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A Study of the Linear Viscoelastic Properties of Cyclic Polystyrenes Using Creep and Recovery Measurements

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ABSTRACT: The viscoelastic behavior of macrocyclic polystyrene fractions having molecular weights ranging from 1.9×10^4 to 3.9×10^5 was studied. Measurements of zero shear viscosity and recoverable compliance were made on Strasbourg fractions, Akron fractions, and two of the former which were refractionated. Also, studies of the effects of blending of up to 15.8% linear chains with the refractionated Strasbourg fractions were carried out. These studies show that the presence of linear chain contaminants in the macrocyclic fractions has the effect of decreasing the plateau compliance, $J_N{}^\circ = 1/G_N{}^\circ$, and increasing the steady-state value of the recoverable compliance $J_e{}^\circ$. Also, the presence of small amounts of linear contaminant increases dramatically the viscosity of the cyclic fractions. The recovery response of the cyclic fractions was used to qualify those having molecular weights above 44 000 as "good", "moderate", or "poor" cycles. The results of analysis of the good and moderate fractions give a picture of the cycles as showing "classical" viscoelastic behavior; i.e., the steady-state recoverable compliance increases with increasing molecular weight and attains a constant value at high molecular weights ($M_w > 1.8 \times 10^5$), as do linear polymers. The plateau compliance of the cycles is about 2 times that of the linear chains. The limiting value of the steady-state recoverable compliance of the rings is also approximately 2 times that of the linear polymer. We find that the zero shear viscosity–molecular weight relation is well described by an equation of the form $\eta = AM + BM^\alpha$ where $\alpha \simeq 3.9$, which is somewhat higher than the 3.4 power obtained for entangled linear chains. Results from dilute solution characterization of the Akron cycles are presented and compared with literature values. Anomalies in the behavior are discussed and the use of dynamical properties in dilute solution as a means of determining the quality of cyclic fractions is questioned.

I. Introduction

There has been considerable interest recently[1-7] in the dynamics of melts of cyclic macromolecules due to the perception that, unlike their linear counterparts, chains in the form of uncatenated rings cannot reptate. On simply the basis of their presumed inability to reptate, the cyclic molecules provide the opportunity to address several basic questions. First, is the viscosity–temperature relationship for the cyclic and linear molecules the same? Second, what is their viscosity–molecular weight relationship and how does it compare with that of the linear (presumed to be reptating) analogue? Third, does the difference in the topology of rings result in differences in other viscoelastic properties such as the level of the plateau modulus or the steady-state recoverable compliance?

While there appears to be little doubt that above approximately 40 000 molecular weight, the cyclic and linear macromolecules obey the same Vogel or WLF type viscosity–temperature relationship,[1] there is a controversy about the molecular weight dependence of the viscosity. McKenna et al.[1] report that the melt viscosity of polystyrene (PS) macrocycles follows a power law dependence with weight average molecular weight, M_w, where the M_w exponent is similar to that obtained for linear polystyrenes. Roovers,[3] on the other hand, reported a stronger than power-law dependence of viscosity on molecular weight.

The possible reasons for the differences between the results from different groups revolve around two points, both of which relate to the ringlike nature and quality of the fractions used for the viscosity measurements. The ringlike nature of the fractions has been deduced primarily from measurements of intrinsic viscosity at or near the Θ temperature and in good solvent conditions. Because the intrinsic viscosity at T_Θ reported by Roovers[3] vary with a power in molecular weight which is significantly less than one-half,[8,9] it has been argued[1] that the Roovers cycles may contain a significant percentage of permanent knots. If this percentage were to increase with increasing molecular weight, it would lead to more compact chains relative to unknotted rings and possibly to lower viscosities. Such a behavior is not observed with the Strasbourg[1,10-12] cycles or cyclic molecules synthesized elsewhere.[13-16] This will be further discussed in the section on dilute solution properties.

Knotted chains alone, however, would not explain the differences in the results for macrocyclic melts reported by Roovers[3] and those of McKenna[1] et al. Rather, it is necessary to invoke both knots and contamination by linear chains or high molecular weight rings in the Roovers cyclic fractions to explain the discrepancy between the results. As has been shown by McKenna and Plazek,[2] the addition of small quantities of linear chains can greatly increase the viscosity of cyclic fractions. Furthermore, there is evidence, which we present in this paper, that the high molecular weight Roovers cycles contain a contami-

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nant which we expect increased the viscosity. Thus, we will argue that the results of Roovers[3] appear to follow a stronger than power-law behavior because of the combined effects of knotting and an increasing amount of linear contamination with increasing molecular weight, the evidence for the latter being stronger.

In addition to the interest in the zero shear viscosity of cyclic molecules, the expectation that the cyclic macromolecule of a given molecular weight is smaller, both theoretically[17-21] and based on intrinsic viscosity measurements for cyclic polystyrenes,[1,8,9,12-14] poly(dimethylsiloxanes),[6,15] and polycarbonates[16] than are the linear molecules of the same molecular weight, suggests that the melt topologies for cyclic and linear molecules may be different. In fact, Roovers[3] has reported that the plateau modulus for cyclic polystyrenes is one half that of linear polystyrenes. From rubber elasticity arguments this would imply that the entanglement molecular weight of the cycles is twice that of the linear chains. In this study, we confirm this result. On the other hand, the critical molecular weight for entanglement coupling, M_c, from viscosity measurements was reported by one of us[1] to be approximately the same for cyclic and linear polystyrenes. Here we present new data which suggest that M_c of the cycles is significantly higher than that of linear chains.

In this study we address the fraction quality issue by carrying out measurements of the recoverable compliance after steady shearing flow for several cyclic polystyrene fractions. The fractions come from three sources: those synthesized by two of us (L.J.F. and B.J.H.) and referred to as the Akron fractions; those synthesized and fractionated at the Institut Charles Sadron, referred to as the Strasbourg fractions; and two Strasbourg fractions which were refractionated by us at the University of Pittsburgh. Furthermore, we will report results on the effects of blending up to 15.8% linear chains with the refractionated Strasbourg samples.

There are four salient features that emerge from our study. (1) We demonstrate that the recoverable compliance is a sensitive measure of the presence of a contaminant in the cyclic fractions and characterize the Strasbourg and Akron cyclic fractions as "good", "moderate", or "poor" based on these measurements. (2) The zero shear viscosity of the cyclic macromolecules characterized as "good" and "moderate" results in a power-law dependence on M_w somewhat greater than that obtained previously;[1] i.e., the exponent is 3.8–3.9 rather than 3.4. Furthermore, the results suggest that M_c for the cyclic fractions is approximately 58 000, which is higher than the value reported previously by McKenna et al.[1] for cyclic polystyrenes and approximately twice that of linear polystyrenes.[2,3] (3) It is found, in agreement with results reported by Roovers[3] from dynamic measurements, that the plateau modulus for the cycles is approximately half that for the linear chains. (4) Small amounts of linear chains added to cyclic fractions of the same molecular weight decrease the plateau compliance toward the linear value and greatly enhance the zero shear viscosity of the cyclic melt.

An additional feature of this work arises from our examination of the dilute solution properties of the Akron cyclic fractions and their comparison with properties reported in the literature. There are several anomalies observed in the behavior of cyclic macromolecules which cannot be accounted for presently. We suggest that much work still needs to be done in order to establish the exact behavior of macrocyclic polymers, both in dilute solution and in the melt.

In the following sections we will describe the synthesis and dilute solution characterization of the Akron fractions and compare these latter with literature reports for cyclic polystyrenes. We will then describe the measurement of the recoverable compliance after steady shearing flow on the cyclic fractions. Following this we will show how the recoverable compliance measurements are sensitive to fraction contamination. Subsequently we will report the results from the reduced curves of recoverable compliance versus time for all of the fractions for which measurements are available and compare the results with those obtained for linear polystyrenes of similar molecular mass. We will then examine the behavior of the blends. This will be followed by an examination of the Roovers data which demonstrates that not only are his high molecular weight samples contaminated but also the data suggest that his samples may be knotted. We will also discuss the results for the viscosity molecular weight behavior of what we consider to be "good" polystyrene macrocycles.

II. Experimental Methods

A. Materials. 1. Strasbourg Macrocycles. The synthesis and dilute solution properties of the polystyrene macrocycles made at the Institut Charles Sadron in Strasbourg (CRM) have been reported elsewhere.[1,10-12] [We thank Drs. P. Rempp, G. Hild, and P. Lutz of the Institut Charles Sadron, Strasbourg, France, for making the Strasbourg fractions available to us. We also want to thank Dr. Lutz for light scattering molecular weight and intrinsic viscosity measurements on the samples which we refractionated.] Two of these fractions were found to be contaminated, presumably by small amounts of linear chains, as described subsequently, and were refractionated by precipitation from benzene and methanol at the University of Pittsburgh. These fractions are designated PS2829[4] and PS2780[3,4] where the numbers in brackets indicate the fraction number. In addition, we obtained a fraction which corresponded to the CRM fraction PS2774 for which dilute solution and melt results had been reported previously.[1] However, this fraction was a higher cut from the same fractionation (i.e. F8 versus F7) and as will be reported had different properties. The molecular weights and intrinsic viscosities in cyclohexane and THF of the Strasbourg samples are listed in Table I.

2. Synthesis of the Akron Cycles. The macrocyclic polystyrene rings were prepared via anionic polymerization procedures using vacuum-line techniques. The initiator used was a difunctional species containing lithium as the counterion. The preparative procedures and the general guidelines used in synthesis of the Akron macrocycles are given in Appendix 1.

B. Methods of Characterization of the Akron Fractions. 1. Size-Exclusion Chromatography (SEC). Waters* Ana-Prep GPC and Waters* 150C ALC/GPC instruments were used to obtain all of the chromatograms for which data are reported in this work. [*Certain commercial materials and equipment are identified in this paper by an asterisk to specify the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Science and Technology or that the materials and equipment identified are necessarily the best available for the purpose.] Tetrahydrofuran (THF) was used as the carrier solvent at 30 °C with a differential refractometer detector. Flow rates were maintained at or near 1 mL/min. The concentrations used were in the range 0.0625–0.250 wt %.

2. Light Scattering. Weight-average molecular weights were measured by use of the Chromatix* KMX-6 low-angle laser light scattering photometer. The instrument was equipped with an He–Ne laser emitting at 633 nm. Toluene was used as the solvent at ambient temperatures.

The LALLS KMX-6 instrument was also used when coupled with the Waters 150-C ALC/GPC instrument and the Chromatix*/Digital* microprocessor interface. THF at 30 °C was used as the solvent, and the MOLWT2* program was used for all calculations.

3. Θ Temperature. The Sofica* PGD light scattering photometer was used to determine the Θ temperature of the linear

Table I
Sample Designations, Molecular Weights, and Intrinsic Viscosities of Strasbourg Polystyrene Macrocycles[1]

macrocyclic fraction	$10^{-4}M_w$,[a] g mol^{-1}	M_w/M_n[b]	$[\eta]$, dL g^{-1} cyclohexane 35 °C	$[\eta]$, dL g^{-1} THF 25 °C
PS2653	1.11	1.09	0.0555	0.070
HA50	1.25	1.30	0.0565	0.081
PS2857[h]	1.94	1.16	0.0755	0.1005
PS2648	2.70[c]		0.0870	
PS2654	3.78[d]	1.13	0.0990	
HA49[h]	4.40	1.08	0.119	0.182
HA51	5.05	1.17	0.125	0.215
PS2774[F7][e]	7.94	1.12	0.159	
PS2774[F8][e,g,h]	7.30			0.242
PS2829[h]	10.6		0.178	0.355
PS2829[4][f,h]	10.6	1.13		0.325
HA53	11.7	1.12	0.221	0.410
PS2780[h]	18.2	1.10	0.235	0.530
PS2780[3,4][f,h]	18.5	1.12	0.230	0.470

[a] By light scattering. [b] By size exclusion chromatography. [c] By neutron scattering. [d] This sample has also been reported by Hadziiaonnou et al.[27] to have a value of $M_w = 4.2 \times 10^4$ by light scattering and 4.5×10^4 by neutron scattering. [e] Different fractions from Strasbourg fractionation of polycondensate resulting from the cyclization reaction. [f] Samples refractionated by us at the University of Pittsburgh. [g] Previously unreported result. The measurements were kindly made by Dr. Pierre Lutz at the Institut Charles Sadron in Strasbourg. [h] Samples for which viscosity in steady shearing flow and recovery after steady shearing flow were measured.

and cyclic fractions. Unpolarized light of wavelength 435.8 nm was used with cyclohexane as the solvent. All samples were centrifuged at 8500 rpm for 1 h in a thermostated chamber to remove dust and impurities. Solutions were transferred directly from the centrifuge tubes to the light scattering cells by using a heated syringe. The scattering intensities were measured as a function of concentration at an angle of 90° at several temperatures above and below the Θ temperature. The Θ temperature was determined by plotting the second virial coefficient, A_2, versus temperature and determining the temperature at which $A_2 = 0$.

4. **Intrinsic Viscosities.** Intrinsic viscosities were measured by using Cannon Ubbelohde* type viscometers having capillary sizes of 50, 75, and 100. No kinetic energy corrections were made. Toluene solutions were run at 35.0 °C, and cyclohexane solutions were run at the Θ temperature of the sample as determined from the light scattering measurements.

C. Creep and Recovery Measurements. The creep and recovery data described in this work were obtained by using a magnetic-bearing torsional creep apparatus (MBTCA).[24] This instrument consists of a magnetically suspended rotor, which applies known torques to one end of a cylindrically shaped sample (i.e. parallel plate geometry). The instrument has several advantages which make possible the accurate characterization of the creep and recovery responses of small quantities of sample. First, the magnetic bearing is essentially frictionless, thus permitting the determination of the creep and recovery behavior over long periods of time. Second, the lower platen is adjustable, permitting manipulation of the sample shape after installation of the sample. Third, the atmosphere of the system is controllable, capable of being evacuated to a moderate vacuum (0.001 Torr) or purged with nitrogen. Fourth, the sample can be visually observed at all times during the testing.

The polymeric samples were molded in an apparatus consisting of an evacuated precision glass tube and two steel cylinders. The material was heated to ca. 150 °C and compressed into a disk shape corresponding to the size platen in the test machine (6.35-mm diameter). Total sample weight was of the order of 50 mg.

After the sample was inserted into the creep instrument, the sample chamber was evacuated to a pressure of less than 0.01 Torr and heated to a temperature of ca. 120 °C for 2–4 h to remove residual solvent, moisture, and entrapped gas. Samples were then heated in nitrogen to a temperature at which the viscosity was 10^5–10^6 P and reevacuated, at which point the remaining residual moisture etc. cause the sample to foam. The bottom platen was raised simultaneously to keep the foaming sample in the platens, and the shape of the sample was then manipulated into cylindrical form by varying the height of the lower platen and applying torque to the sample. Nitrogen was then reintroduced into the sample chamber, and all tests were performed in a nitrogen atmosphere.

Sample deformation was measured via a light lever 11.6 m long. The beam was provided by a low power He–Ne laser reflected off a rectangular mirror attached to the upper (moving) platen, and the beam's displacement was measured on a modified strip chart recorder. The recorder pen was attached to a pair of photocells. The output of the photocells was used to control a servo-circuit which kept the light beam centered between the two cells. The total deflection that could be measured was essentially unlimited since the lower platen in the apparatus can be rotated after sufficient deformation has been reached to drive the pen the width of the chart paper. The resolution was 2.3×10^{-5} radians corresponding to 0.25 mm of displacement on the chart.

The viscosities and compliances were calculated as described in ref 24. Specific volumes were calculated with the expression of Fox and Loshaek given for linear polystyrenes in ref 25:

$$V = 0.767 + 5.5 \times 10^{-4}T \tag{1}$$

without correction for molecular weight, since the rings have no free ends.

The maximum instrument sensitivity allowed absolute compliances of the order 3×10^{-9} cm^2/dyn to be measured.

Two procedures were used for making viscosity and compliance measurements. First, at high temperatures, where steady state could be reached within ~5000 s, a torque was applied to the sample for this length of time and the rate of deformation required for the viscosity calculation recorded. The torque was then removed and the sample allowed to recover. Second, as the times to achieve steady state at low temperatures increased, the method suggested by Leaderman et al.[26] was followed; i.e., steady state was achieved by applying a torque at an elevated temperature. Then the temperature was reduced to the lower value while a constant torque was maintained. Upon reaching and stabilizing the lower temperature, the sample was allowed to creep for several hours during which time the deformation rate required for the viscosity calculation was recorded. The torque was then removed and the recovery measured. The results will be reported as reduced recoverable compliance, $J_R(t)/b_T$ versus reduced time, t/a_T, where $J_R(t)$ is the recoverable compliance, b_T is a vertical shift (due to either small errors in the material geometry measurements[24] or the level of the rubbery plateau[23]), t is time, and a_T is the temperature shift factor required to superimpose the curves obtained at different temperatures to create the reduced curve.[23]

III. Results and Discussion

A. Dilute Solution Properties. (a) Background. Prior work on macrocyclic polymers has used the characterization of the dilute solution properties as a litmus test of the quality of the cyclic fractions.[1,3,8-10] In particular, emphasis has been placed on the ratio of the intrinsic viscosities of the cycles to those of their linear counterparts in a "good" solvent and under near Θ conditions. In those studies it was argued, based on theoretical calculations by several authors,[17-21] that a cyclic chain is more compact and should have a smaller radius of gyration and hydrodynamic radius than a linear chain of the same molecular weight. Therefore, the intrinsic viscosity of the cycles should be similarly lower. The theoretical calculations result in the prediction that $g_\Theta = [\eta_C]_\Theta/[\eta_L]_\Theta = 0.662$ where $[\eta]$ is the intrinsic viscosity, the subscripts C and L refer to the cyclic and linear molecules respectively, Θ refers to the value at the Θ temperature, and g is often referred to as the structure factor. The situation in good solvent conditions is more complicated but similar; i.e., the cycle is expected to be more compact than the linear analogue.

In addition to the intrinsic viscosity ratio, the smaller size of the cyclic molecules is also expected to result in a lower apparent molecular weight (greater elution volume) in size-exclusion chromatography (SEC). Because SEC is carried out in good solvent conditions, the expected ratio of apparent molecular weights is less certain than g_Θ but has been reported to be between 0.71 and 0.81 for cyclic polymers.[8,10]

Finally, cyclic polymers have been reported to exhibit a Θ temperature which is depressed relative to that of their linear counterparts.[8-10,27] The Θ temperature of cyclic polystyrene (as measured by light scattering as the point at which the second virial coefficient A_2 is equal to zero) of cyclic polystyrene in cyclohexane has been reported to be approximately 6 °C lower than for the linear chains (28.5 °C versus 34.5 °C),[8-10,27a] while in decahydronaphthalene (Decalin) it was only depressed by 4 °C (15 °C versus 19 °C).[10] Similar results have been found in deuterated solvents by neutron scattering.[27b] In all cases there appears to have been no effect of molecular weight on the Θ-point depression, although only Roovers[8,9] provides tabulated values. Other experiments have been used to show the ringlike quality of fractions. In particular, neutron scattering results on the Strasbourg cyclic polystyrenes,[10,27b] those of Ragnetti et al.[28] on polystyrene macrocycles and those of Higgins et al.[29] on PDMS cycles, show agreement that the mean square radius of gyration of macrocycles is smaller than that of the linear counterpart.

In the following section we will focus on the dilute solution properties of the Akron cycles because they show anomalous behavior; viz., while the Θ temperature is depressed and the SEC results show that the high molecular weight fractions are ringlike, measurements of the intrinsic viscosities are much less convincing. Furthermore, as presented in the section on rheological properties, the highest molecular weight Akron fractions do not behave like linear chains. Therefore, we present the dilute solution results for the Akron cycles in the next section and compare these to the literature results for other polystyrenes. Of particular interest, we attempt to show that there are anomalies in the results reported by some other groups as well which may suggest that the "quality" of ring fractions based on intrinsic viscosities is not necessarily the litmus test initially conceived. We will briefly discuss possible limitations of the theories and point out the literature studies which address the refinements needed in the theories to obtain better predictions of the dynamical properties of polymers in dilute solutions. Finally we will suggest that ring quality be determined only from static experiments, e.g. scattering measurements of A_2 and R_g, which are not available for the Akron fractions, nor have they both been reported in the studies on ring fractions which appear in the literature.

(b) Dilute Solution Results. The intrinsic viscosities of all of the Akron fractions are presented in Table II. The four samples on which we carried out rheological measurements are marked with the letter a. In Figure 1 we plot [η] versus M double logarithmically for both the cycles and the linear chains in Θ conditions and in good solvent conditions. The important thing to note from Table II and Figure 1 is that, unlike the rings produced by other groups, the Akron rings show relatively little difference in intrinsic viscosity behavior from those of their linear counterparts. While this might be reason to speculate that the Akron fractions are not rings, we will show in subsequent paragraphs that they do exhibit "ringlike" properties in other respects. First, however, we shall consider literature results for the intrinsic viscosities of other polystyrene macrocyclic fractions.

Table II
Intrinsic Viscosity and Θ Temperature Characteristics for Akron Cyclic, R, and Linear, L, Polystyrene Fractions

sample	$10^{-4}\bar{M}$, g mol^{-1}	[η], dL g^{-1} toluene 35 °C	[η], dL g^{-1} cyclohexane $T = T_\Theta$	T_Θ, °C cyclohexane $A_2 = 0$
79L	2.24	0.139	0.113	28.8
79R[a]	2.23	0.124	0.118	25.0
80L	3.12	0.172	0.147	
80R	2.80	0.164	0.134	
70L	4.76	0.239	0.167	28.0
70R[a]	4.39	0.237	0.163	22.0
90L	4.76	0.258	0.174	30.5
90R	4.25	0.262	0.161	27.0
75L	5.41	0.256	0.172	31.8
75R	5.48	0.256	0.180	28.1
76L	6.79	0.300	0.192	31.0
76R	7.31	0.292	0.181	29.9
2013L	7.33	0.354	0.217	28.4
2013R	9.30	0.416	0.242	28.0
20L	9.40	0.401	0.252	34.1
20R	9.50	0.362	0.212	29.6
5L	13.7	0.530	0.295	34.5
5R	14.0	0.460		29.0
1L	18.6	0.634	0.357	
1R	18.6	0.536	0.298	30.0
81L	15.2	0.580	0.320	34.5
81R	19.5	0.593	0.309	30.5
82L	20.0	0.685	0.361	34.4
82R[a]	24.7	0.711	0.334	32.4
83L	41.2	1.16	0.551	34.0
83R[a]	39.1	1.19	0.496	32.5

[a] Samples used in steady shearing and recovery experiments.

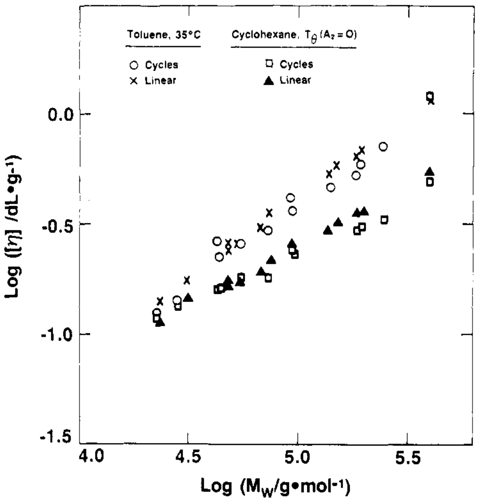

Figure 1. Double logarithmic plot of intrinsic viscosity versus molecular weight for Akron fractions. In toluene at 35 °C: (○) cycles; (×) linear. In cyclohexane at the measured Θ temperature: (□) cycles; (▲) linear.

In Figure 2 we show results from the literature[1,8-14] for the intrinsic viscosities of linear and cyclic polystyrene fractions in good solvent conditions (THF or toluene). Of considerable interest here is the observation that, while most of the values of [η] for the rings are lower than for their linear counterparts, the differences among them vary not only by molecular weight but also, apparently, between laboratories. Furthermore the apparent molecular weight dependence of [η] differs among laboratories. This has already been noted[1] with reference to differences between the Strasbourg rings and the Roovers rings, and the lower slope for the latter was interpreted[1] as indicating the possible presence of knotted chains. Interestingly, at much higher molecular weights the Vollmert and Huang[13] rings show very large reductions in intrinsic viscosity relative to their linear counterparts. Whether this is due also to

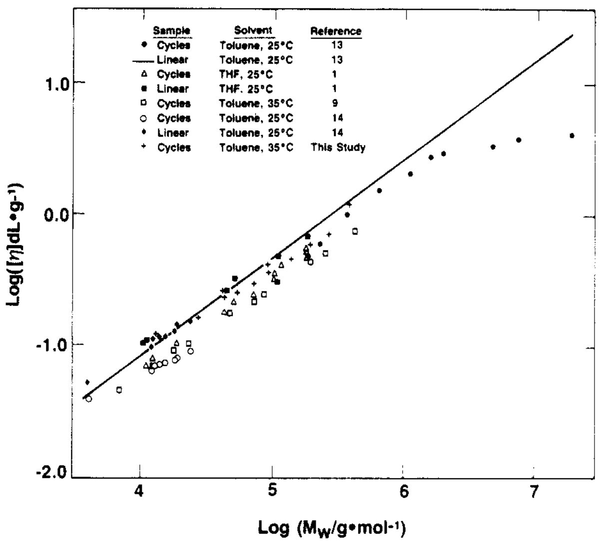

Figure 2. Double logarithmic plot of intrinsic viscosity versus molecular weight for cyclic and linear polystyrenes in good solvent conditions. Solid line: linear polystyrene in toluene at 25 °C calculated from $[\eta] = 9.38 \times 10^{-5} M^{0.738}$ (ref 13). Points: linear polystyrenes: (■) THF, 25 °C (ref 1); (♦) toluene, 25 °C (ref 14); cyclic polystyrenes: (●) toluene, 25 °C (ref 13); (△) THF, 25 °C (ref 1); (□) toluene, 35 °C (ref 9); (○) toluene, 25 °C (ref 14); (+) toluene, 35 °C (this study).

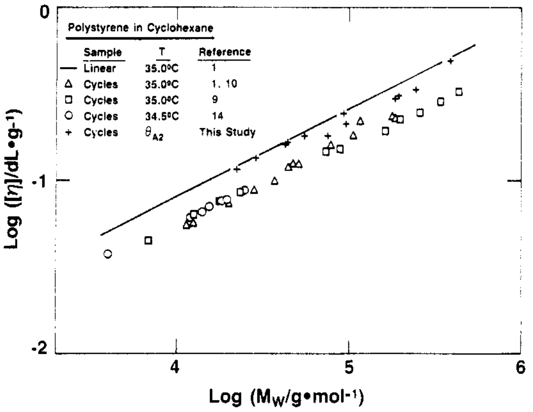

Figure 3. Intrinsic viscosities for cyclic and linear polystyrenes in cyclohexane near the Θ temperature. Solid line: linear polystyrene, calculated from $[\eta]_\Theta = 8.0 \times 10^{-4} M_w^{0.5}$ (ref 1). Cycles: (△) 35 °C (ref 1, 10); (□) 35 °C (ref 9); (○) 34.5 °C (ref 14), (+) measured Θ_{A2} (this study).

knots or to catenation as they[13] speculated is unknown.

In addition to measurements in good solvent conditions, the Strasbourg cycles and Roovers' cycles were characterized in near Θ conditions at the Θ temperature of the linear chain. The Akron cycles were characterized at their Θ temperature [as $A_2 = 0$]. The results for the Strabourg and Roovers cycles near the Θ condition are also shown in Figure 3. The discrepancies here are not enormous, and the slopes of least-squares lines through the data in the two cases are different,[1,10] with that for the Roovers[8,9] cycles showing the lower slope.[1,10] A point worth making here is that Roovers also reports,[9] without showing the data, that at the measured Θ temperature of the rings, his intrinsic viscosity measurements result in a Mark–Houwink exponent of 0.40. Again, are these result due to an increasing presence of knots?

These results show that, although macrocyclic polymers have been reported to exhibit intrinsic viscosity behavior consistent with the theoretical calculations, the results are not uniformly in agreement with the theories. Furthermore, because the discrepancies between the values of the ratios of intrinsic viscosities of the cycles to the linear chains in good solvent vary by as much as 25% (not including the Akron rings), even at low molecular weights, one must ask whether or not the cycles have knots in them and whether the quantity of knots depends not only on synthesis conditions, as previously speculated,[1] but also on the conditions of fractionation. The importance of this will be discussed in section III.A.c.

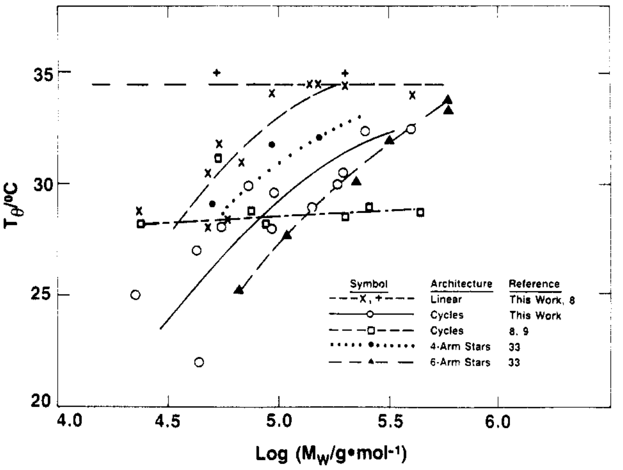

Figure 4. Θ temperature for cyclic, linear, and star-branched polystyrenes versus logarithm of molecular weight. Linear polystyrenes: (– – ×) this work; (– – +) (ref 8). Cycles: (—○) this work; (– – □) (ref 8). Four-arm stars: (··●) (ref 33). Six-arm stars: (– – △) (ref 33).

The Θ temperatures of the cyclic and linear precursor polystyrenes synthesized in Akron are also tabulated in Table II. The Θ temperature is defined as the point at which the second virial coefficient from light scattering measurements equals zero. As seen here, Θ_{A2} for all of the Akron cycles is lowered relative to the linear counterpart. Several comments are in order here. First, the Θ temperatures of these linear chains are depressed relative to normal anionic polystyrenes (Θ = 34.5 °C). This is undoubtedly due to the presence of the dimethylsilane and hexadiene groups on these chains.[30] Second, the amount of depression is dependent upon molecular weight, but less so than in star-branched molecules. This is seen in Figure 4 where T_Θ versus log M_w is shown for the Akron rings and linear chains and for anionic polystyrene,[8] without the hexadiene and dichlorosilane. Also shown are the Roovers[8,9] results for his cyclic polystyrenes and literature results for four- and six-arm star-branched polystyrenes.[33,34] Interestingly, Θ_{A2} is independent of molecular weight for the Roovers cycles and, as noted previously, has been reported to be independent of molecular weight for the Strasbourg cycles.[27b] We are aware of only two theories which predict the Θ-point depression of rings.[35a,b] Both Kosmas[35a] and Tanaka[35b] predict a molecular weight dependence of Θ. Kosmas[35a] predicts a behavior which is similar to that of four-armed stars and for which there is no Θ-point depression at high molecular weights. In the Tanaka[35b] theory, the molecular weight dependence of the Θ-point depression is less dramatic than in the Kosmas[35a] theory and a depression of Θ for the rings remains even at high molecular weights.

The above then is the first anomly for the Akron rings. How does one explain a depressed Θ temperature but intrinsic viscosities which are close to those of linear chains? Furthermore, the Θ-point depression of the Akron rings is in better agreement with the available theories than the Roovers or Strabourg fractions.

The results of measurements on the Akron fractions using size exclusion chromatography are ambiguous. In Figure 5 we plot elution volume, V_e, versus log M_w (de-

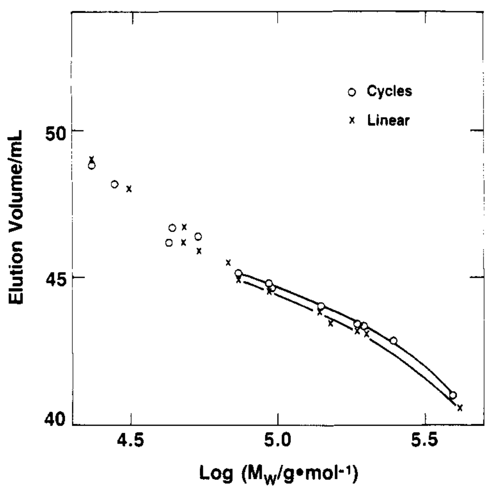

Figure 5. Elution volume in SEC versus logarithm of molecular weight for Akron polystyrene fractions: (O) cyclic fractions; (×) linear fractions.

termined from light scattering) for the Akron fractions. At low molecular weights the values are scattered and we make no comments about the results. Above approximately 70 000 g mol^{-1}, however, the results are much as one would expect for cyclic molecules; i.e., the elution volume of rings is greater than that of linear chains of the same molecular weight. The differences, however, translate into apparent molecular weights for the cycles which are not as great as reported previously by Roovers and Toporowski[8] and by Lutz et al.;[10] i.e., $M_{\mathrm{app}}/M|_{\mathrm{Akron}} \approx 0.9$ versus $M_{\mathrm{app}}/M|_{\mathrm{Roovers}} \approx 0.71$ and $M_{\mathrm{app}}/M|_{\mathrm{Lutz}} \approx 0.81$. We also note that the PDMS studies of Semlyen and co-workers[6] result in a value of $M_{\mathrm{app}}/M \approx 0.8$.

In this section we have shown that the Akron cyclic fractions exhibit anomalous properties. While they are ringlike based on the fact that the Θ temperature is lower than that of their linear counterparts and the elution volume of the Akron rings (at high molecular weights) in SEC measurements is greater than for the linear chains, there is little difference in the intrinsic viscosities between the cyclic and linear polymers. In addition, we will show subsequently that in rheological tests the Akron cycles which were studied are different from linear chains of the same molecular weight and they behave very much like the Strasbourg cyclic fractions which we studied. The question which arises then is: can these anomalous properties be explained? We are not in a position to answer this conclusively, but we will speculate in the next section on the possible reasons for differences between the properties of the cyclic fractions from different groups. In addition we will present a series of thoughts about the theoretical calculations and why experimental results on rings might not agree with them.

(c) Comments on the Dilute Solution Properties of Macrocyclic Polymers. In the preceding paragraphs we have presented dilute solution properties for the macrocyclic polystyrenes synthesized by various groups and noted that there are discrepancies among the results and furthermore that the Akron cycles show anomalous behavior in that the intrinsic viscosities overall are nearly the same as for the linear chains, and yet they show the ringlike property of a depressed Θ temperature relative to their linear analogues. Also, above about 70 000 g mol^{-1}, the Akron cycles show greater elution volumes in size exclusion chromatography, as expected for ringlike molecules. Furthermore, we have rheological measurements, to be presented in the next section, for four of the Akron fractions which show that these are definitely not (pure) linear chains and that their behavior is ringlike. As a result we wish to speculate on possible reasons for the anomalous behavior of these fractions and for the discrepancies among the dilute solution results from the various laboratories which might occur independently of the macrocyclic fractions containing a linear contaminant.

Our basis for these speculations arises from several considerations dealing with the theoretical analyses used to calculate the properties of polymer chains, both linear and cyclic, in dilute solution. These speculations will be particularly important in discussing the dynamical properties, e.g. intrinsic viscosity, SEC behavior, etc., although one of them may be important for the static properties as well.

First, we consider that the calculations available for the dynamical properties of polymer chains depend upon the Kirkwood–Riseman[36] theory and the calculations are generally made tractable by using the preaveraging approximation to the Oseen tensor.[18] Even at the Θ temperature, where the chains are often modeled as ideal Gaussian chains, the preaveraging approximation can introduce errors into the value of the hydrodynamic radius, R_{H}. These errors might affect the expected relative values between linear and cyclic chains for dynamical properties obtained by intrinsic viscosity and SEC measurements. There has been much discussion[37–45] in the literature concerning the magnitude of the corrections due to preaveraging. For linear chains they have been estimated by Zimm[44] using Monte Carlo simulations to be of the order of 12%, while Fixman[45] estimates them to be of the order of 8%. We know of no calculation which estimates the preaveraging corrections for rings. Furthermore, in a survey by Schmidt and Burchard,[46] it is found that the experimental measurements on linear polystyrene give discrepancies with theory in the neighborhood of 15–20%.

Another source of difficulty in the calculations of dynamical properties in dilute solution arises from the presence of residual or ternary interactions at the Θ temperature. The magnitude of these effects is uncertain, although recent renormalization group calculations[40] and Monte Carlo simulations[39,43] suggest that they could be as large as 10%.

These errors may not be sufficient to account for all of the discrepancies in the reported data, as other effects such as draining and excluded volume become important in good solvent conditions. The sum of all of these things may or may not account for the anomalies in the behavior of the Akron fractions. They do, however, suggest that dynamic properties in dilute solution may not be the "litmus" test for ring quality previously thought and static properties such as mean square radius of gyration, penetration function, and second virial coefficient may be more appropriate tests. The reader is referred to Douglas and Freed[41] for a discussion of these properties as tests of theory. Unfortunately few of the macrocyclic fractions have been characterized in this way. Radius of gyration of small cyclics, in particular, requires neutron scattering experiments, as light scattering is limited to the high molecular weight range.

Even here, though, it is possible to pose an additional question—can the presence of knots[47,48] affect the measured versus the theoretical properties of the macrocycles? Intuitively one would answer yes, and then the obvious difficulty arises of characterizing the knots. For example, we noted previously that the Roovers[8,9] samples showed evidence of being more compact (less expanded) at high molecular weights than the fractions from other groups (see discussion of intrinsic viscosity). One possible interpretation of such a rsult is the presence of knotted rings. However, the presence of knots in rings poses a complicated question for the experimentalist because such things as the conditions during the ring closure stage of synthesis ("poor" solvent favoring more knot formation) or the actual amount of fractionation (can knotted rings separate preferentially from unknotted rings?) almost certainly have an effect on the actual state of knottedness of each cyclic fraction.

From the theoretical side, the models available for calculating the properties of rings have generally used Gaussian statistics.[17-21,48] This implies that the conformation calculations include "phantom" conformations that may not be available for the real rings if they were successfully synthesized in an unknotted state. The results, then, of the calculations of these phantom chains would have an excess of knots over the unknotted real chains. The real chains would then be expected to be expanded relative to the theoretical predictions. Does then agreement with the Gaussian chain theory actually imply that the cyclic fractions chosen for study have the appropriate number of knots? Since the magnitude of such effects is not known, we cannot answer this question, but pose all of the above possibilities in at least partial explanation of the diversity of dilute solution results obtained by the various groups working with macrocyclic molecules. It may also explain some of the "anomalous" behavior of the Akron fractions.

B. Recoverable Compliance Measurements. (a) General. The measurement of the recoverable compliance in the terminal flow regime is a sensitive measure of the monodisperse quality of polymeric fractions. The reason for this is that the slope $d \log (J_R)/d \log (t/a_T)$ for narrow fractions approaches zero at the steady-state recoverable compliance $J_e°$ plateau while for fractions which contain even small amounts of high molecular weight material,[49] the $J_e°$ value is too high and/or the slope does not go to zero in the time range of the measurements. Since the quality of the cyclic fractions from different groups has been the subject of a controversy which strongly affects the interpretation of the viscosity molecular weight results obtained by the different groups, we took several of the Strasbourg fractions and four of the Akron fractions described above and measured the recoverable compliance after steady shearing flow. In addition, as will be explained below, two of the Strasbourg samples were refractionated and experiments were carried out by using these fractions as well. Finally, we also obtained a fraction from Strasbourg which corresponds to the same synthesis as for the PS2774 reported previously but which had a higher fraction number (i.e. F8 versus F7 for the previous one) and was therefore, possibly, different.

(b) Illustration of Recoverable Compliance as a Sensitive Measure of Fraction Quality. In early work on the recoverable compliance, J_R, of linear macromolecules, Plazek and O'Rourke[49] were able to demonstrate that the steady-state value of the recoverable compliance can be a sensitive measure of small amounts of high molecular weight impurities in the sample. Moreover in dealing with the cyclic polystyrene fractions, we can illustrate this effect by showing the recoverable compliance master curves for the PS2829 and PS2780 Strasbourg samples before and after refractionation in Figures 6 and 7. As can be seen the behavior of the refractionated samples is quite different from that of the original fractions. [Note these original fractions were made by combining several of the narrowest fractions obtained by fractionation at the Institut Charles Sadron in Strasbourg. Recombination was carried out because the Strasbourg viscometer required a minimum of 1 g of material for viscosity measurements versus the ≃50 mg required for the MBTCA.] Not only is a steady-state value of the recoverable compliance attained for the refractionated materials, but we see that the curves cross. As will be shown in the section on blends, the low J_R values in the "plateau" or shoulder region of the curves for the original samples is consistent with the presence of linear chains. The fact that no steady-state value, $J_e°$, is attained within the same time scale as for the refractionated samples indicates that either the linear chains are of high molecular weight or the terminal times of linear chains in rings are very long. Furthermore, we note that the intrinsic viscosities of the refractionated samples are only slightly lower than for the original samples while the molecular weight remains unchanged (see Table I). Thus the amount of contaminant, of whatever molecular weight, was undoubtedly small. Finally, as will be discussed subsequently, the zero shear melt viscosities of the refractionated samples are significantly lower than for the original fractions, consistent with a viscosity enhancement of the cycles blended with small quantities of linear chains, to be discussed next.

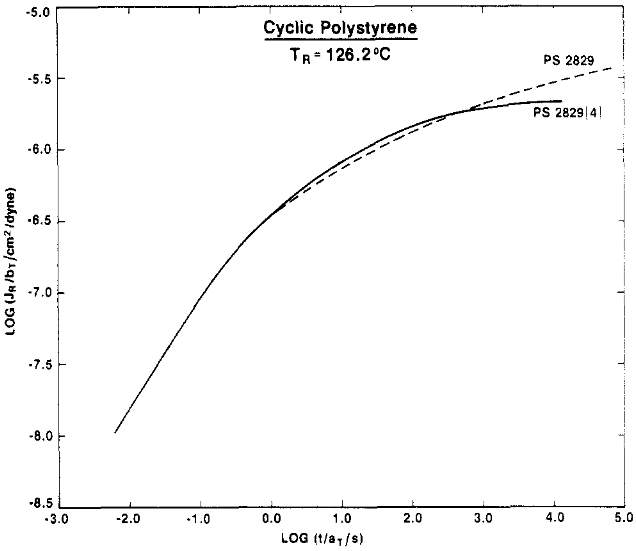

Figure 6. Master curves for recoverable compliance versus reduced time in double logarithmic representation for cyclic polystyrene fractions: dashed line, PS2829; solid line, PS2829[4], which was refractionated; reference temperature T_R = 126.2 °C. Differences interpreted to be due to presence of linear and high molecular weight contamination of unrefractionated sample. (See text for discussion.)

(c) Behavior of Blends of Linear and Cyclic Molecules of Similar Molecular Mass. The observation that refractionation of the PS2829 and PS2780 samples leads to a change in both the recoverable compliance behavior and the viscosity (to be discussed in the section on viscosity) of the cyclic molecules leads us to carry out several experiments designed to determine the effect of small amounts of linear polymer on the behavior of the PS2829[4] and PS2780[3,4] refractionated samples. Parts of this work have been reported elsewhere.[2,4] Here we report the results from recoverable compliance measurements on blends of linear fractions having approximately the same molecular mass as the PS2829[4] and PS2780-[3,4] cyclic fractions. The characteristics of the cycles and linear chains with which they were blended are shown in Table III.

In Figure 8 we present a comparison of recoverable compliance reduced curves for the PS2829[4] refractionated sample with that for a blend of 4.75% of the L-5

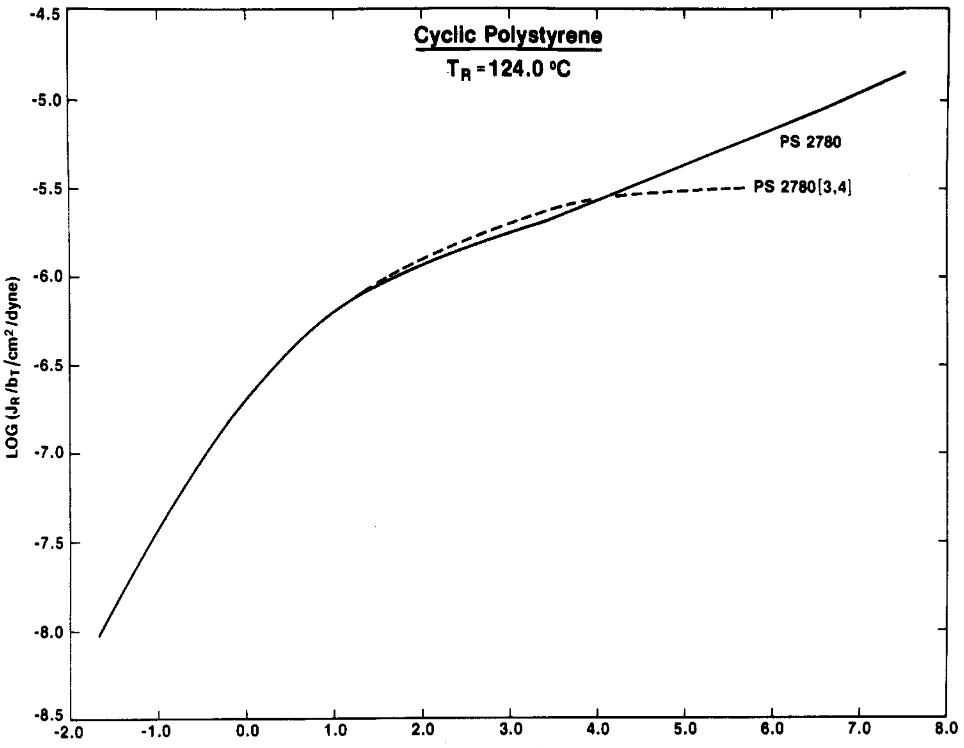

Figure 7. Master curves for recoverable compliance versus reduced time for cyclic polystyrene fractions: solid line, PS2780; dashed line, PS2780[3,4], which was refractionated; T_R = 124.0 °C. Differences interpreted to be due to presence of linear and high molecular weight contamination of unrefractionated sample. (See text for discussion.)

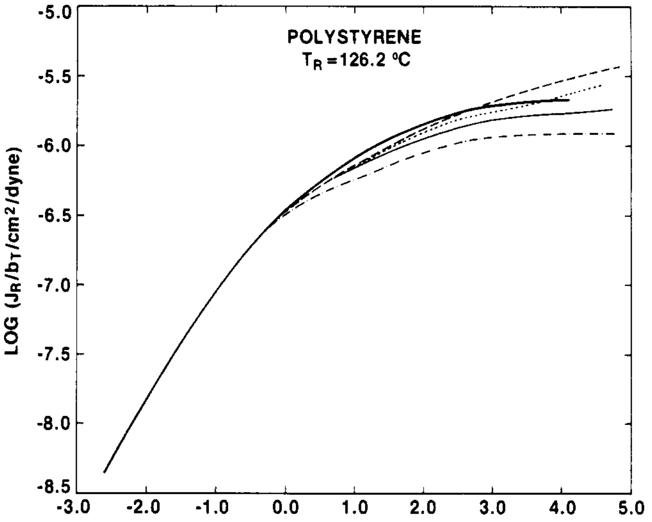

Figure 8. Double logarithmic plot of recoverable compliance versus reduced time for cyclic and linear polystyrene fractions and their blends (T_R = 126.2 °C). Long dashed line is for unrefractionated cyclic fraction PS2829. Bold solid line is for refractionated cyclic fraction PS2829[4]. Light solid line is for refractionated cyclic fraction PS2829[3]. Short dashed line is for a blend of 94.25% PS2829[4] cycles with 5.75% linear fraction L-V. Dashed–dotted line is for linear fraction L-V. (See text for discussion.)

linear polystyrene fraction with he PS2829[4] cycles. In Figure 9 we present a similar comparison of the reduced curves for the PS2780[3,4] cyclic fraction with blends of 5.75 and 14.8% of the L-2 linear polystyrene with the PS2780[3,4] cycles. Also shown in Figures 8 and 9 are the reduced curves for the relevant linear fractions as well as for the original unrefractionated samples.

The major result from these experiments is that the recoverable compliance measured in the rubbery plateau region for the blends is lower than for the cycles. This

Table III
Characteristics of Cyclic and Linear Polystyrene Fractions Used in Blend Study

fractn designatn	type molecule	$10^{-5}M_w$, g mol^{-1}	M_w/M_n	[η], dL g^{-1}
PS2780	cyclic	1.82	1.10	23.5[a]
PS2780[3,4]	cyclic	1.85	1.12	23.0[a]
L-II-2	linear	1.89	1.01	36.9[b]
PS2829	cyclic	1.06	1.16	17.8[a]
PS2829[4]	cyclic	1.06	1.13	
L-V	linear	1.22	1.05	29.7[b]

[a] In cyclohexane at 35.0 °C. [b] In cyclohexane at 34.5 °C.

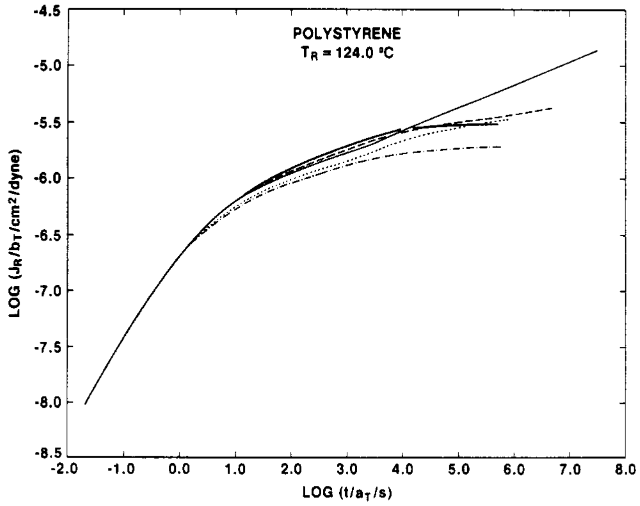

Figure 9. Double logarithmic plot of recoverable compliance versus reduced time for cyclic and linear polystyrenes and their blends (T_R = 124.0 °C). Light solid line is for unrefractionated cyclic sample PS2780. Bold solid line is for refractionated sample PS2780[3,4]. Long dashed line is for blend of 95.2% PS2780[3,4] with 4.8% linear fraction L-II-2. Short dashed line is for blend of 84.25% PS2780[3,4] with 15.75% linear fraction L-II-2. Dashed dotted line is for linear sample L-II-2. (See text for discussion.)

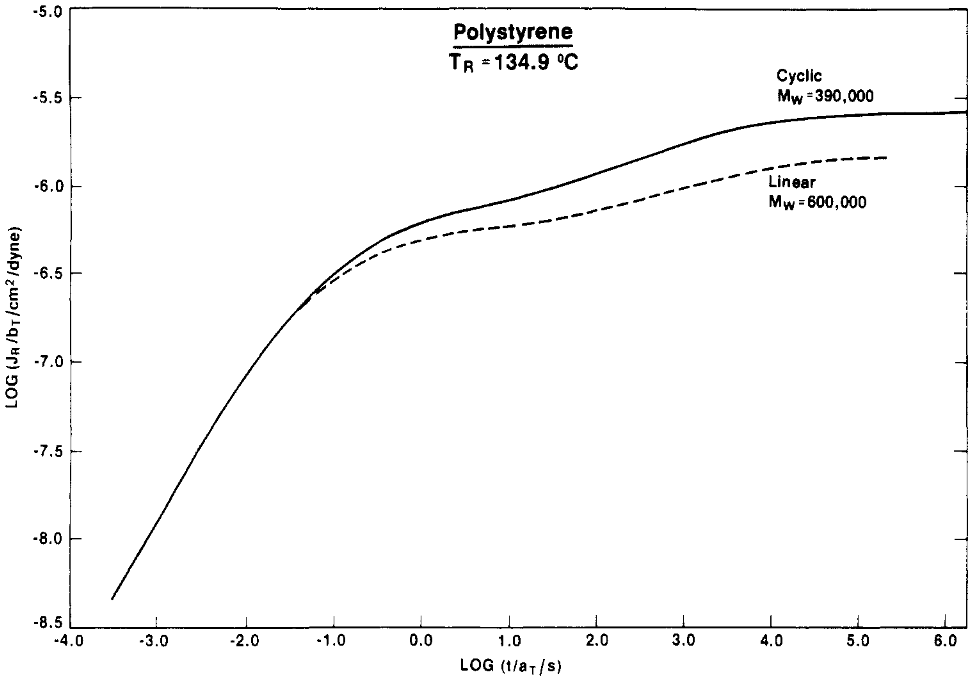

Figure 10. Double logarithmic plot of recoverable compliance versus reduced time for cyclic polystyrene fraction 83R (M_w = 390 000) compared with that of a linear polystyrene fraction A19 (M_w = 600 000), as indicated. Curves superpose in dispersion region, i.e. at short times. The differences are interpreted as showing the 83R to be a good cyclic fraction with $G_N° = 1/J_N°$ half that of the linear chain and $J_e°$ cycles ≈ $2J_e°$ linear. (See text for discussion.)

confirms the assertion made in section b above that linear chains constitute at least part of the contamination of the original PS2829 and PS2780 fractions. However, in the blends, molecular weights of the linear chains are approximately the same as for the cycles, the terminal relaxation times for cyclic and linear chains can be seen to be approximately the same, and the values of the steady-state recoverable compliance appear to increase upon addition of the linear chains. This effect does not appear dramatic, but the measurements required to establish the value of $J_e°$ in the blends were not successfully completed.

One other experiment relevant to the problem we are addressing here was carried out. The third cut from the refractionation of the PS2829 sample, designated as PS2829[3], was molded and placed in the testing machine, and the recoverable compliance was measured. For this fraction, the behavior was similar to that of the blends; i.e. the rubbery region showed a lower recoverable compliance while the value of $J_e°$ was virtually unchanged. This is also shown in Figure 8. This result suggests that the fractionation of linear chains from the cycles is extremely delicate. In Table IV we give the total weights of the original PS2829 and PS2780 fractions and the amount of material in each cut from the refractionation.

An important aside here is that these two fractions in their "as received" state have been used by other workers to study neutron scattering,[27b] and diffusion,[5] behavior of rings. It is not known how important this is for the interpretation of the results. As we will show, it is quite important for the zero shear viscosity.

Table IV
Fraction Masses for Macrocyclic Samples PS2780 and PS2829 Refractionated[a] at University of Pittsburgh

sample	fractn no.	$10^{-5}M_w$, g mol^{-1}	mass
PS2829	original	1.06	0.850
	[1,2]		0.410
	[3]		0.164
	[4]	1.06	0.276
PS2780	original	1.82	0.970
	[1]		0.159
	[2]		0.250
	[3,4]	1.85	0.558

[a] By fractionate precipitation (coascervation) from benzene and methanol.

(d) Behavior of a "Good" Cyclic Fraction. The above described studies of the recoverable compliance behavior of the polystyrene macrocycles provide a considerable amount of information toward the development of criteria for the determination of the quality of a cyclic fraction. However, because of the relatively low molecular weight of these samples, the rubbery plateau in the recoverable compliance reduced curves is generally poorly developed. Therefore, it is illustrative to examine the behavior of a "good" fraction of high molecular weight to elucidate the important points in evaluating the quality of the fraction vis-à-vis its ringlike nature.

To do this, we plot in Figure 10 the recoverable compliance reduced curve for the 83R Akron fraction of 3.9 × 10^5 molecular weight. [Although this sample shows anomalous dilute solution behavior, its rheological properties are definitely not those of a linear chain. Furthermore, examination of the recoverable compliance curve for fraction PS2780[3,4] shows the rubbery "inflection" at log $J_N°$ = −5.9, which is the same as that for the 83R sample and consistent with log $G_N°$ = 5.9 reported by Roovers.[3]] It is compared in the figure with the behavior of a 6 × 10^5 molecular weight linear polystyrene fraction.[49] First we note that both the cyclic and linear fractions exhibit smooth behavior and the steady-state value of the recoverable compliance, $J_e°$, is attained. However, the $J_e°$ value for the cyclic fraction is approximately twice that of the linear fraction [i.e., log $J_e°|_{\text{cycles}}$ = −5.6; log $J_e°|_{\text{linear}}$ = −5.85). The attainment of a steady-state value, $J_e°$, implies that the fractions are narrow. Furthermore the fact that the $J_e°$ value for the 83R fraction is approximately the same as that for the PS2780[3,4] sample (see Figure 7) is indicative that at these molecular weights $J_e°$ is no longer increasing as M_w increases, similar to what is observed in narrow molecular weight linear fractions.[22,49,50] In addition, both the cyclic sample and the linear sample exhibit well-developed rubbery plateaux. Plazek[51] has shown that the plateau compliance $J_N°$ measured by taking the inflection point on the log J_R/b_T – log t/a_T plot agrees well with that determined by integration under the first peak of the retardation spectrum. In this instance the rubbery compliance of the cyclic fraction is approximately twice that of the linear one, i.e. log $J_N°|_{cycles} = -5.95$ and log $J_N°|_{linear} = -6.2$. This agrees with the finding of Roovers from dynamic measurements that the rubbery modulus for the cycles is approximately half that of the linear chains and implies from rubber elasticity arguments that the molecular weight between entanglements, M_e, for the cycles is about twice that of the linear chains.

(e) Criteria for Evaluating the Quality of Cyclic Fractions from Recoverable Compliance Measurements. The evaluation of the quality of the cyclic fractions is based upon the assumption that the fractions themselves are composed primarily of ringlike molecules. The recoverable compliance measurements make it possible to look for two types of contamination in relatively small quantities. First, the presence of a high molecular weight tail in the sample can be detected from the magnitude of the steady-state recoverable compliance. $J_e°$ for the cycles appears to be approximately 2 times the value for the linear counterparts, at least above 10^5 molecular weight. (We note, however, that any high molecular weight tail may be either linear or cyclic molecules.) Second, the presence of linear chains can be seen in the recoverable compliance measurements. The presence of linear chains manifests itself by changing the compliance behavior near the rubbery plateau by displacing the plateau of the cycles toward that of the linear chains. Furthermore, the presence of small amounts (~5%) of linear chains in the cyclic fraction is sufficient to cause a measurable reduction in the plateau if it is well developed or in the shoulder region if the plateau is not well developed. (See Figures 8 and 9.)

Thus, the recoverable compliance response of the cyclic fraction upon comparison with the behavior of a similar linear fraction presents a sensitive tool for evaluating the quality of the fractions. The fraction quality can be judged not only for the presence of high molecular weight species but also for the presence of linear chains. In the following section we evaluate the quality of the remaining Strasbourg and Akron fractions for which we have had the opportunity to measure the recoverable compliance after steady shearing flow.

(f) Evaluation of the Quality of the Cyclic Fractions from Recoverable Compliance Measurements. In this section we present results from measurements of the recoverable compliance of the remaining Akron and Strasbourg cyclic fractions studied here, compare these with the behavior of similar molecular weight linear fractions and then judge the cyclic fraction quality based upon the criteria described above. We start with the highest molecular weight samples, which are the most easily evaluated, and in order of decreasing molecular weight evaluate each sample.

In Figure 11 is shown the compliance master curve for the 82R Akron fraction of cyclic polystyrene of molecular weight 247 000. Also shown for comparison is the master curve for the 83R cyclic fraction as we had no data for a 247 000 molecular weight linear polystyrene. There are several things to be noted from this figure. First, although a steady-state value of recoverable compliance is attained for the 82R cycles, the value is somewhat higher than that of the higher molecular weight 83R cycles. Since it is expected that $J_e°$ should reach a limiting value at high molecular weights, we interpret this result as evidence of some sort of higher molecular weight material in the sample. (In fact, GPC traces for the 82R cycles indicate that there is a small amount of material which appears to correspond to double molecular weight rings.) Furthermore, the rubbery plateau region for the 82R cycles while exhibiting a sharp feature at approximately log $t/a_T = 3.12$ is higher by a factor of approximately 2 than what would be expected for a linear fraction. Such behavior is consistent with the contamination giving rise to the high $J_e°$ value corresponding to high M_w cycles rather than linear chains; otherwise the rubbery region would be pulled toward that of the linear chains (see discussion on the refractionated samples and on the blends of cycles and linear chains above). In spite of the fact that the 82R fraction is a narrow one (from M_w/M_N), exhibits a measurable steady-state recoverable compliance, and is apparently predominantly rings, the presence of the high molecular weight tail requires us to classify this fraction as "moderate" in quality. This is particularly so since it is unknown what effects ring polydispersity might have on the viscosity of these fractions.

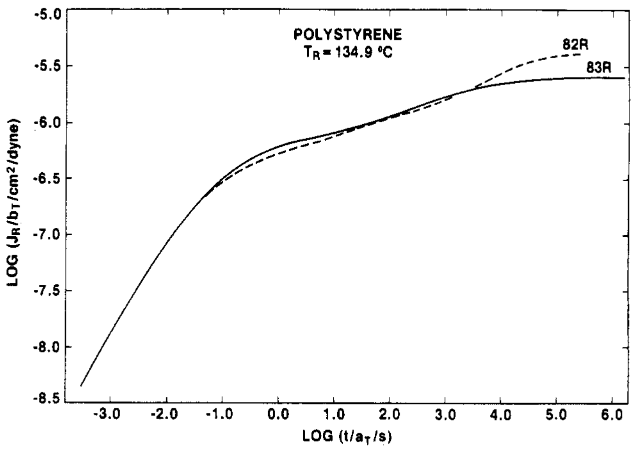

Figure 11. Double logarithmic plot of recoverable compliance versus reduced time for two Akron cyclic polystyrene fractions, as indicated (82R, M_w = 247 000; 83R, M_w = 390 000). The differences are intepreted to mean that the 82R is slightly contaminated by linear chains (low shoulder) and a high molecular weight species (high steady-state recoverable compliance). (See text for discussion.)

In Figure 12 we display a plot of the Strasbourg PS2774[F8] recoverable compliance curve obtained at 119.9 °C. This is the fraction having a molecular weight of 73 000. Also shown are results for a fraction of linear polystyrene of similar molecular weight. As can be seen the cyclic fraction exhibits a steady-state recoverable compliance, which is approximately two times that of the linear fraction (log $J_e°|_{2774} = -5.75$). It is, however, lower than that of the higher molecular weight samples. As this molecular weight is too low to see a well developed rubbery plateau, we simply remark that if there were linear chains present, we would expect the shoulder portion of the reduced curve to be pulled toward the linear sample, flattening the curve. This sample is judged to be a "good" quality fraction.

In Figure 13 is displayed a plot of the recoverable compliance reduced curves for the Akron 70R and the Strasbourg HA49 cyclic fractions, both of which have molecular weights of 4.4×10^4. Also shown is the reduced curve for a similar molecular weight linear polystyrene. There are several things to be noticed about this figure. First both of the cyclic fractions exhibit larger recoverable compliances than does the linear material. However, the 70R material, in exhibiting a slight reduction of compliance in

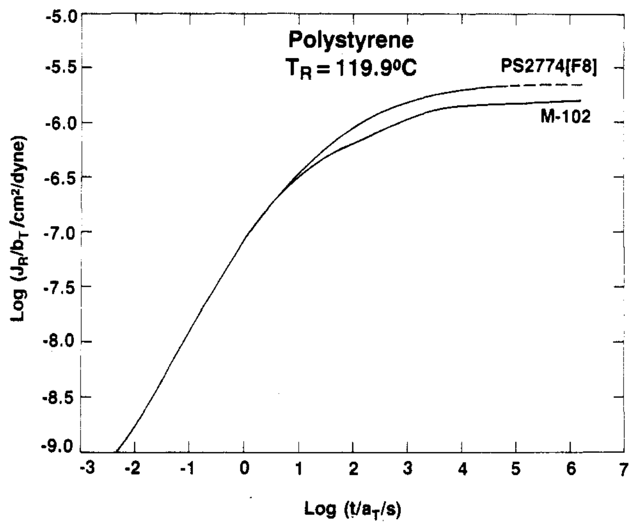

Figure 12. Double logarithmic plot of recoverable compliance versus reduced time for PS2774[F8] cyclic fraction (M_w = 73 000) and linear fraction M-102 (M_w = 94 000). Dashed line is estimated value for the PS2774[F8] fraction. Differences in the curves illustrate the consistency of results, i.e. that the linear chains show a low shoulder region (or rubbery plateau) and lower value for $J_e°$ than do cyclic fractions.

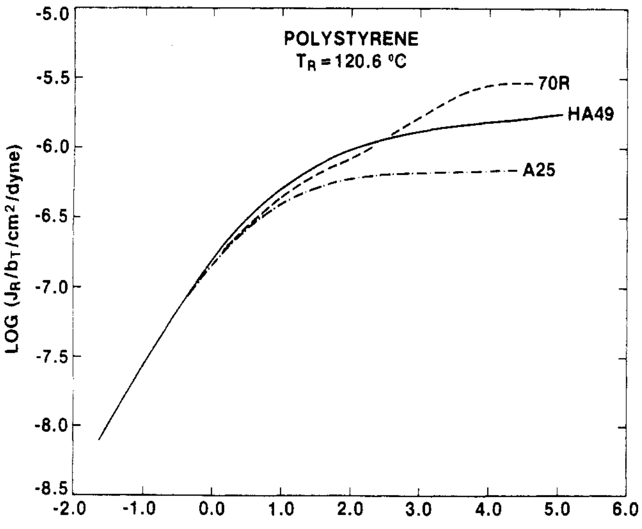

Figure 13. Comparison of steady-state recoverable compliance versus reduced time for two cyclic polystyrene fractions (70R and HA49, M_w = 44 000) and a linear fraction (A25, M_w = 46 000). Curves are interpreted as follows: The HA49 is a "good" cyclic fraction as indicated by the fact that steady state is nearly attained and the recoverable compliance rises above that of the linear fraction. The 70R is only a "moderate" fraction because the shoulder region is lower than for the HA49 and the $J_e°$ value is higher than the HA49. (See text for discussion.)

the shoulder region of the compliance master curve, exhibits evidence of contamination by linear chains. Furthermore, the high value of the steady-state recoverable compliance for the 70R fraction relative to that of the HA49 fraction (log $J_e°|_{70R}$ = 5.5; log $J_e°|_{HA49}$ = −5.7) indicates the presence of a higher molecular weight species. As a result of the compliance behavior we judge the 70R fraction to be a "poor" fraction. On the other hand, behavior of the HA49 sample appears to justify its characterization as a "good" quality cyclic fraction.

In Figure 14 are displayed the data from recoverable compliance measurements for the PS2857 cyclic fraction of 19 400 molecular weight. Interestingly, as has been observed for linear polystyrenes of low molecular weight, the curves are not superposable except at low values of compliance. Note that the plateau value of the recoverable compliance approaching steady state decreases as temperature decreases which implies that the time–temperature reduction (i.e. thermorheological simplicity) does not apply. Such behavior has been observed by Plazek and O'Rourke[49] for low molecular weight linear polystyrenes. In Figure 15 we plot log $J_e°$ versus $T - T_g$ for a linear polystyrene of molecular weight 16 400 and the value of J_R of the PS2857 cyclic fraction ($M_w = 1.94 \times 10^4$) at (or extrapolated to) log t/a_T = 3.0, since the steady state was not reached for this fraction.[52] However, on the basis of the curvature of the data we expect that these isochronal values are not too far from the steady state. In any event, examination of Figure 15 shows that both the linear and cyclic polymers show a decrease in $J_e°$ as $T - T_g$ approaches zero. This behavior has been extensively discussed by Plazek and O'Rourke[49] and attributed to a "freezing out" of relaxation mechanisms near T_g by Ngai, Plazek, and Deo.[53]

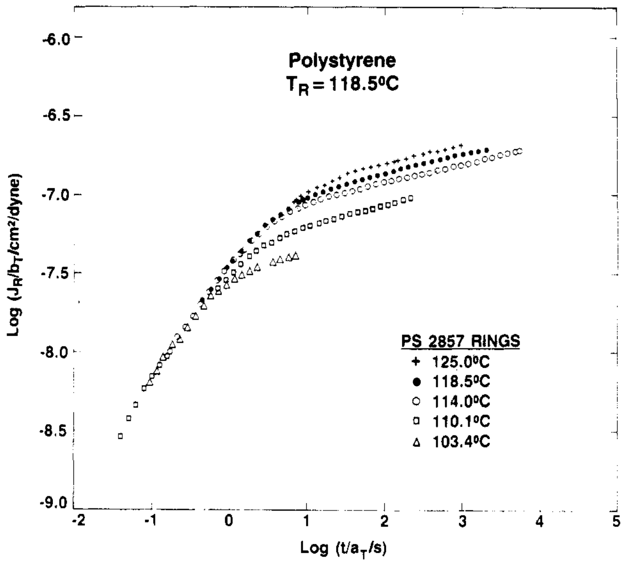

Figure 14. Double logarithmic plot of recoverable compliance versus reduced time for PS2857 cyclic fraction (M_w = 19 400). The spreading of the curves is similar to what has been observed for low molecular weights linear polystyrene close to T_g (see text).

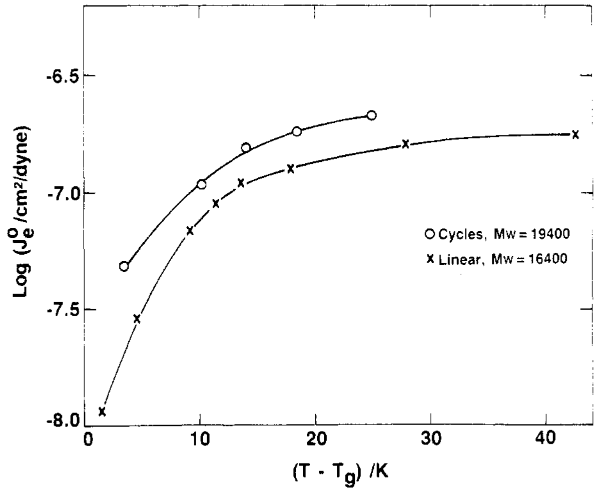

Figure 15. Logarithm of the steady-state recoverable compliance versus $T - T_g$ for low molecular weight linear (M_w = 16 400) and cyclic (M_w = 19 400) polystyrene fractions. Value of $J_e°$ for cycles is actually value of J_R at log t/a_T = 3.

On the basis of this the behavior of the PS2857 depicted in Figure 15, this sample appears to be of "good" quality. However, the position of the T_∞ is apparently too high on

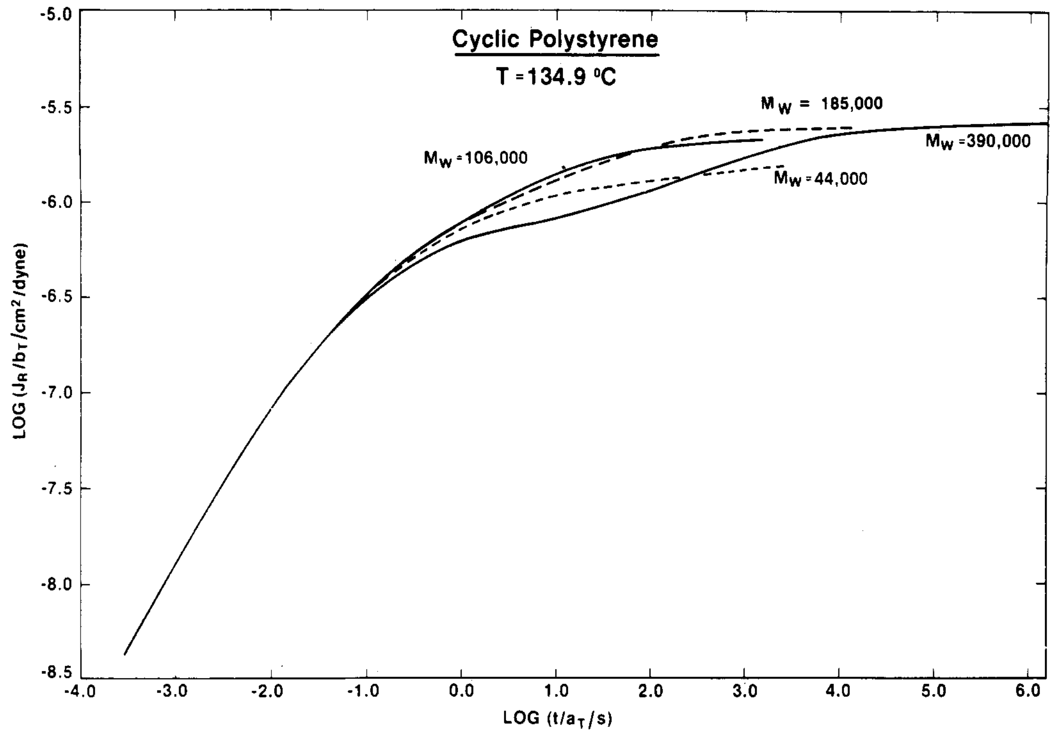

Figure 16. Comparison of recoverable compliance master curves for cyclic fractions HA49 (M_w = 44 000), PS2829[4] (M_w = 106 000), PS2780[3,4] (M_w = 185 000), and 83R (M_w = 390 000). Note that from a classical viewpoint these curves show that rings exhibit linearlike behavior. J_e° increases with increasing molecular weight and becomes constant at high molecular weights with the rubbery plateau only becoming evident at higher molecular weights.

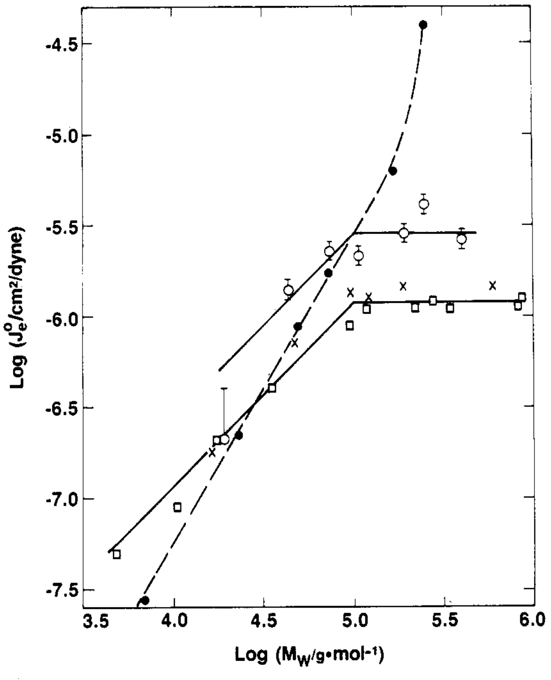

Figure 17. log J_e° versus log M_w for cyclic and linear polystyrenes. Linear: (□) ref 3; (×) ref 49 and results reported in this work. Cycles: (●) ref 3; (○) this work. Large error bar on sample of M = 19 400 is due to these being an estimate which includes both time and temperature dependence since actual steady state was not attained. Note that the results for Roovers[3] cycles are significantly different in character from those of the cycles reported here or the linear chains.

the basis of a Vogel[1,23,54]-type analysis of the zero shear viscosity of this sample. Therefore, this sample is treated as "moderate" in quality.

Insufficient recoverable compliance data were obtained for the Akron 79R fraction of 2.2×10^4 molecular weight to comment on its quality in a strict sense. We do note that the T_g from DSC measurements is approximately 93 °C rather than the 103 °C obtained in the same way on the Strasbourg cyclic polystyrenes (i.e. DSC). This could be due to either the presence of low molecular weight linear contaminants or the bulky group used to couple the ends of the chain together in the Akron fractions. As we will see, the viscosity of this sample, upon correction for the change in T_g, will fall where it should for a cyclic material of this molecular weight. We cannot, however, strictly categorize the "quality" of this fraction.

A final graph presented in this section shows the comparison of the recoverable compliance reduced curves for four of the "good" fractions studied here. In Figure 16 we show the reduced plots for fractions HA49, PS2829[3], PS2780[3,4], and 83R. These show "classical" behavior.[23,49,50] At low molecular weights the recoverable compliance increases at a decreasing rate until a steady-state value is attained. As M_w increases, the steady-state value J_e° increases and one also observes the appearance of a rubbery "shoulder" in the reduced curve. At the highest molecular weights, the rubbery plateau is well developed and J_e° has attained a constant value, independent of further increase in molecular weight. We will discuss this behavior further in the next section where we also "evaluate" the Roovers[3] fractions.

(g) Evaluation of the Roovers Fractions Based on His Reported Dynamic Data. The fractions of cyclic polystyrene for which Roovers[3] presented viscosity data were characterized by him using oscillatory shearing histories. He reported values of J_e° for his samples based on extrapolations of the storage modulus, G', to zero frequency. He also obtained values of the plateau modulus G_N° by integration of the loss modulus G'' over reduced frequency. In Figure 17 we depict the values of J_e° versus M_w in a double logarithmic representation for the "good" and "moderate" Strasbourg and Akron fractions and for the Roovers fractions. Also shown are values of J_e° for linear fractions.

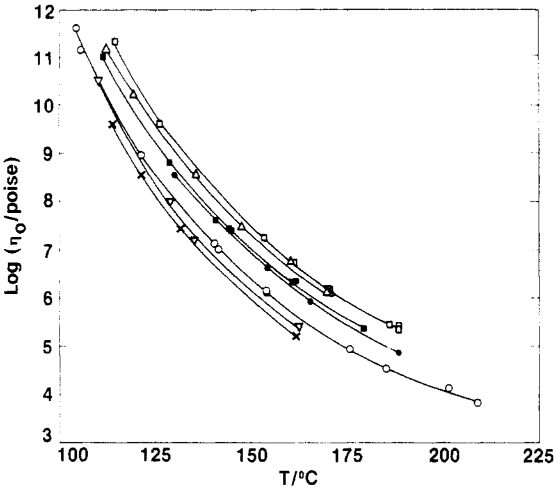

Figure 18. Logarithm of zero shear viscosity versus temperature for cyclic polystyrenes and their blends with linear chains of the same molecular weight: (□) PS2780;[1] (●) PS2780[3,4];[1] (■) 4.8% L-II-2 in 95.2% PS2780[3,4];[2] (△) 15.8% L-II-2 in 84.2% PS2780[3,4][2] (this study); (○) PS2829;[1] (×) PS2829[4];[2] (▽) 5.75% L-V in 94.25% PS2829[4][2] (this study).

Table V
Zero Shear Viscosity (η_0) Data for Cyclic Polystyrenes and Blends of Cyclic and Linear Polystyrenes of Similar Molecular Mass

T, °C	log η_0, P
79R	
$M_w = 2.2 \times 10^4$	
106.0	7.762
125.8	5.627
142.3	4.300
PS2774 [F7][1]	
$M_w = 7.94 \times 10^4$	
137.0	6.818
139.4	6.566
145.1	6.118
150.0	5.777
156.8	5.345
164.1	4.891
169.9	4.546
174.7	4.376
184.8	3.982
193.1	3.671
204.0	3.307
211.4	3.140
217.6	2.975
PS2774[F8]	
$M_w = 7.30 \times 10^4$	
119.9	8.187
131.3	6.830
148.1	5.399, 5.370
148.2	5.351, 5.330
168.1	4.261
PS2829[1]	
$M_w = 1.06 \times 10^5$	
104.4	11.579
105.5	11.142
121.4	8.957
140.3	7.110
141.3	6.999
153.8	6.129
154.0	6.064
175.7	4.925
185.0	4.544
209.1	3.828
PS2829[F4][1]	
$M_w = 1.06 \times 10^5$	
113.7	9.621
121.3	8.549
126.2	8.030
131.8	7.447
142.4	6.498
161.5	5.223
PS2829[F3]	
113.7	10.146
118.7	9.412
128.0	8.397, 8.542
140.9	7.240, 7.234
166.0	5.561
94.25% PS2829[F4] with 5.75% L-V	
Cycles, $M_w = 1.06 \times 10^5$; Linear, $M_w = 1.22 \times 10^5$	
110.3	10.570
128.2	7.971
135.6	7.231
144.0	6.568, 6.590, 6.589
162.3	5.383
PS2780[1]	
$M_w = 1.82 \times 10^5$	
114.4	11.336
126.2	9.603
153.2	7.235
153.2	7.228
170.3	6.176
170.7	6.159
170.7	6.114
186.1	5.469
188.2	5.392
188.2	5.375
PS2780[3,4][1]	
$M_W = 1.85 \times 10^5$	
124.0	9.289
130.2	8.555
154.4	6.635
165.2	5.928
188.4	4.864
95.2% PS2780[3,4] and 4.8% L-II-2	
Cycles, $M_w = 1.85 \times 10^5$; Linear, $M_w = 1.89 \times 10^5$	
111.0	10.991
128.4	8.812
144.1	7.437
144.6	7.392
151.4	6.940
160.4	6.294
160.8	6.306
178.7	5.382, 5.374
84.2% PS2780[3,4] and 15.8% L-II-2	
111.8	11.125
119.2	10.195
135.4	8.554
148.0	7.467, 7.505, 7.527
160.2	6.787, 6.766
169.6	6.134

The differences between the results for the Strasbourg/Akron fractions and those of Roovers are quite large. At high M_w the Roovers macrocycles show a value of $J_e°$ over 10 times greater than that of the Strasbourg/Akron group and he was unable to measure the value of his $M_w = 3.34 \times 10^5$ fraction. Furthermore, at lower molecular weights one observes that the Roovers macrocyclic fractions exhibit values of $J_e°$ which are lower than for the linear chains. This is surprising and the trend in results is difficult to explain. Here we speculate that it may be due to a high fraction of knots in all of the Roovers cycles (due to either excessive fractionation or ring closure in poor solvent conditions) and an increasing amount of linear chain contamination as the molecular weight increases.

Examination of the dynamic data from Roovers should, in principle, enable us to determine whether or not these high molecular weight species are cyclic or linear. Roovers reports the values of $G_N°$ for the R18DD, 3.34×10^5 molecular weight cyclic sample to be half that of linear chains. He further observes that upon a 150 °C heat treatment in benzene in a pressure vessel of this sample that $G_N°$ increases to 0.7 times the value for linear polystyrene. He interpreted this increase in $G_N°$ in terms of improved entanglements. We, however, feel that the partial degradation of the sample into linear chains is responsible for such an increase in plateau modulus.

Unfortunately, Roovers does not present enough information and sample by sample comparison of his cyclic fractions with linear chains to judge whether or not the plateau region is affected by the high molecular weight contaminant. Thus, we cannot judge whether or not the contaminant contains linear chains. In any event, these three fractions are definitely not "good" ones and, on the basis of simply the high value of $J_e°$, we would judge them to be worse than our "moderate" sample 82R of 2.47×10^5 molecular weight.

C. Zero Shear Viscosities. (a) Temperature Dependence. The temperature dependence of the viscosity of the cyclic macromolecules has been dealt with elsewhere.[1] The data reported here, with the exception of the 79R sample, the PS2774[F8] sample, and the blends, were used in the previous analysis. Therefore, we merely note that the temperature dependence of all of the cycles, independent of molecular weight and with the exceptions of the 79R sample and PS2857, obey the same Vogel[54] or WLF[55] type of relation as the linear chains above their M_c. The new results for fraction PS2774[F8] and 79R are tabulated in Table V. Also listed in the table are the viscosities of the blends of linear polystyrenes with the PS2780[3,4] and PS2829[4] cycles. The temperature dependences of the blends of linear and cyclic molecules are depicted in Figure 18 along with the curves corresponding to the original PS2780 and PS2829 fractions and refractionated PS2780[3,4] and PS2829[4] samples.

An interesting feature of the temperature dependence of the viscosity of cyclic polystyrenes is the observation that it is independent of molecular weight, at least to molecular weights of 1.1×10^4. This is contrary to the behavior of linear polystyrene molecules for which the glass transition changes at low molecular weights and superposition of the viscosity curves requires a shift along the temperature abscissa in addition to the vertical shift along the log η_0 ordinate below a molecular weight of approximately 4×10^4.

The 79R Akron sample of 2.2×10^4 molecular weight, however, does not follow this rule. Rather superposition of the viscosity curves requires a temperature shift, ΔT, of approximately 10 °C. This corresponds well with the observation that the glass temperature by DSC is approximately 10 °C lower than for the Strasbourg cyclic molecules. There are two possible reasons for this. First the sample could be contaminated with low molecular weight material or the presence of the dichlorosilane at the ring closure site or the hexadiene group in the chain. In any event, when the viscosities of the samples are discussed, those for this sample will be corrected for the change in T_g, i.e. the ΔT required to superimpose the viscosity curves.

(b) Effects of Fraction Quality on Zero Shear Viscosity. The recoverable compliance measurements described earlier allowed us to evaluate the quality of the cyclic fractions. In this section we describe the effects of fraction quality on the melt viscosity. We do this by considering three different sorts of experiments. First, the PS2829 and PS2780 samples which were shown to be contaminated, most probably by high molecular weight linear chains were refractionated and showed significant (approximately a factor of 3) decreases in viscosity, without a change in molecular weight. This was the first indication we had that the presence of linear chains could significantly increase the viscosity of the cyclic fractions. Also, the refractionated samples PS2829[4] and PS2780[3,4] showed compliance behavior which we interpreted as being consistent with that of "good" cyclic fractions.

Second, we took the PS2829[4] and PS2780[3,4] "good" fractions and intentionally blended them with linear chains of the same molecular mass. The recoverable compliance behavior of the cycles due to the presence of the linear chains changed which aided us in evaluating the quality of the other fractions (see Discussion, section B). In addition, the presence of even a small quantity of linear chains results in a significant increase in the viscosity of the cyclic fractions.

Due to the fact that there is only a limited amount of data, we chose to present the effects of changing blend composition on the viscosity of the mixtures as the ratio of viscosity at a given composition to the viscosity of the refractionated samples (nominally 100% cycles); i.e., η_0/η_{100}. Figure 19 shows a plot of log (η_0/η_{100}) at 160 °C versus log (ϕ_c), where ϕ_c is the weight concentration of the cyclic molecules. The results suggest that small quantities of linear chains in the cyclic fractions have a dramatic effect on the viscosity. The line of slope −5.6 in Figure 19 underlines this effect. Of course at a zero concentration of cyclic chains the viscosity would tend toward that of the linear fraction (dashed and solid traces at the vertical axis). We note here that the reason for the difference between the positions of the reduced viscosity lines for the two linear fractions stems primarily from the fact tht the L-5 linear fraction has a molecular weight of 1.22×10^5 versus 1.06×10^5 of the PS2829[4] cyclic fraction. The L-2 linear fraction has a molecular weight more nearly the same as that of the PS2780[3,4] cyclic fraction with which it was blended.

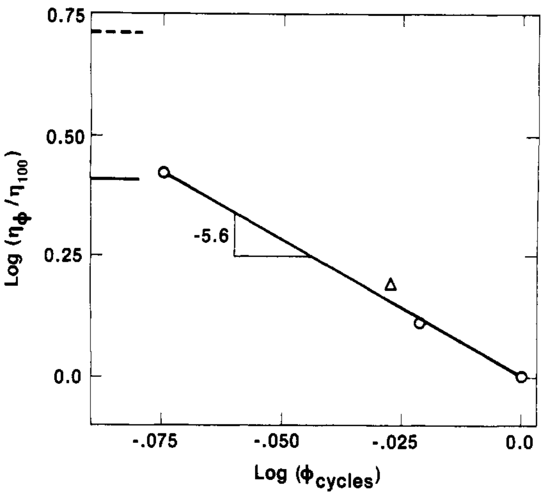

Figure 19. Double logarithmic plot of reduced viscosity versus concentration of cyclic molecules for blends of linear and cyclic molecules. Circles represent result for blends of L-II-2 linear polymer with PS2780[3,4]. Triangle is for a blend of L-V linear polymer with PS2829[4] cyclic polymer. Broken line is reduced viscosity for 100% L-V linear fraction. Solid line is for 100% L-II-2 linear fraction.

Third, we found, quite by chance, that the position of a cut in the refractionation next to a "good" fraction does not necessarily mean that it is also a good fraction. Thus, upon refractionation of the PS2829 sample we obtained four cuts and the fourth was shown, as described previously, to be a good fraction based on the recoverable compliance measurements. However, cut 3 on sample PS2829[3] exhibits behavior typical of a poor fraction based on recoverable compliance measurements (see Figure 8). The viscosity of this fraction was found to be nearly identical with that of the original PS2829 sample (Table V). This value is also close to that for linear chains of the same molecular weight.

In a similar experiment, we obtained a sample of the PS2774[F8] which had a molecular weight of 7.3×10^4. As it happens, the sample for which viscosity data had been previously obtained (and reported)[1] was PS2774[F7]. As discussed previously, the limited recoverable compliance results available for the PS2774[F8] sample show it to be a "good" fraction. Unfortunately, the PS2774[F7] sample was not available for compliance measurements. However, the [F8] sample had a much lower viscosity than did the [F7] sample, as shown in Table V. We, therefore, now think that the PS2774[F7] sample was probably slightly contaminated by linear chains.

(c) The Molecular Weight Dependence of the Zero Shear Viscosity. In the introduction we discussed that the molecular weight dependence of the zero shear viscosity of cyclic polystyrene molecules is controversial. In section III.B we described our measurements of the recoverable compliance of several cyclic polystyrene fractions from Strasbourg and Akron. On the basis of information from studies on refractionated samples and blends of linear chains with cyclic fractions, we were able to categorize the samples as "good", "moderate", or "poor". We used data for $J_e°$ reported by Roovers[3] to categorize his samples as well. Thus, we were able to use data for samples of "good" and "moderate" quality to study the effects of molecular weight on the melt viscosity of cyclic polystyrenes. Because there has been no controversy about the behavior of low molecular weight cycles, we include data for all of these samples.

In Figure 20 we present the viscosity–molecular weight dependence of the "good" and "moderate" cyclic macro-

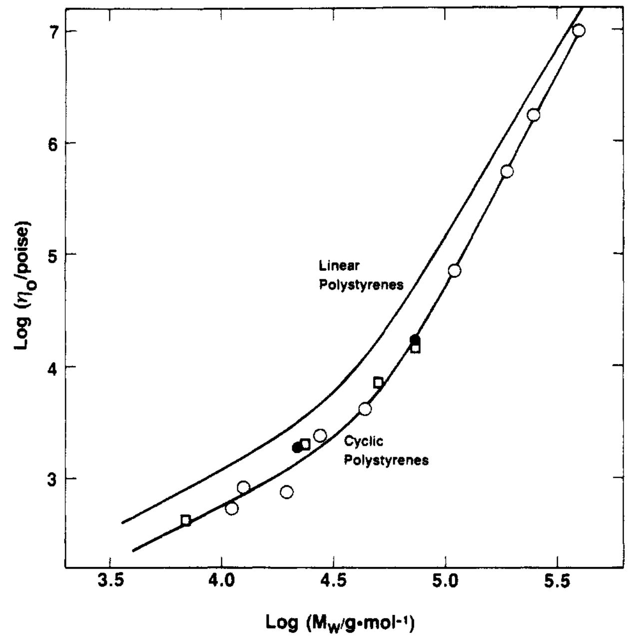

Figure 20. Double logarithmic plot of zero shear rate viscosity versus molecular weight for linear and cyclic polystyrenes at $T - T_g = 69.5$ °C. The upper solid line is for linear polystyrenes (from ref 1). Open squares are data for cyclic molecules from Roovers.[3] Open circles are data for cyclic polystyrenes reported previously (ref 1) and which we show in this paper follow our classification as "good" or "moderate" fractions. (Below M_w = 44 000 we make no effort to classify samples.) Two solid points are for previously unreported data. Curve through cyclic data obtained by nonlinear least-squares fit[56] to eq 2 for the data represented by the open and filled circles. These are the Akron and Strasbourg fractions.

Table VI
Parameters from Least-Squares Analysis of Viscosity–Molecular Weight Data for Cyclic[a] and Linear[b] Polystyrene Fractions at T_g + 69.5 °C

η–M_w equation	mol wt range, g mol^{-1}	parameter values[c]	M_c estimate[d]
	Cyclic Polystyrenes[a]		
$\eta = AM + BM^\alpha$	1.11×10^4 to 3.91×10^5	A: 0.058 (±0.006)	4.92×10^4
		B: $1.29 \times 10^{-15\,e}$	
		α: 3.91 (±0.26)	
$\eta = CM^\beta$	<4.8×10^4	log C: −3.02 (±0.61)	
		β: 1.44 (±0.14)	5.83×10^4
$\eta = BM^\alpha$	<4.8×10^4	log B: −14.22 (±0.15)	
		α: 3.79 (±0.028)	
	Linear Polystyrenes[b]		
$\eta = AM + BM^\alpha$	3.3×10^3 to 1.2×10^6	A: 0.112 (±0.01)	
		B: $8.84 \times 10^{-13\,e}$	$3.71 \times 10^{4\,f}$
		α: 3.43 (±0.06)	
$\eta = CM^\beta$	<40 000	C: g	
		β: 1.5	$4.40 \times 10^{4\,f,g}$
		B: g	
$\eta = BM^\alpha$	>40 000	α: 3.37	

[a] Strasbourg fractions: PS2653, HA50, PS2857, PS2648, HA49, PS2774[F8], PS2829[4], and PS2780[3,4]. Akron fractions: 79R, 82R, and 83R. [b] A compilation of data reported in ref 1. [c] Values in parentheses represent estimates of the standard deviation on the parameter given by the Dataplot[56] nonlinear least-squares data analysis package available at NIST. [d] M_c is estimated as the abscissa of the intersection of the high and low M asymtotes for the equation $\eta = AM$ + NIST. and the intersection of the lines CM^β and BM^α for the simple power law fits. [e] Because the parameter B in the equation $\eta = AM + BM^\alpha$ is extremely small and the estimates highly sensitive to the value of α, the standard deviations on B do not mean very much and, therefore, are not reported. [f] These values of M_c for linear polystyrene are higher than normally reported in the literature, see, e.g., Ferry[23] where $M_c \simeq (2.4–3.0) \times 10^4$ g/mol. Here we report the higher values based upon a consistent analysis technique for the cyclic and linear polymers. [g] The values of C and B were not given in ref 1, and M_c is obtained graphically from Figure 12 in ref 1.

molecules at T_g + 69.5 °C, where we assume T_g = 100 °C for the bulk of the samples. For the samples of Roovers and the 79R sample from this study for which a T_g depression was observed, the viscosity is corrected by the appropriate amount to account for the changing segmental mobility. The data for the PS2857 sample is corrected for an increase in T_g of 4 °C. Also shown is the least-squares curve obtained by analysis of data for linear polystyrenes from several literature sources and reported by McKenna et al.[1]

It is obvious from the data of Figure 20 that there is not a great difference in behavior between the cyclic and linear molecules. Over the entire range of molecular weights, at constant $T - T_g$, the cycles exhibit a somewhat lower viscosity than do the linear chains. At low molecular weights this difference is approximately a factor of 2. At the highest molecular weights the difference diminishes to approximately 20%.

We have analyzed the viscosity–molecular weight relation of the "good" and "moderate" Akron and Strasbourg cycles in two ways. First, because the transition from unentangled to entangled behavior is not very abrupt, we have fitted[56] the data to a form

$$\eta = AM + BM^\beta \tag{2}$$

which was found previously[1] to describe the η–M data for both linear and cyclic macromolecules. Second we chose to analyze the data as two power laws—one for the unentangled polymer and one for the entangled polymer.

$$\eta = CM^\alpha \qquad M < 48\,000 \tag{3a}$$

$$\eta = BM^\beta \qquad M > 48\,000 \tag{3b}$$

The results of analyses of the viscosity molecular weight data for the cyclic fractions according to eq 2, 3a, and 3b are shown in Table VI. Also shown for comparison are the results reported previously[1] for linear polystyrenes. The curves in Figure 20 are the result of the fits to eq 2. Importantly the analysis of the cyclic data does not include the Roovers points which are depicted in Figure 20, although this does not dramatically affect the results.

The value of the critical molecular weight for entanglement coupling, M_c, for the macrocycles was obtained by taking the intersection of the asymptotes at low and high molecular weight in eq 2 and the intersection of eq 3a and 3b. These are reported in Table VI along with those for the linear chains. As can be seen, the M_c for the cycles is greater than for the linear chains, in contradiction to what was reported previously by McKenna et al.[1] This result arises primarily because the data point for the PS2774[F8] sample was lower than that for the PS2774[F7] sample, and, as discussed previously, we judged the [F8] sample to be the "good" fraction. This result also makes the estimate of M_c for the cycles consistent with the value of M_e obtained from the level of the rubbery plateau, i.e., greater than the value for the linear chains.

We note that the molecular weight dependence of the viscosity of the cyclic polystyrenes above M_c is somewhat higher than for the linear materials; i.e., β in eq 2 or 3b is 3.8–3.9 for the cycles versus 3.4 for the linear chains.

On the basis of this analysis of the viscosity data, we conclude that the cyclic and linear macromolecules exhibit similar Rouse-like behavior below M_c. The viscosity of the cycles below M_c is $^1/_2$ that of the linear chains. M_c for the cycles is approximately 1.8 times greater than for the linear

Table VII
Chain End Concentration for Equal Probability of Cyclization

M_w, g mol^{-1}	$C_{eq}(\Theta)$, g/mL	C_{eq}(good solvent), g/mL	$C_{eq}(\Theta)$, mol/L
2.0×10^4	5.9×10^{-3}	4.0×10^{-3}	2.9×10^{-4}
5.0×10^4	3.7×10^{-3}	2.0×10^{-3}	7.5×10^{-5}
1.0×10^5	2.6×10^{-3}	1.2×10^{-4}	2.6×10^{-5}
2.0×10^5	1.9×10^{-3}	7.1×10^{-4}	9.5×10^{-6}
4.0×10^5	1.3×10^{-3}	4.2×10^{-4}	3.3×10^{-6}

chains. Above M_c, the cycles and linear chains both exhibit a power law dependence on molecular weight. The power law exponent for the cyclic molecules is greater than is that for the linear chains, i.e., 3.8–3.9 versus 3.4. We do not find a stronger than power law dependence of the viscosity on molecular weight above M_c.

IV. Summary and Conclusions

As discussed in the Introduction, the characterization of the viscoelastic behavior of melts of cyclic polystyrene molecules is of great interest due to the perception that such molecules cannot reptate. Furthermore, comparison of such parameters as the magnitude of the rubbery plateau and steady states recoverable compliance (J_N° and J_e°, respectively) provides information about melt topology and the breadth of the viscoelastic spectrum. Unfortunately, the viscosity–molecular weight behavior of cyclic polystyrene molecules has been controversial and the results differ due, as we have shown, primarily to the nature of the fractions, i.e., presence of linear chains, knots, etc.

In this study we have addressed the question of the fraction quality by carrying out measurements of the recoverable compliance after steady shearing flow for several cyclic polystyrene fractions from three sources: those synthesized by two of us (L.J.F. and B.J.H.) and referred to as Akron fractions; those synthesized at the Institut Charles Sadron in Strasbourg and referred to as Strasbourg fractions; and two Strasbourg fractions which were refractionated by us. Furthermore we have examined the effects of blending up to 15.8% linear chains on the properties of the two CRM cyclic samples which we refractionated.

In these studies we have made evident several things. First, we have demonstrated that measurement of the recoverable compliance of cyclic fractions is a sensitive tool for characterizing the quality of the fractions. The presence of linear chains results in a rubbery region in the compliance curve which is reduced relative to that of the "good" cycles. The value of the steady state recoverable compliance, J_e°, is a good measure of the presence of high molecular weight species (linear or cyclic) in an otherwise narrow fraction. Second, the recoverable compliance measurements make possible the "rating" of the fraction quality as "good", "moderate", and "poor". Thus, we were able to rate five Strasbourg and Akron fractions of high molecular weight as "good" and one as "moderate". Furthermore, examination of the dynamic mechanical data

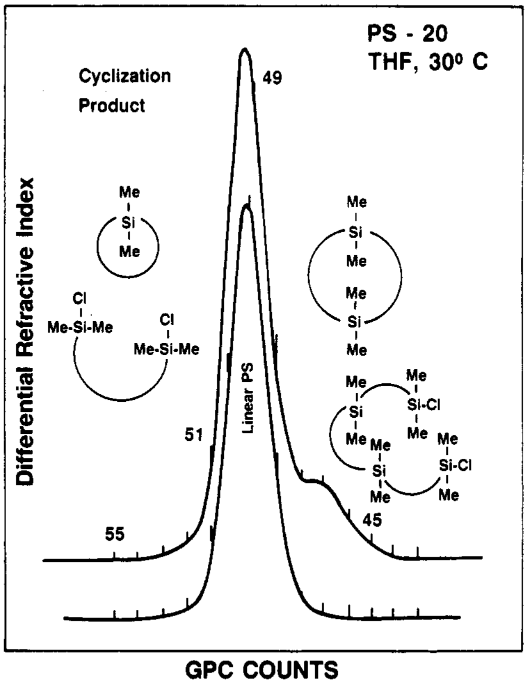

Figure 21. SEC chromatogram for cyclization products and linear polystyrenes.

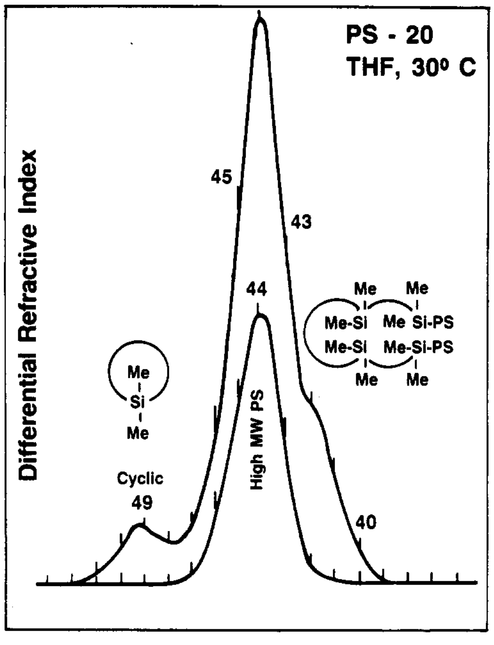

Figure 22. SEC chromatogram for macrocyclic and high molecular weight polystyrenes.

Table VIII
Cyclization Products

sample	percent cyclic	percent linear	monomer concn, g/mL	polymer concn, g/mL	cyclization time, days
79	33	67	1.5×10^{-2}	6.4×10^{-4}	15
80	67	33	1.7×10^{-2}	5.5×10^{-4}	9
70	76	24	1.7×10^{-2}	3.5×10^{-4}	6
90	77	23	1.7×10^{-2}	3.5×10^{-4}	10
75	33	67	1.43×10^{-2}	2.6×10^{-4}	2
20	85	15	9.5×10^{-3}	1.0×10^{-4}	28
5	43	57	1.03×10^{-2}	7.4×10^{-5}	5
1	67	30	1.07×10^{-2}	5.7×10^{-5}	4
82	100	0	1.41×10^{-2}	5.7×10^{-5}	3
83	100	0	1.41×10^{-2}	3.4×10^{-5}	5

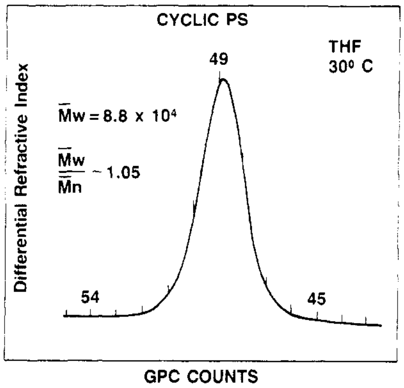

Figure 23. SEC chromatogram for fractionated macrocyclic polystyrenes.

obtained on melts of cyclic polystyrene samples by Roovers[3] has enabled us to categorize his two highest MW samples as "poor". Third, the zero shear viscosity of cyclic macromolecules characterized as "good" and "moderate" fractions results in a power law dependence of the viscosity on MW somewhat greater than that obtained previously;[1] i.e., the exponent is approximately 3.8–3.9 for the cycles versus 3.4 for the linear chains. Furthermore, the results suggest that M_c for the cyclic fractions is approximately 5.8×10^4 versus approximately 3×10^4 for linear polystyrene chains.[23] This is higher than the values estimated for M_c for cyclic polystyrene by McKenna et al.[1] previously.

Fourth, the value of the plateau modulus for the cycles is found to be half that of the linear chains. This confirms Roovers[3] findings for his samples. We also find that the limiting value of the steady-state recoverable compliance at high MW of the cyclic polystyrene fractions is approximately 2 times that for the linear polystyrenes.

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A special thanks is given to Pierre Lutz, Girard Hild, and Paul Rempp at the Institut Charles Sadron who synthesized the Strasbourg rings, made them available to us for rheological characterization, and then carried out dilute solution measurements on the refractionated samples. Finally thanks to Jack Douglas of NIST for many stimulating discussions about dilute solution properties and renormalization group and its relevance to our observed "anomalous" behavior.

Appendix 1. Synthesis of the Akron Cycles

The preparation of the macrocyclic polystyrenes was accomplished via the use of a difunctional initiator based on *trans*-2,4-hexadiene (Wiley Organics*). The procedures of preparations have been given elsewhere.[57] After isolation of the oligomeric initiator ($\mathrm{DP}_n = 2–6$), a few units of styrene per active center were added in order to enhance the solubility of the initiator in the polymerization media.

All polymerizations and the subsequent manipulations involving ring formation were conducted under high vacuum conditions in 2-L Pyrex reactors.[31a] Monomer and solvent purifications were carried out by using techniques described previously.[58] Prior to polymerization the reactor and its contents (monomer and solvent) were purged by using a dilute solution of dialkylmagnesium. The polymerization medium of choice was a 50/50 (v/v) mixture of benzene and cyclohexane. A typical recipe for such an experiment involved ca. 1.6 L of cosolvent and 10–20 g of styrene. The monomer concentration was controlled by the need to enhance the probability of intramolecular coupling at the expense of the corresponding intermolecular (chain extension) reaction. To this end the Jacobson and Stockmayer[59] predictions were followed as has been outlined by Roovers and Toporowski.[8]

A multistep synthetic route used in the macrocyclic preparation facilitated the examination of the reaction products after each step. This was accomplished principally by the use of size-exclusion chromatography (SEC).

A several gram sample was removed from the reaction flask following the polystyrene polymerization and analyzed by SEC. This served to produce the linear (L) polystyrene series. This sample was also used to check for a monomodal distribution and molecular weight before proceeding. Polymerization products with bimodal distributions were discarded. After the cyclization process, another sample was obtained for SEC evaluation. The approximate percentages of cyclized and chain extended products was determined from these results. An example of the linear "parent" and cyclization products are shown in Figure 21 for sample 20. The relative peak elution counts for these two samples, 49.1_5 for the linear material and 49.6_5 for the unfractionated cyclic polymer, serve as semiquantitative proof that cyclization took place.

The linear series was considered to be 100% polystyrene with the initiator fragment in the chain center. The cyclization product was potentially composed of the desired cyclic product, the linear polystyrene of parent molecular weight terminated with dimethyldichlorosilane, and chain-extended products of cyclic and linear nature in molecular weight multiples of the parent molecular weight. The high intensity peak in Figure 21 of the cyclized product represents the parent molecular weight fraction while the lower intensity peak represents the chain extended (or double cycle) fraction.

An additional step of adding a high molecular weight polystyryllithium of approximately 5–10 times the parent molecular weight was used as a scavenger reaction to eliminate the chlorosilane terminated linear contaminates. This step, developed by Geiser and Höcker,[14,60] was used to couple the parent molecular weight component with the high molecular weight scavenger producing a higher molecular weight species which could be separated by fractionation. An SEC chromatogram of material resulting from this step is shown in Figure 22. All cyclic samples were prepared in this manner. The macrocyclic polystyrenes of the linear parent molecular weight were separated from chain extended and high molecular weight components by successive fractionation until a monomodal SEC chromatogram was obtained. These samples composed the R series macrocyclic polystyrenes. Sample 20-R is shown in Figure 23.

Additional sources of contamination were considered and are described briefly. The potential of the existence of monofunctional chlorosilane or a dimethyldichlorosilane derivative would possibly prohibit the elimination of linear polystyrene contaminates by the scavenger reaction described previously.

The purity of the dimethyldichlorosilane coupling agent was examined by density and infrared spectroscopy measurements. The density values of dimethyldichlorosilane are listed below and compared to those of poly(dimethylsiloxane), the major product of a condensation reaction of dimethyldichlorosilane with water. For example, 10% content of poly(dimethylsiloxane) as contaminant would result in a density of 1.057 g/mL.

	density
dimethyldichlorosilane	
26 °C	1.065 g/mL—experimental; this study
25 °C	1.065 g/mL—ref 61
poly(dimethylsiloxane)	
25 °C	0.98 g/mL—ref 62

The concept of coupling two chains ends of a linear molecule together to form a cyclic structure must take into consideration the concentration of active centers and polymer molecular weight. The competing reaction of chain extension is favored in moderately concentrated solution, and cyclization only becomes favored at very low concentrations of reactive chain ends. In the case of a polycondensation reaction, Jacobson and Stockmayer[59] examined this problem and found the probability of cyclization to depend on the molecular weight, concentration of polymer, and the mean square end to end distance of the chain in solution.

The concentration for equal probability of inter- versus intramolecular condensation is given by

$$C_{\mathrm{eq}} = \left(\frac{3}{2}\right)^{3/2} \frac{M}{2N_{\mathrm{a}}} \left(\frac{1}{\langle r \rangle^2}\right)^{3/2}$$

where C_{eq} = monomer concentration (g/mL), M = molecular weight, N_{a} = Avogadro's number of molecules, and $\langle r \rangle^2$ = mean square end to end distance. Several points are obvious from this equation. (1) The higher the molecular weight, the lower the chain end concentration necessary for the same degree of cyclization. (2) Decreased chain dimensions for a given molecular weight favor cyclization, i.e. cyclization if favored in a Θ solvent. (3) The effective polymer concentration decreases with extent of reaction for an irreversible process. This results in a lower effective concentration of reactants as the total process proceeds and results in a higher probability of cyclization.

Equal probability concentrations (C_{eq}) for several molecular weights of polystyrene in thermodynamically good and theta solvents are presented in Table VII. Also the equiprobability chain end concentration is calculated where the chain end concentration for equal probability of chain cyclization and chain extension is given by $Ce_{\mathrm{eq}} = C_{\mathrm{eq}}/M_{\mathrm{w}}$. From Roovers and Toporowski[5]

$$\langle r^2 \rangle_\Theta = 6\langle S^2 \rangle = 6(7.9 \times 10^{-18} M) \qquad (\Theta \text{ solvent})$$

$$\langle r^2 \rangle = (6.5\epsilon + \epsilon^2)\langle S^2 \rangle = 6.88(1.66 \times 10^{-18} M^{1.77}) \qquad (\text{good solvent})$$

The respective concentrations used in this work are listed in Table VIII. Also included are the approximate percentages of cyclized and chain extended products calculated from the SEC analysis. We have no explanation for the very high degrees of cyclization in the 82R and 83R samples of high molecular weight, where the cyclization yields under constant conditions would normally be expected to be lower.

Appendix 2. Some Cautions and Some More Anomalous Results

Throughout this paper we have presented our results assuming that our fractions are "good" and the final conclusions are stated on the basis of the data presented in the paper. However, often in science more is learned from the results which do not fit into our preconceived notions. Therefore we wish to present here a description of results from experiments on two of the cyclic fractions which we cannot explain and which may, in the long term, be important to our understanding of the behavior of macrocyclic polymers. They complete our report of our efforts to characterize polystyrene macrocycles.

In two cases, we attempted to carry out repeat experiments to obtain better measurements of the steady-state recoverable compliance of our samples. In both cases, we did this by changing the geometry of the sample by using a larger platen than the $^1/_4$ in. diameter one normally used. This would allow large torques to be applied and in principle increase the angle measured during recovery. It would also decrease the effects of residual torque present in the magnetic elevation system on the measured recovery as both samples were of relatively low viscosity in the temperature range of interest. We found in both cases that the samples had changed tremendously from the prior results. Because the changes were so great, we assumed that we had damaged the samples. Here is what we observed:

For sample PS2857 of molecular weight 1.94×10^4 and sample PS2774[F8] of molecular weight 7.3×10^4 the recovery was approximately an order of magnitude greater than that obtained previously and we did not attain steady state after long times. We have no means of explaining this behavior and can speculate only what we either did damage the samples or (and) the (damaged?) macrocycles have two different possible modes of behavior.

Also we must put in a note of caution here concerning the conclusions made in this work. We have adopted an approach which assumed that the behavior of the cyclic macromolecules should be similar to that of the linear chains, i.e., $J_{\mathrm{e}}°$ increases with M_{w} and then becomes constant above M_{c}. Should subsequent work demonstrate that this is not so, then the results from the samples 82R, a "moderate" fraction and from 83R a "good" fraction would need to be reconsidered. The problem of the behavior of macrocyclic molecules is one which is far from resolved, and we feel strongly that much of the work which has been carried out by us and others needs to be redone (keeping in mind what we have now learned) to clear up the ambiguities in results and explain the anomalies in behaviors of rings produced by different groups.

Note Added in Proof. In an interesting article,[63] J. Roovers has reported the synthesis and properties of polybutadiene rings. He reports viscosities of rings which are up to an order of magnitude lower than those of the linear counterparts. We find their results difficult to reconcile with our results and use this fact to emphasize the need for further study.

Registry No. Polystyrene, 9003-53-6.

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