg mol,[16,17] there is no rubbery plateau in the storage modulus. (Moreover, M_e may be larger for rings.[4,18]) At all frequencies below the softening zone (wherein $G' \approx G''$), the loss tangent exceeds unity. At the lowest measured frequencies, proportionality between $G'(\omega)$ and ω^2 was not attained (the resolution of the rheometer is insufficient). However, the dynamic viscosity, $G^*(\omega)/\omega$, did become constant, yielding a value for the zero shear rate viscosity, η_0, equal to 1.62×10^8 Pa s at 379.2 K.

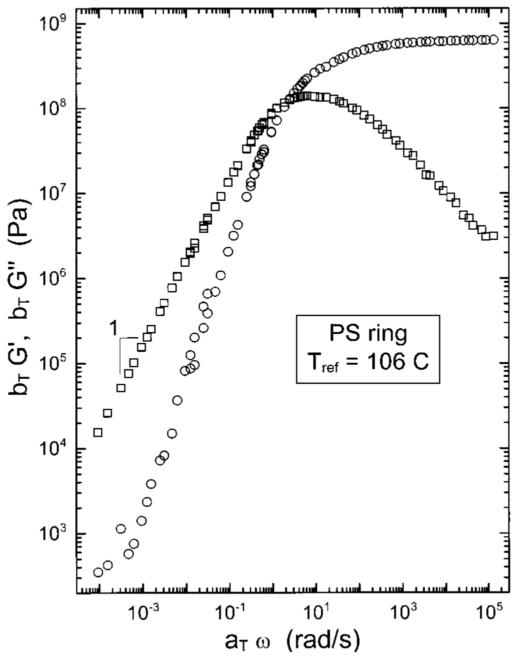

Figure 2. Dynamic mechanical storage (circles) and loss (squares) moduli for PS ring measured at 379.2 K (data at $\omega < 13$ rad/s) and 367.2 K (data at $a_T\omega > 4$ rad/s). The latter were shifted to superimpose. (For clarity, not all points are shown.) The glassy plateau approaches a value ≈ 1 GPa, quite comparable to glassy modulus of linear PS.[15] At the lowest frequencies, the quantity G''/ω becomes constant, although terminal flow ($G' \propto \omega^2$) has not been attained.

This viscosity can be compared to the results of McKenna et al.,[19] who reported a master equation describing both the temperature and molecular weight dependences of the terminal viscosity for cyclic PS

$$\log \eta_0 = -11.04 + \frac{689}{T - 323.3} + 1.74 \log M_w \quad (2)$$

For $M_w = 4.6$ kg/mol, this gives $\log \eta_0$ (Pa s) $= 7.7 \pm 0.7$ at 379.2 K, which is within error equal to the value measured herein, $\log \eta_0 = 8.21$. There is a large uncertainty in the former, since eq 2 represents data obtained over a wide range of molecular weights and temperatures.

According to the Rouse model, the viscosity of an unentangled, linear polymer should be twice that of its cyclic counterpart.[11,19] Results for linear PS are available from Plazek and O'Rourke,[15] although comparison to the ring viscosity requires interpolating data for linear PS having molecular weights different from M_w of our sample. The result suggests that the viscosity of a linear PS of equivalent molecular weight is indeed larger than measured herein for the ring, although the difference is substantially more than the expected factor

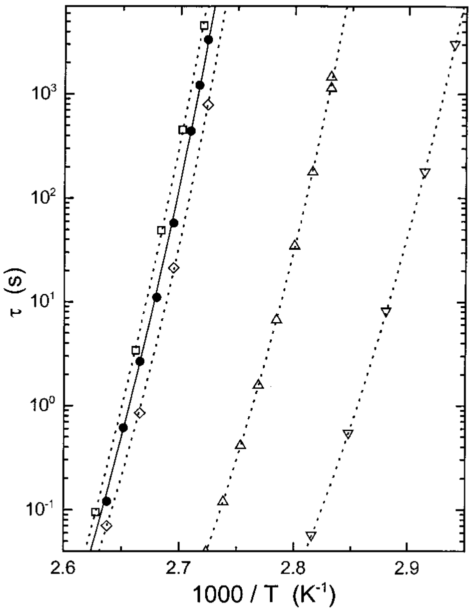

Figure 3. Segmental relaxation times from dynamic mechanical spectroscopy for the PS ring (●) and for linear PS with M_w equal to 3.7 (▽), 6.4 (△), 90 (◇), and 3840 kg/mol (□). The curves are fits to eq 3.

Table 1. Polystyrene Ring

M_w (kg mol)	T_g (K)	T_{ref} [a] (K)	log τ_0 (s)	B	T_0 (K)	m
4.6	374 ± 0.2	371	−17.15	2119	322.6	148

[a] Temperature at which segmental relaxation time equals 100 s.

of 2. However, the need to adjust the linear data for the M_w dependence of T_g introduces substantial error into the estimated η_0 for linear PS.

Local Segmental Relaxation. As seen in Figure 2, there is a dispersion in the loss modulus, associated with local segmental relaxation. The breadth of this peak was invariant to temperature over the measured range and equivalent to that found[6] for high molecular weight linear PS. From the frequency of the maximum in the loss modulus, ω_{max}, we obtain a relaxation time for local segmental motion, $\tau = 1/\omega_{max}$. These segmental relaxation times are plotted in Arrhenius fashion in Figure 3 along with the fit to the Vogel–Fulcher equation[20]

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{3}$$

The best-fit parameters are listed in Table 1. Also displayed in Figure 3 are the segmental relaxation times for linear PS of molecular weights encompassing that of the ring. Consistent with the high T_g of the latter, τ for cyclic PS are essentially equal to those of high molecular weight (>10^3 kg/mol) linear PS.

More interesting is the effect of temperature on these relaxation times. As seen in the figure, the curves for the ring and the high molecular weight linear PS appear to be parallel. To quantify the temperature dependences, we divide the temperatures by the respective value, T_{ref}, at which $\tau = 100$ s for each sample. This defines an effective glass temperature, more appropriate for dynamic data than a calorimetric T_g. Arrhenius plots using a T_{ref}-normalized temperature variable have been shown to be a self-consistent means to classify and distinguish segmental relaxation behavior of polymers.[21–24] From the slope at T_{ref}, a steepness index, m (often referred to as the "fragility"[25] or "cooperativity index"[26]), is obtained. In terms of the Vogel–Fulcher parameters, this parameter is given by[27]

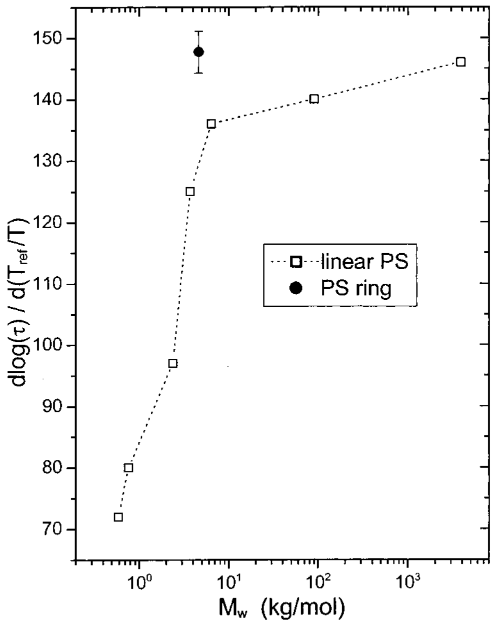

Figure 4. Steepness index at T_{ref} determined (eq 4) for linear PS and the PS ring. The dashed line is only a visual aide.

$$m \equiv \left.\frac{d\log(\tau)}{d(T_{ref}/T)}\right|_{T=T_{ref}} = \frac{B/T_{ref}}{(\ln 10)(1 - T_0/T_{ref})^2} \tag{4}$$

This steepness index is plotted for the PS ring in Figure 4 along with results for linear PS (some taken from ref 6 and some measured herein).

As seen in the figure, linear PS exhibits a systematic decrease in normalized temperature dependence with decreasing molecular weight. This is quite different from the behavior of more flexible polymers, such as poly(propylene oxide),[28] poly(phenylmethylsiloxane),[28] and poly(dimethylsiloxane),[29] for which the normalized temperature dependences of segmental relaxation times are independent of chain length. The stiffer PS chain, with its bulky pendant groups, is more constrained in its local motion, and it is this enhanced intermolecular cooperativity that gives rise to a larger value of m.[30–36]

Drawing on the general correlation between the temperature dependence of segmental relaxation and the degree to which the chemical structure engenders steric constraints on the local motion, we previously suggested[6] that the smaller m of low molecular weight PS reflects the presence of a high concentration of chain ends. The greater degree of configurational freedom conferred by the chain ends alleviates constraints on the local dynamics, thus reducing the temperature dependence.

Accordingly, if this explanation is correct, the PS ring, lacking this excess mobility, will exhibit a steepness index much closer to that of high molecular weight, linear PS. This is exactly what is observed in Figure 4; the PS ring exhibits a value quite close to the asymptotic m for high molecular weight linear PS. Thus, the previously reported dependence of m on molar mass for linear polymers[6] is indeed a chain end effect. Note that similar considerations appear to govern the molecular weight dependence of the glass temperature itself; to wit, polymers with high T_g's (reflecting more constrained local motion) tend to have more molecular weight-dependent glass temperatures (reflecting constraint mitigation from chain ends).[37]

Summary

We find that for a low molar mass ring PS the glass temperature and the steepness index describing the temperature dependence of segmental relaxation are equivalent to the high molecular weight limiting values for linear PS. This behavior can be ascribed to the absence of chain ends and the associated configurational freedom, which give rise to a molecular weight dependence of these properties in linear polymers. Thus, chain stiffness and (the related) intermolecular constraints govern the temperature dependence of local segmental relaxation.

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References and Notes

(1) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834.
(2) Roovers, J. *Polym. News* **1993**, *18*, 197.
(3) Di Marzio, E. A.; Guttman, C. M. *Macromolecules* **1987**, *20*, 1403.
(4) Muller, M.; Wittmer, J. P.; Cates, M. E. *Phys. Rev. E* **1996**, *53*, 5063.
(5) Brown, S.; Lenczycki, T.; Szamel, G. *Phys. Rev. E* **2001**, *63*, 52801.
(6) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31*, 4581.
(7) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.
(8) Lee, H. C.; Lee, H.; Wonmok, Lee; Chang, T.; Roovers, J. *Macromolecules* **2000**, *33*, 8119.
(9) Cho, D.; Park, S.; Kwon, K.; Chang, T.; Roovers, J. *Macromolecules*, in press.
(10) Ueberreiter, K.; Kanig, G. *J. Colloid Sci.* **1952**, *7*, 569.
(11) Roovers, J. *Macromolecules* **1985**, *18*, 1359. The present ring PS, prior to purification using HPLC at the chromatographic critical condition, is identical to the sample identified as R17H in this earlier publication.
(12) Gan, Y.; Dong, D.; Hogen-Esch, T. E. *Macromolecules* **1995**, *28*, 383.
(13) Liu, X.; Chen, D.; He, Z.; Zhang, H.; Hu, H. *Polym. Commun.* **1991**, *32*, 123.
(14) Yang, A. J.-M.; Di Marzio, E. A. *Macromolecules* **1991**, *24*, 6012.
(15) Plazek, D. J.; O'Rourke, V. M. *J. Polym. Sci., Part A2* **1971**, *9*, 209.
(16) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(17) Fetters, L. J.; Lohse, D. J.; Colby, R. H. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; American Institute of Physics: Woodbury, NY, 1996.
(18) Roovers, J. *Macromolecules* **1988**, *21*, 1517.
(19) McKenna, G. B.; Hadzlioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 498.
(20) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980; p 289.
(21) Oldekop, W. *Glastech. Ber.* **1957**, *30*, 8.
(22) Laughlin, W. T.; Uhlmann, D. R. *J. Phys. Chem.* **1972**, *76*, 2317.
(23) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222.
(24) Bohmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.
(25) Angell, C. A. *Science* **1995**, *67*, 1924.
(26) Roland, C. M.; Santangelo, P. G.; Plazek, D. J.; Bernatz, K. M. *J. Chem. Phys.* **1999**, *111*, 9337.
(27) Bohmer, R.; Angell, C. A. *Phys. Rev B* **1993**, *48*, 5857.
(28) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 5765.
(29) Roland, C. M.; Ngai, K. L. *Macromolecules* **1996**, *29*, 5747.
(30) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 5315; **1992**, *25*, 1844.
(31) Ngai, K. L.; Roland, C. M. *Macromolecules* **1993**, *26*, 6824.
(32) Ngai, K. L.; Roland, C. M. *Macromolecules* **1993**, *26*, 2688.
(33) Roland, C. M. *Macromolecules* **1994**, *27*, 4242.
(34) McGrath, K. J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1995**, *28*, 2825.
(35) Santangelo, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1996**, *29*, 3651.
(36) Roland, C. M.; Ngai, K. L. *J. Non-Cryst. Solids* **1997**, *212*, 74.
(37) Boyer, R. F. *Macromolecules* **1974**, *7*, 142. Cowie, J. M. G. *Eur. Polym. J.* **1975**, *11*, 297.

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