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Melt Properties of Ring Polystyrenes†

Recently, narrow molecular weight distribution ring polystyrenes with molecular weights between 7000 and 450 000 have been prepared and characterized and some of their dilute solution properties have been described.[1,2] As an example of the purity of the ring polymers, the sedimentation boundaries of a ring polymer (R19D) and a synthetic mixture of the ring and its linear precursor are compared in Figure 1. There is presently speculation about the melt properties of large entangled rings because neither the reptation mechanism of linear polymers nor the chain retraction prominent in star polymers is expected to be effective in rings. Indeed, both relaxation mechanism require the existence of chain ends. The melt viscosities of unentangled low molecular weight poly(dimethylsiloxane) rings are approximately half those of linear polymers,[3] in agreement with the modified Rouse normal mode analysis.[4]

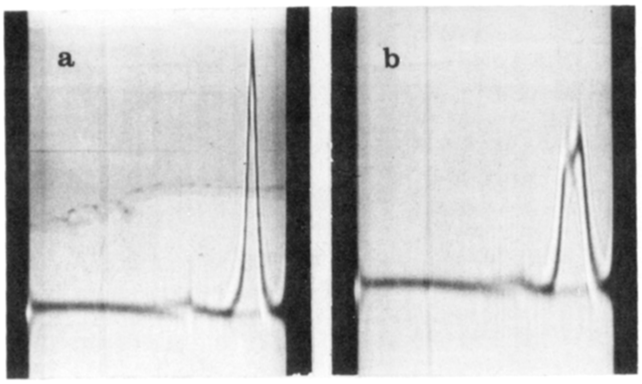

Figure 1. (a) Ultracentrifugation boundary of ring polystyrene R19D in cyclohexane at 35 °C and 60 000 rpm. Sedimentation from left to right. (b) Same as (a) for a synthetic mixture of R19D and 20% linear percursor. Due to the Johnston–Ogston effect the slower sedimenting 20% linear polymer appears as almost 50% of the total.

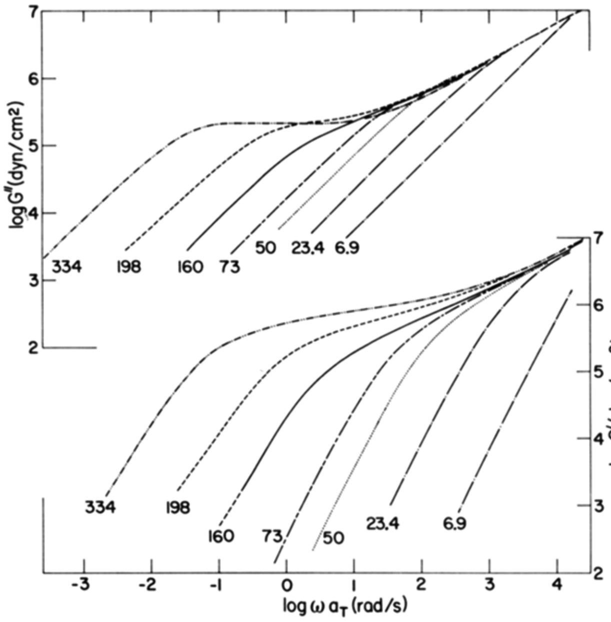

Figure 2. Moduli–frequency master curves for the ring polymers at T_r = 169.5 °C. Numbers indicate molecular weight ($\times 10^{-3}$) of the polymers.

The glass transition temperature (T_g) of the rings was measured with a Du Pont 1090 thermal analyzer in the DSC mode. The heating rate was 10 °C/min. In Table I, $\Delta T_g = T_g(\infty) - T_g$ is given, where $T_g(\infty)$ is the high molecular weight limit of T_g. The experimental $T_g(\infty)$ for ring and linear polystyrene is the same. The true glass transition temperature of polystyrene was taken equal to 100 °C. From Table I it can be seen that the dependence of ΔT_g on molecular weight is less for rings than for linear polymers. This is in qualitative agreement with the hypothesis that T_g is inversely proportional to the chain-end concentration.[5] The reason for the residue decrease of T_g with decreasing molecular weight of the rings is not known.

The storage (G') and loss (G'') moduli of the melts were measured with a Rheometrics mechanical spectrometer in the dynamic mode. Measurements as a function of frequency (ω) were made at temperatures between T_g + 40 °C and T_g + 110 °C. Master curves at the reference temperature T_r = 169.5 °C were constructed by horizontally shifting the moduli–frequency curves at the other temperatures by a_T. Master curves are shown in Figure 2. Vertical shifts smaller than $(\rho_r T_r)/(\rho T)$, where ρ is the density of the melt, were only applied above T_g + 90 °C. No evidence of degradation during melt measurements was found by GPC. The observed zero-shear viscosities, $\eta_0 = \lim_{\omega \to 0} (G''/\omega)$, of the ring and linear polymers at T_r are given in Table I and plotted double-logarithmically against M_w on the left-hand side of Figure 3. Except for the low molecular weight ring, η_0 of the rings is less than that of the linear polymers. The isothermal data were converted to iso-free volume data. The temperature dependence of η_0 and a_T was found to be given by log a_T = log η_0 = $B/[2.303\alpha_f(T - T_0)]$.[6] The slopes of plots of log a_T vs. $1/(T - T_0)$, where T_0 and T_g − 55 °C, gave 764 ± 15 K for all linear and ring polymers except PS10 and PS5. With B = 1, α_f, the thermal expansion coefficient of the fractional free volume, is 5.7×10^{-4} K^{-1}, in good agreement with published data.[7,8] Zero-shear viscosities at T_g + 69.5 °C (fractional free volume f = 0.071) are also given in Table I. For PS10, $T_0 = T_g - 51.5$ °C, $\alpha_f = 5.95 \times 10^{-4}$, and f = 0.071 at 158.4 °C. For PS5, $T_0 = T_g - 45.3$ °C, α_f = 6.4 $\times 10^{-4}$, and f = 0.071 at 147.7 °C. From the right-hand side of Figure 3 it can be seen that for linear polystyrene under iso-free volume conditions $\eta_0 \propto M_w$ below M_w = 38 000 and $\eta_0 \propto M_w^{3.4}$ above 38 000. For the rings, values

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Table I
Melt Properties of Ring and Linear Polystyrenes

<table>
<tr><th>sample</th><th>$M_w \times 10^{-5}$</th><th>ΔT_g</th><th>$\eta_0^{169.5}$, P</th><th>$\eta_0^{T_g+69.5}$, P</th><th>$J_e^\circ \times 10^6$, cm²/dyn</th></tr>
<tr><td colspan="6">Linear</td></tr>
<tr><td>PS5 bis</td><td>0.048^b</td><td>18.8</td><td>9.4×10</td><td>6.9×10^2</td><td>0.05</td></tr>
<tr><td>PS10</td><td>0.105</td><td>10.1</td><td>3.9×10^2</td><td>1.2×10^3</td><td>0.09</td></tr>
<tr><td>PS17</td><td>0.171^b</td><td>5.5</td><td>1.3×10^3</td><td>2.4×10^3</td><td>0.21</td></tr>
<tr><td>PS30f3</td><td>0.35_5</td><td>2.7</td><td>5.9×10^3</td><td>7.8×10^3</td><td>0.40</td></tr>
<tr><td>PS90</td><td>0.95</td><td></td><td>8.6×10^4</td><td>9.6×10^4</td><td>0.89</td></tr>
<tr><td>PS100f2^a</td><td>1.15</td><td>0.7</td><td colspan="2">$1.6_7 \times 10^5$</td><td>1.08</td></tr>
<tr><td>PS150f2</td><td>2.16</td><td></td><td colspan="2">1.6×10^6</td><td>1.10</td></tr>
<tr><td>C6bb^a</td><td>2.75</td><td></td><td colspan="2">3.1×10^6</td><td>1.20</td></tr>
<tr><td>PS350</td><td>3.46</td><td></td><td colspan="2">7.6×10^6</td><td>1.10</td></tr>
<tr><td>PS830</td><td>8.0</td><td></td><td colspan="2">1.4×10^8</td><td>1.15</td></tr>
<tr><td>C7bb^a</td><td>8.6</td><td>0.0</td><td colspan="2">1.5×10^8</td><td>1.25</td></tr>
<tr><td colspan="6">Ring</td></tr>
<tr><td>R17H</td><td>0.069^c</td><td>3.2</td><td>3.0×10^2</td><td>4.3×10^2</td><td>0.028</td></tr>
<tr><td>R7F</td><td>0.12^c</td><td>2.5</td><td></td><td></td><td></td></tr>
<tr><td>R16E</td><td>0.18^c</td><td>1.9</td><td></td><td></td><td></td></tr>
<tr><td>R1F</td><td>0.234</td><td>1.0</td><td>1.8×10^3</td><td>2.0×10^3</td><td>0.22</td></tr>
<tr><td>R4DB</td><td>0.50</td><td>0.4</td><td colspan="2">6.7×10^3</td><td>0.86</td></tr>
<tr><td>R8DC</td><td>0.73</td><td></td><td colspan="2">1.4×10^4</td><td>1.7</td></tr>
<tr><td>R18D</td><td>1.60</td><td></td><td colspan="2">7.4×10^4</td><td>6.0</td></tr>
<tr><td>R10DD</td><td>1.98</td><td></td><td colspan="2">6.2×10^5</td><td>(39.)^d</td></tr>
<tr><td>R12D</td><td>2.58</td><td>0.0</td><td colspan="2"></td><td></td></tr>
<tr><td>R19D</td><td>3.34</td><td></td><td colspan="2">7.5×10^6</td><td>*e*</td></tr>
</table>

[a] Reference 10. [b] M_n. [c] From GPC of linear precursor. [d] Estimation. [e] Could not be determined experimentally.

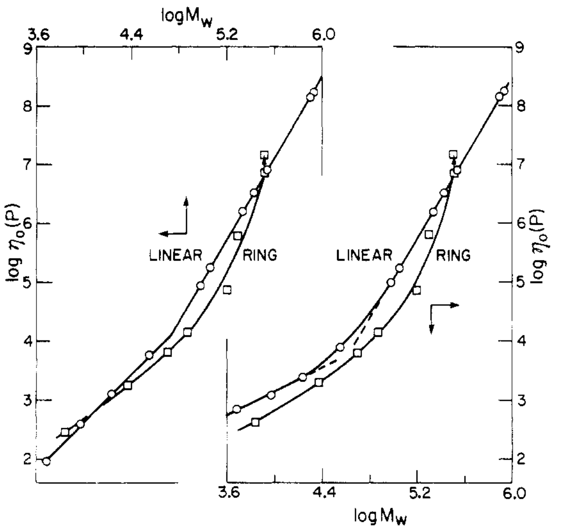

Figure 3. Left-hand side: double-logarithmic plot of η_0 vs. M_w at T_r = 169.5 °C. Right-hand side: double-logarithmic plot of η_0 vs M_w at T_r = 169.5 °C under iso-free volume conditions. See text for an explanation of arrow.

of η_0 are all lower than for the linear polymers. At low molecular weight, $(\eta_0)_r/(\eta_0)_l \approx 0.5$, in accordance with the modified free-draining Rouse model.[4] Our viscosity data for *low* molecular weight rings agree with those quoted by McKenna when his results are divided by 13.8 to correct for the different reference temperature.[9] However, at high molecular weight $(\eta_0)_r/(\eta_0)_l > 0.5^{3.4}$, the ratio expected when the viscosity depends only on the size of the polymer. Note that the random flight model for rings gives $g_r = (\langle S^2\rangle_0)_r/(\langle S^2\rangle_0)_l = 0.5$. Also, for the high molecular weight rings η_0 has a stronger dependence on M than $M^{3.4}$ and at M_w = 340 000 $(\eta_0)_r/(\eta_0)_l \approx 1$. These results suggest that high molecular weight polystyrene have large enhancements of viscosity.[10,11]

At this point it is useful to compare the master curves of a ring and a linear polymer in Figure 4 (R19D and PS350: $M_w \approx 340000$, $\eta_0 = 7.5 \times 10^6$ P). It can be seen that values of G'' of the ring are lower than for the linear polymer over the entire plateau zone. Indeed, determination of the plateau modulus, G_N°, according to $G_N^\circ = (2/\pi)\int_{-\infty}^{\infty}(G'' - G_s'')\ln\omega\, d\omega$, where G_s'' is the contribution from the glassy state to G'', reveals that for R19D $(G_N^\circ)_r \approx {}^1/_2(G_N^\circ)_l$. This is qualitatively confirmed by the lower value of G' of the ring, e.g., at log (ωa_T) = 2. A similar conclusion is drawn from the data of the other entangled rings, although the evaluation of G_N° is not very accurate. Since M_e, the molecular weight between entanglements, is given by $\rho RT/G_N^\circ$, it follows that the apparent M_e for the rings is about twice that for the linear polymer. It has been shown for a large variety of branched polymers that M_e depends only on the chemical nature of the polymer and is practically independent of their large-scale architecture.[10-12] The low value of $(G_N^\circ)_r$ could therefore mean that rings occur as double strands. This is a very unlikely configuration, however. Alternatively, it is conceivable that the rings are not fully entangled at the time of the measurements, due to their very slow interdiffusion.[13] Such a nonequilibrium state can be observed with ultrahigh molecular weight polystyrene.[14] It is expected that the equilibration time strongly increases with the molecular weight of the ring.

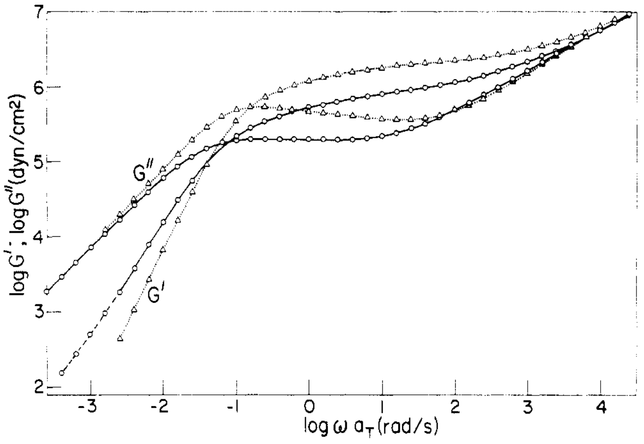

Figure 4. Comparison of the moduli–frequency master curves. Full lines: ring R19D; dotted lines: linear PS350.

To increase the entanglements of the ring samples solutions of about 50% polymer in benzene were prepared and slowly evaporated. In the case of R4DB (M_w 50 000) no change in η_0 was observed. It is concluded that the observed melt viscosities of the lightly entangled rings (MW < 10^5) are probably true values. R19D was treated similarly. When the polymer content reached 90%, the sample was placed for 3 h at 150 °C in a pressure vessel in a benzene atmosphere. All residual benzene was removed under vacuum at room temperature. After this treatment the melt viscosity of R19D increased by a factor of 2 (arrow in Figure 3) and $(G_N^\circ)_r$ had risen from $0.5(G_N^\circ)_l$ to $0.7(G_N^\circ)_l$. Unfortunately, the ultracentrifuge pattern of the sample indicated that some degradation had occurred during the treatment and subsequent measurements (30% linear polymer with the same molecular weight as the ring and 20% low molecular weight material). Nevertheless, the increased melt viscosity indicates that the increased entanglement of the rings outweighs the effects of low molecular weight linear material in the sample. Of course, it is not established that in the limit $(G_N^\circ)_r = (G_N^\circ)_l$.

Ring polymers with MW > $(M_c)_l/g_r \approx 7 \times 10^4$ are expected to be effectively entangled. However, because of the low values of $(G_N^\circ)_r$ the measured viscosities of the large entangled rings are probably only minimum values that differ increasingly from the true η_0 as the molecular weight increases. For the same reason, the values of the recoverable compliance J_e° of the rings ($J_e^\circ = 1/\eta_0^2 \lim_{\omega\to 0} (G'/\omega^2)$) given in Table I are probably only apparent. Note, however, that for the lowest molecular weight ring $J_e^\circ \approx {}^1/_2(J_e^\circ)_l$, in accord with the Rouse model.[4]

In conclusion, it can be said that the observed melt viscosities are minimum values which show enhanced η_0 over linear polymers of the same *size*. Therefore, these data provide partial indirect evidence for the tube model and reptation.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

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Observations of a "Gel" Phase in Binary Mixtures of Semifluorinated *n*-Alkanes with Hydrocarbon Liquids

Semifluorinated *n*-alkanes, $F(CF_2)_n(CH_2)_mH$ (F*n*H*m* in our notation) have been the subject of a number of recent studies in both the melt[1] and solid state.[2-4] Results indicate that only partial disordering of the molecular chain occurs in the melt, with a partial ordering maintained in the fluorocarbon portion of the molecule. When these materials crystallize, several different morphologies result,[2] depending on the fluorocarbon-to-hydrocarbon ratio (n/m) in the molecule.

An investigation of binary mixtures of semifluorinated *n*-alkanes in hydrocarbon liquids has revealed[5] the existence of a new phase which exhibits gel-like characteristics and henceforth will be referred to as a "gel". This phase results when a mixture of an F*n*H*m* compound and various hydrocarbon liquids (see Tables I and II) is heated above the melting point of the corresponding F*n*H*m* to form a homogeneous fluid and then allowed to cool to room temperature. Once the gel is formed, the transition between the gel phase and an isotropic, transparent fluid is reversible. The temperature, T_c, at which this transition occurs and the opacity of the gel phase depend upon the concentration of the components in the mixture. This transition temperature above which the mixture is visibly transparent also corresponds (±2 °C) to an endotherm easily measured by differential scanning calorimetry (DSC). However, in comparison to the melting endotherm observed for the neat F*n*H*m*, the endotherm of the gel transition is broad (extending over some 40 °C compared to 10 °C for the solid) and skewed toward the low-temperature side, indicating that a gradual disordering occurs over this range prior to the temperature of the endotherm minimum. In addition, the enthalpies (per mole of F*n*H*m*) of the observed gel transitions have been found to be consistently larger than that found for the melting of the pure solid.

Macroscopically the "gel" phase is manifested by an extremely large zero-shear viscosity, which reverts to that of a low-viscosity liquid upon heating above T_c. When this "gel" phase was vigorously shaken it remained intact. In fact, it could also be inverted in a tube and left for several days without any noticeable flow. Microscopically the gel was observed to exhibit birefringence between crossed polarizers which disappeared above T_c. Under high magnification the presence of what appeared to be a microfibrillar morphology was also noted.

Table I
F*n*H*m* + Decane

n	*m*	gel formed
12	2	no
12	4	no
12	6	marginal
12	8–20	yes
14	0	no

Table II
F10H12 + Solvent

solvent	gel formed	solvent	gel formed
octane	yes	perfluorooctane	no
decane	yes	cyclodecane	yes
dodecane	yes	caprylic acid	yes
tetradecane	yes	PEO-400	no
hexadecane	yes	2-methylnonadecane	yes
perfluorocyclohexane	no	decalin	yes