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grateful for timely discussions with C. Cohen, B. A. Smith, and P. F. Green.

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Viscoelastic Properties of Polybutadiene Rings[†]

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ABSTRACT: The linear viscoelastic properties of a series of linear and three ring polybutadienes have been studied. It is observed that melt viscosity of a pure ring is about 10 times smaller than that of the linear polymer with the same molecular weight. The plateau modulus is similarly 5 times smaller. Rings contaminated with 20–25% linear polymer have the same melt viscosity as linear polymers, although their plateau modulus is only about one-half times that of the linear polymer. Synthetic mixtures of ring and linear polymers were used to complete a study of the effect of linear impurities on the melt properties of rings. The data are compared with data obtained previously on polystyrene ring samples.

Introduction

Ever since the introduction of the reptation model[1] for the relaxation and diffusion of long linear polymers in the melt and in concentrated solutions, a wide search has gone on to determine the range of validity of this powerful concept. Research has proceeded in two directions. In one approach the application of the reptation model to linear polymers has been finetuned by the introduction of tube renewal[2] and contour-length fluctuation[3] effects. Experiments have been performed to evaluate the former by studying relaxation of linear polymers in networks,[4] by studying binary mixtures of linear polymers,[5–7] and by measuring the diffusion rates of linear polymers in various linear matrices.[8] Contour-length fluctuations are shown to be very important in the relaxation of low molecular weight polymers in the range $M = 2\text{–}5M_e$,[9] where M_e is the molecular weight between entanglements, and to disappear gradually for $M > 200M_e$.[10] The other approach taken consists of modifying the polymers with long branches and making ring polymers. For example, the central branch point of star polymers prevents reptation,[11] and arm retraction, an extended countor-length fluctuation, becomes the prominent relaxation mechanism,[11–14] for which substantial experimental evidence has been gathered.[15–18] The role of tube renewal in stars is also being documented.[19,20] It has been shown that in long-chain comb polymers the longest relaxation times are associated with the tube renewal relaxation of backbone segments between branches.[21]

In entangling ring polymers neither reptation nor arm retraction are expected to operate and since tube renewal is a second relaxation process driven by a primary relaxation process such as reptation or arm retraction it is not clear how rings in rings can relax and diffuse. A number of theoretical papers have recently appeared on the general subject of relaxation and diffusion of rings. Klein has introduced the distinction between pinned (with entanglements on the inside of the ring) and unpinned rings and estimated their concentrations.[22] Diffusion and relaxation would occur mainly by the unpinned fraction. Others explore the statistics and dynamics of rings in networks and touch upon the more difficult problem of rings in rings and rings in linear polymers.[23,24] A study of diffusion of rings in linear polymers found rings to diffuse slower than linear polymers, almost with the rate expected for a tube renewal mechanism.[25]

With respect to viscoelastic measurements two sets of data have been published recently on the molecular weight dependence of the melt viscosity, η_0, of ring poly-

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styrenes.[26,27] While the data for low MW rings ($M_w < 5 \times 10^4$) of the two laboratories agree with each other and with the theoretical prediction that $(\eta_0)_r = {}^1/_2(\eta_0)_l$, the values of η_0 for high MW rings ($5 \times 10^4 < M_w < 3.9 \times 10^5$) obtained in the two laboratories are substantially different and have been differently interpreted.

The Strasbourg group found that the melt viscosities of high MW ring polymers followed a $M^{3.4}$ dependence as do linear polymers and that at constant MW $(\eta_0)_l > (\eta_0)_r > {}^1/_2(\eta_0)_l$. They found also that the MW for the onset of entanglement effects in η_0 is almost identical for linear and ring polymers. These results are important because the Strasbourg interpretation puts doubt on the reptation mechanism as the dominant long-time relaxation mechanism for long linear polymers.[26,28] Indeed, if the melt behavior of ring and linear polymers is a similar as found by the Strasbourg group, a common relaxation mechanism should be favored.

The melt viscosities of rings obtained in our laboratory are substantially lower than those of linear polystyrene in the range $5 \times 10^4 < M_w < 2.0 \times 10^5$ while one ring with $M_w = 3.34 \times 10^5$ had $(\eta_0)_r \approx (\eta_0)_l$. The result of these data was that the melt viscosities of low MW but "entangled" polystyrene rings are thought to be lower than for linear polymers. However, the melt viscosity of rings shows a stronger, possibly exponential, MW dependence than the power law dependence observed for linear polymers at high molecular weight.

An important note was subsequently published by McKenna and Plazek,[29] showing that the melt viscosity of a ring polymer increases rapidly on addition of small amounts of linear polymer. They found

$$(\eta_0)_r \propto \phi_r^{-5.6} \tag{1}$$

for $\phi_r > 0.85$ where ϕ_r is the volume fraction of ring polymer. They added linear polymer with approximately the same MW as the ring, a practice that has been followed throughout the work to be described. This is in agreement with a qualitative experiment that showed that degradation of a ring increased η_0.[27]

The sensitivity of the melt viscosity to traces of linear polymer suggests that lower values of $(\eta_0)_r$ should be retained. E.g., the relatively large scatter in the $(\eta_0)_r$–M_w plot[27] may be caused by the presence of variable small amounts of linear impurities that are not detected by other techniques.

Recently, three ring polybutadienes and a number of reference linear polybutadienes with the same microstructure have been prepared.[30] A high-resolution SEC column set has been used to determine quantitatively the amount of linear impurity in the ring polymers. It is therefore now possible to correlate unambiguously the melt viscosities and other properties such as the plateau modulus, G_N^0, and zero-shear recoverable compliance, J_e^0, with the linear polymer content of the rings. Synthetic mixtures of ring and linear parent polymer were also made and studied. The high MW ring polystyrenes, when still available, were analyzed in the high-resolution SEC column set and the melt data correlated with the weight fraction of linear polymer.

It is worth noting that, although the synthesis of ring polybutadienes is inherently more difficult than the synthesis of ring polystyrenes,[30] there are major advantages to their study. As will be shown, the entanglement molecular weight of the polybutadienes prepared with potassium naphthalene initiator is 2750 compared to 18 000 for polystyrene. Relatively low MW polybutadienes have all the rheological characteristics of entangled polymers. Moreover, at room temperature all polybutadienes are well above their T_g, and slow relaxation and diffusion processes, if important, are not frozen in on ordinary storage as happens with polystyrene. Finally, the melt properties can be measured at or near room temperature and the risk of polymer degradation is reduced.

Table I
Viscoelastic Melt Properties of Linear Polybutadienes at 26.2 °C

sample	$10^{-4}M_w$	η_0, P	$10^7 J_e^0$, cm^2/dyn	$10^{-6}G_N^0$, dyn/cm^2	$10^{-6}G''_{max}$, dyn/cm^2
KPBD 29	2.05	1.46×10^4	2.3_8		
31PC	3.6_3	1.4×10^5	2.8_2		2.1_5
32PC	4.4_0	2.1×10^5	2.9_5	7.8	2.0_4
34PC	5.7	6.7×10^5	2.8_5	8.6	2.1_3
26	8.6	$2.8_3 \times 10^6$	2.8_2	8.7	2.1_5
28	23.2	1.1×10^8	(3.1_6)	8.7	2.1_7

Table II
Viscoelastic Melt Properties of Ring Polybutadienes and Their Mixtures with the Linear Parent Polymer at 26.2 °C

sample	$10^{-4}M_w$	ϕ_l	n_0, P	$10^7 J_e^0$, cm^2/dyn	$10^{-6}G_N^0$, dyn/cm^2
KPBD31B4	3.8	0.25	1.5×10^5	7.6	
KPBD32B4	4.2	0.20	2.4×10^5	9.5	4.0 ± 0.2
A		0.36	3.8×10^5	8.0	5.0
B		0.46	4.3×10^5	8.0	5.1
C		0.60	$4.8_5 \times 10^5$	7.2	6.3_5
D		0.73	$4.3_5 \times 10^5$	7.2	7.4
KPBD34B3	6.0_7	0.0	6.3×10^4	33.9	1.3
A		0.07	$2.9_5 \times 10^5$	17.2	1.9
B		0.14	5.8×10^5	14.4	2.5_5

Table III
Melt Properties of Ring Polystyrenes at 169.5 °C[27]

sample	$10^{-5}M_w$	ϕ_l	η_0, P	$(\eta_0)_r{}^a/(\eta_0)_l$	$10^{-6}G_N^0$, dyn/cm^2
R18D	1.60	0	7.4×10^4	0.136	0.58
R10DD	1.98	0.12	6.2×10^5	0.55	0.85
R19D	3.34	*b*	7.5×10^6	~1.0	1.0_6
R19Drepeat[c]	3.34	0.50	1.5×10^7	~2.0	1.4

[a] Based on $(\eta_0)_l = 1.4 \times 10^{-12} M^{3.38}$ for linear polystyrene at 169.5 °C. [b] Linear contamination unknown; the sample was degrading during the low-frequency (high-temperature) measurements; the original sample contains 5–10% linear polymer. [c] See ref 27 for experimental procedure; ϕ_l was also determined by UC sedimentation analysis.

Experimental Section

The synthesis and dilute solution characterization of the linear and ring polybutadienes has been described previously.[30] The microstructure is 63% 1,2, 30% trans-1,4, and 7% cis-1,4. The weight average MW of the samples is given in Tables I and II. Intrinsic viscosity measurements in toluene gave $g'_r = [\eta]_r/[\eta]_l = 0.63$ for KPBD34B3.[30] The values of $g'_r = 0.70$ and 0.71 for KPBD31B4 and KBPD32B4, respectively, are indicative of contamination with linear polymer.[30] High-resolution SEC[30] allows a reasonably accurate determination (within 3%) of the fraction of linear polymer in the rings or in synthetic mixtures. Values of ϕ_l are given in Tables II and III. The contaminant is almost exclusively the linear parent polymer.

The linear viscoelastic properties were measured with a Rheometrics mechanical spectrometer (Model 605M) in the dynamic mode between parallel platens. Shear loss (G'') and storage (G') moduli were determined as a function of frequency from ω = 0.01 to 100 rad/s for temperature between 88 and −25 °C. Master curves were constructed by superimposing the experimental moduli obtained at different temperature onto the moduli at the reference temperature, 26.2 °C. In order to obtain superposition the moduli are corrected by a small factor, b_T. Horizontal shift factors are applied to the frequency axis, their temperature dependence is given by

$$\log a_T = \frac{650 \pm 20}{T - T_\infty} \tag{2}$$

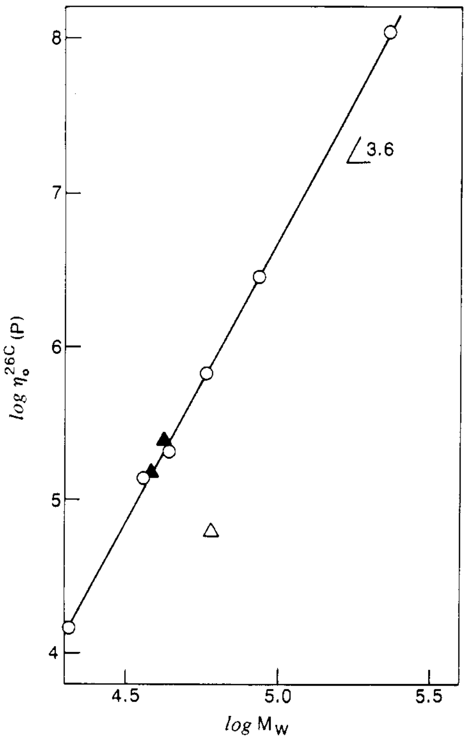

Figure 1. log–log plot of η_0 versus M_w for linear and ring polybutadienes at 26.2 °C. The full triangles indicate rings contaminated with 20–25% linear polymer. The open triangle is KPBD34B3.

where $T_\infty = T_g - 55$. T_g of the polybutadienes is −40 °C, as measured by DSC and extrapolated to zero heating rate. The limiting low shear rate properties are calculated by [31]

$$\eta_0 = \lim_{\omega\to 0} \frac{G''(\omega)}{\omega} \qquad (3)$$

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega\to 0} \frac{G'(\omega)}{\omega^2} \qquad (4)$$

and the plateau modulus is obtained by

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{+\infty} [G''(\omega) - G''_s(\omega)] \, d \ln \omega \qquad (5)$$

where $G''_s(\omega)$ is the contribution from the transition region.

Results and Discussion

The melt characteristics of the linear polybutadienes are given in Table I. The zero-shear viscosity is plotted double logarithmically against molecular weight in Figure 1. The zero-shear viscosity at 26.2 °C is given by

$$\eta_0 = 2.8 \times 10^{-12} M_w^{3.65} \qquad (6)$$

From Table I it can be seen that the zero-shear recoverable compliance of the linear polybutadienes is 2.8×10^{-7} cm^2/dyn. Sample KPBD28 has a slightly wider molecular weight distribution which accounts for a 10% higher value of J_e^0. The MW of KPBD29 is probably close to M_c', the MW at which the dependence of J_e^0 changes from proportional to independent of molecular weight.

Values of G_N^0 of the linear samples are collected in Table I. The molecular weight between entanglements is calculated from

$$M_e = \rho RT / G_N^0 \qquad (7)$$

where $\rho = 0.89$ is the density,[32] R the gas constant, and T the absolute temperature. For the 63% 1,2-polybutadiene $M_e = 2600$ from eq 7. An estimate of G_N^0 can also be obtained from the empirical relation[32]

$$G_N^0 = 3.56 G''_{\max} \qquad (8)$$

used by Carella to determine values of M_e for polybutadienes of different microstructures. Values of $G''_{\max}$, the maximum G'' in the terminal zone, are given in Table I. Relation 8 leads to $M_e = 2900$. It is noteworthy that the numerical factor in eq 8 depends on the molecular weight distribution of the sample. The originally proposed coefficient is 4.83.[31] In view of the experimental uncertainty in both values of M_e an average $M_e = 2750$ has been adopted.

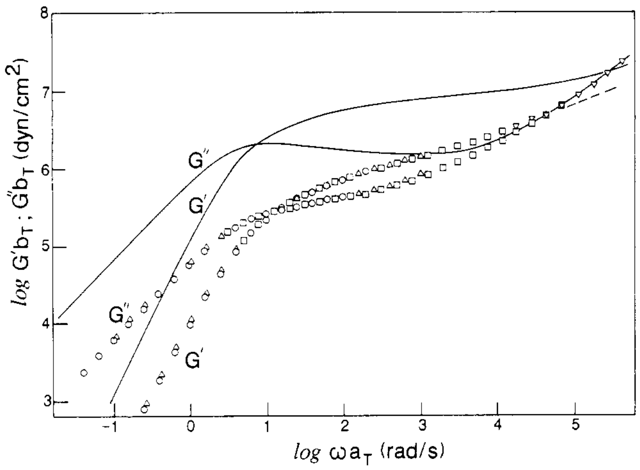

Figure 2. Comparison of the dynamic moduli of ring KPBD34B3 (symbols) and the linear parent polymer KPBD34PC (lines) at 26.2 °C. Symbols: ○, 26.2 °C; △, 7 °C; □, −10.3 °C; ▽, −25 °C. For clarity one-half of the experimental points were omitted.

The product $J_e^0 G_N^0 = 2.3$ is a measure of the width of the terminal relaxation time distribution.[33] The value obtained here is slightly larger than for very narrow MW distribution 1,4-polybutadienes.[16]

The melt properties of the ring polybutadienes are collected in Table II. The shear-moduli master curves of a ring are compared with those of the linear parent polymer in Figure 2. The low values of G'' and G' in the plateau and terminal zone should be noted.[27] As can be seen in Figure 1 the melt viscosities of two rings KPBD31B4 and KPBD32B4, which contain 25 and 20% linear polymer respectively, are almost identical with η_0 of linear polybutadiene. On the contrary the melt viscosity of KPBD34B3, which is free of linear polymer, is more than 10 times smaller than $(\eta_0)_l$. These results are in qualitative agreement with the large increase of η_0 of polystyrene rings when small amounts of linear parent polymer are added.[29]

In order to obtain more quantitative information on the effect of linear polymers on the melt viscosity of rings the three highest polystyrene rings for which melt viscosities are available[27] were analyzed by SEC. The results are given in Table III together with values of η_0 at 169.5 °C.[27] A comparison of the ratio $(\eta_0)_r/(\eta_0)_l$ given in Table III with ϕ_l shows clearly that for the purest ring R18D, $(\eta_0)_r/(\eta_0)_l = 0.13$ quite similar to the result obtained for the best polybutadiene ring, while for the other polystyrene samples $(\eta_0)_r/(\eta_0)_l$ increases with ϕ_l. It appears therefore that only two ring polymers, R18D and KPBD34B3, are sufficiently pure to yield reliable values of η_0.

Further progress in understanding the effect of linear polymer on the melt viscosity is made by inspection of a plot of $(\eta_0)_r/(\eta_0)_l$ for all available polystyrene and polybutadiene samples against the "nominal" number of entanglements per chain M_w/M_e in Figure 3. The MW's of

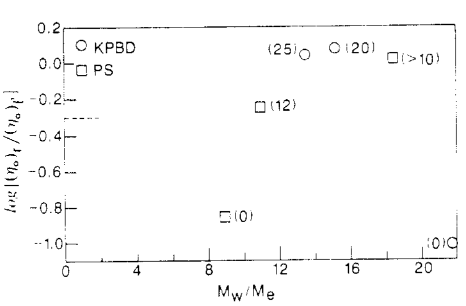

Figure 3. log of $(\eta_0)_r/(\eta_0)_l$ as a function of the nominal number of entanglements per chain. The numbers in parentheses indicate the percent linear polymer in the sample. The dashed line is the low MW limit.

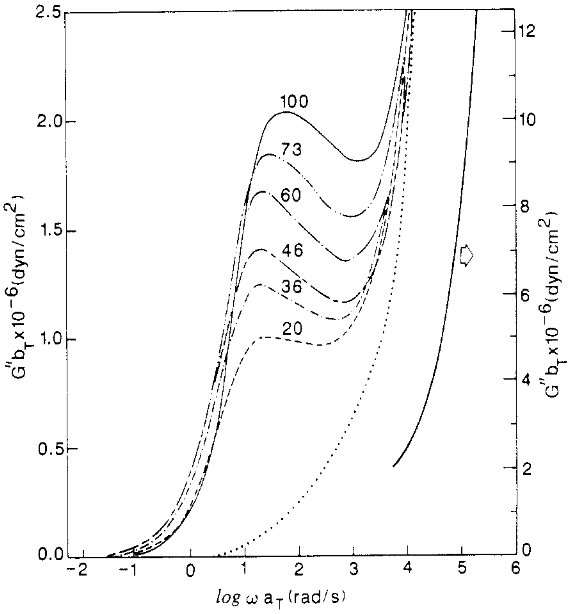

Figure 4. G'' plotted against the logarithm of the frequency for the synthetic mixtures made with KPBD32B4 and KPBD32PC. Reference temperature is 26.2 °C. Dotted line is $G''_s(\omega)$ in eq 5.

the good rings bracket all other samples. Samples with 20–25% linear polymer have $(\eta_0)_r/(\eta_0)_l \approx 1$ in this molecular weight range. Figure 3 indicates that to a first approximation, $(\eta_0)_r/(\eta_0)_l$ of "perfect rings" is independent of the ring MW in the range $8 < M_w/M_e < 22$.

A number of synthetic mixtures of ring with linear polybutadienes have been prepared. Some $G''(\omega)$ curves are presented in Figure 4. Their composition and the melt characteristics are given in Table II. Values of $(\eta_0)/(\eta_0)_l$ are plotted against $\phi_r = (1 - \phi_l)$ in Figure 5. Although there is some scatter in the experimental data, the overall picture that evolves from Figure 5 is that η_0 of a ring polymer increases on addition of linear polymer to $\phi_l = 0.5$. At the $\phi_l = 0.5$, $(\eta_0)/(\eta_0)_l \approx 2.3$. At $\phi_l > 0.5$, $(\eta_0)/(\eta_0)_l$ decreases, presumably to unity at $\phi_l = 1.0$. The same data are plotted logarithmically in Figure 6. For $0.1 < \phi_l < 0.2$ the dependence of η_0 on ϕ_l can be represented by $\eta_0 \propto \phi_r^{-5.6}$ as proposed by McKenna (eq 1).[29] However, for lower fractions of linear polymer, $0 < \phi_l < 0.1$ the dependence is much stronger.

In order to understand why the melt viscosities of ring polymers are so low and so strongly affected by the presence of linear polymer, it is useful to consider the values of G_N^0 for the rings and the mixtures with linear polymer. G_N^0 has been determined from data as shown in Figure 4 with eq 5. Values of G_N^0 for the polybutadiene samples are given in Table II, and those for polystyrene are given in Table III. It should be mentioned that the accuracy of G_N^0 for the present rings is not very high because of the important overlap of the plateau and transition zones. For pure rings $G_N^0 \approx 0.2(G_N^0)_l$ and G_N^0 increases with increasing weight fraction of linear polymer. See Figure 7. Since G_N^0 is inversely proportional to M_e (eq 7), it appears that at constant MW rings have five time less entanglements than linear polymers. A similar reduction in the entanglement density of a linear polymer, e.g. by dilution at constant monomeric friction constant,

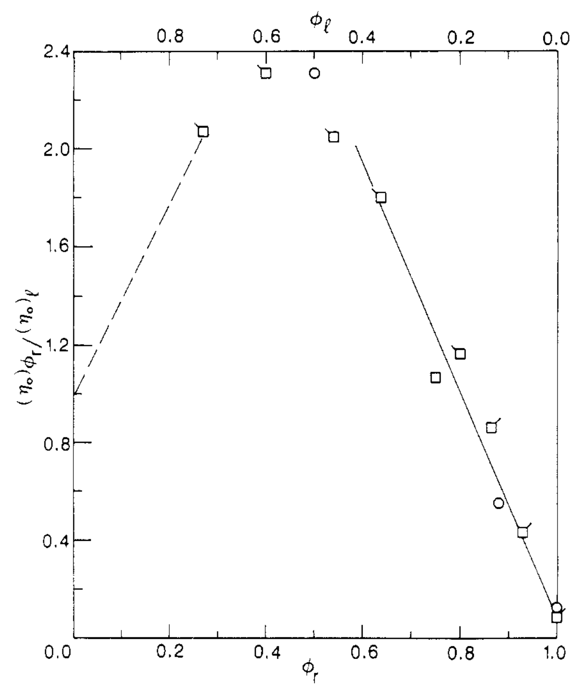

Figure 5. Ratio $\eta_0/(\eta_0)_l$ as a function of the volume fraction of ring for all samples: ○, polystyrenes; □, KPBD31B4; ◻̵, KPBD32; and ◻́, KPB34.

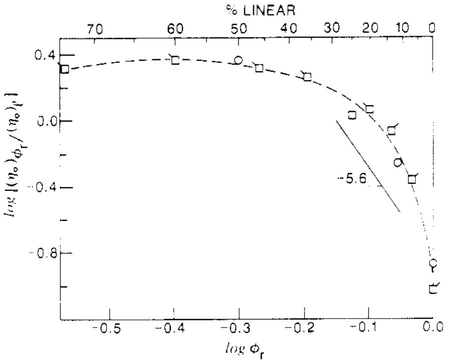

Figure 6. log–log plot of $\eta_0/(\eta_0)_l$ versus volume fraction of the ring. Symbols as in Figure 5.

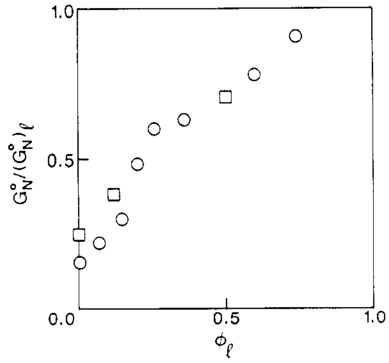

Figure 7. Dependence of G_N^0 on the fraction of linear polymer in the ring: □, polystyrene; ○, polybutadiene.

would produce a $5^{3.38} = 230$ fold decrease in the melt viscosity, and even larger decreases are expected in the case of entangled stars.[34] Unfortunately, such simple comparison cannot be made between the melt viscosity of a linear and a ring polymer. G_N^0 and η_0 are related to each other by integral equation involving the spectrum of relaxation times $H(\tau)$, according to[31]

$$G_N^0 = \int_{-\infty}^{+\infty} H(\tau) \ln \tau \qquad (9)$$

$$\eta_0 = \int_{-\infty}^{+\infty} \tau H(\tau) \ln \tau \qquad (10)$$

The absence of a maximum in $G''(\omega)$ at low frequencies (Figure 2) indicates that the spectrum of relaxation times at long times is larger for the ring than for the entangled linear polymer.

At this point it is not clear why rings appear to have such small number of entanglements. It seems to indicate that the ring structures are collapsed in a ring environment.[24] More likely, the ring structure prevents a mutual interpenetration of the chains (pinning,[22] threading[24,25]) possibly because all cocatenation is forbidden. It is unlikely that the reduced entanglement is caused by the high segment density in the rings alone because stars[17] and combs[21] with higher segment densities have normal values of G_N^0.

The rapid increase of G_N^0 on addition of linear polymer to the rings suggests that linear polymers entangle readily with the rings. Of course, the rapid increase in η_0 should be primarily caused by the increased number of entanglements per chain. It is worth noting that $(\eta_0)/(\eta_0)_l$ levels off at a value of 2.3. This is close to the increase in η_0 that is expected when tube renewal effects are eliminated from the relaxation of linear polymers.[5] The presence of rings could indeed have such an effect on linear polymer. However, the actual values of η_0 in the intermediate range of ϕ_l must be the result of more complex interactions that are not easily resolved by viscoelastic measurements.

In Table II the values of J_e^0 for the rings and their mixtures are collected. Surprisingly, the pure ring has the highest value of J_e^0 and J_e^0 decreases on addition of linear polymer. This behavior is indicative of a wide spectrum of relaxation times in the long time range for ring polymers. Addition of linear polymer causes a narrowing of the terminal spectrum of relaxation times, as can be deduced from the development of a maximum in G'' on addition of linear polymer. In contrast to these results, McKenna and Plazek found that J_e^0 decreased on purification of a ring sample.[29] The high value of J_e^0 quoted for R10DD[27] is almost certainly due to decomposition of the sample at 192 °C. Similarly, no constant value of J_e^0 could be obtained for R19D.[27]

Conclusion

It has been confirmed that the melt viscosity of ring polymers is unexpectedly sensitive to the presence of traces of linear polymer and that few perfect ring samples are presently available. The low melt viscosity of ring polymers has a low MW limit $(\eta_0)_r/(\eta_0)_l = {}^1/_2$ (see Figure 3) which is well-established.[26,27,35] In the molecular weight range studied here $(\eta_0)_r/(\eta_0)_l \approx 0.1$. For one poly(bisphenol A carbonate) ($M_w = 240\,000$; $M_w/M_e = 140$) a 30-fold reduction in the melt viscosity has been observed,[36] suggesting that the low η_0 phenomenon persists to very high molecular weights. The strong increase of $(\eta_0)_r$ with increasing MW previously found for polystyrene rings[27] is due to increasing contamination with linear polymer due to degradation.

The low melt viscosity appears mainly caused by a lack of entanglement in ring–ring systems. When the polymers are compared at constant entanglement density, rings may well relax slower than linear polymers. Addition of linear polymers increases the entanglement density as shown by the increasing values of G_n^0, and thereby the melt viscosity increases. At present, there appears to be no need to invoke knotted ring polymers[26] to explain their viscoelastic behavior.

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