Dilute Solution Characterization of Cyclic Polystyrene Molecules and Their Zero-Shear Viscosity in the Melt

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ABSTRACT: Narrow fractions of polystyrene molecules in the form of uncatenated rings (cycles) were synthesized by reacting bifunctional living linear precursors with an appropriate coupling agent at very low concentrations. The cyclic molecules were separated from the simultaneously formed linear polycondensates by fractionate precipitation. The molecular weights of the cycles ranged from 11 100 to 185 000, thus encompassing the critical molecular weight for entanglements in linear polystyrene. The ring-like nature of these fractions has been investigated by a variety of techniques, including the limiting viscosity number in a good and in a Θ solvent as well as neutron scattering in deuteriated cyclohexane. These measurements, part of which are reported here in some detail, display a gratifying agreement with the theoretical predictions reported earlier for uncatenated cyclic polymers. The zero-shear melt viscosities of these cyclic fractions and several others prepared by Fetters and Hostetter to extend the molecular weight range to 390 000 were measured over a wide range of temperatures and compared with the viscosities of linear polystyrenes of similar molecular weights. Above the critical molecular weight for entanglement coupling, no major differences were found between the temperature dependence or the molecular weight dependence of the cyclic polymers and those of their linear counterparts. For the same molecular weight, however, the cycles exhibit somewhat lower melt viscosity values than do the linear molecules. The results are critically compared with those reported by Roovers on similar polystyrene cycles and briefly discussed in terms of recent molecular theories based on snake-like motion (reptation) of chains along a curvilinear tube formed by the constraints of the surrounding entangled matrix.

Introduction

Recent theories[1,2] of the flow behavior of entangled polymer chains model their motion as "reptation" along a curvilinear "tube" formed by the constraints of the surrounding matrix. The constraints result from interactions with neighboring chains which also reptate along their own tubes, and Klein[3] has considered a self-consistent model that accounts for "tube renewal" mechanisms due to the migration of chain ends within the matrix. This mechanism modifies the "primitive paths" of the tubes and releases the initial constraints.

Clearly, a closed cyclic or ring molecule cannot reptate in the conventional sense since it has no chain ends. Therefore, its motion in response to a shear stress might be expected to differ appreciably from that of its linear counterparts. In the instance of the motion of cyclic molecules in a matrix of linear chains, one can readily envisage the nonreptating cycles behaving as "obstacles" around which the linear chains must move. Thus the cycles would not contribute actively to the diffusion process; rather their translation would be determined by the motion (reptation) of the linear chains. This problem was treated by Klein,[4] who predicted that the diffusion of the cyclic molecules in a matrix of linear chains is determined by the tube renewal processes of the latter alone. More recently, Klein[5] has extended his analysis to the problem of diffusion of rings in a network of fixed obstacles.

If reptation and the concomitant tube renewal processes were the only modes (or major modes) of motion available to macromolecules, one would expect that as the concentration of cyclic molecules increased in the matrix of linear chains, the motion of the cycles would become more and more hindered. On the basis of this straightforward interpretation of the reptation model[1–4] one could conjecture that the melt viscosity of entangled ring molecules might be substantially greater than that of their linear counterparts, while the corresponding self-diffusion coefficient might be expected to be much smaller. Klein[5], however, does suggest that such effects might be suppressed until high molecular weights. The situation would not be appreciably modified by accounting for the "tube leakage" effects, as described by Graessley,[6] since this process results merely in the fluctuation of the path of the chain ends, which are absent in ring molecules. Although a generalized tube leakage[5] or amoeba-type motion can also be envisaged for the cycles, to our knowledge no theoretical treatment of the dynamics of uncatenated ring molecules in a matrix of similar rings has been proposed.

On the other hand, there is a substantial body of literature[7–13] dealing with the theory of chain conformation and dilute solution behavior of cyclic macromolecules relative to their linear counterparts. Consequently, there has been much recent effort devoted to the synthesis and dilute solution characterization of ring molecules.[14–23] In particular, Semlyen et al.[14–18] have reported extensively on the synthesis and characterization of poly(dimethylsiloxane) (PDMS) rings. Their findings tend to confirm that the chain statistics of the rings and consequently their dilute solution behavior (limiting viscosity number, sedimentation coefficient, etc.) fully agree with the earlier theoretical predictions.[7–13]

The investigations of Semlyen et al. also include measurements of the melt viscosities, η, of cyclic PDMS molecules.[17,18] Although their results are limited to molecular weights, M_w (weight average), smaller than 28 000, which is just above the critical molecular weight, M_c, for entanglement coupling for PDMS ($24\,500 < M_c < 27\,000$),[24,25] they do show important differences in the molecular weight dependence of the viscosities of cyclic and linear molecules. Actually, at room temperature, the reported values of η are higher for the cycles than for the linear chains for $M_w \leq 4000$, where there is a crossover, and for $4000 < M_w < 28\,000$ the viscosity of cycles is lower than that of the linear fractions.

No explanation for this behavior has been attempted by the authors,[17,18] although the values of η were not reduced to the same segmental mobility in order to separate the molecular weight dependence of η from the contribution

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of temperature, T. In fact, for linear chains, the latter increases below M_c, as the number-average molecular weight, M_n, decreases. This effect is generally attributed to the increased contribution of chain ends to the overall mobility,[25] whereas this extra contribution must be absent in the cycles. As a consequence, the conventional glass transition temperature T_g of the rings would be expected to be independent of M_n. In fact, Semlyen[16] has found that the T_g of the PDMS rings remains constant with decreasing molecular weight and actually increases below 2000 molecular weight.

Also several groups have reported the successful synthesis of sharp fractions of cyclic polystyrenes[19-23] in a wide range of molecular weights. Their ringlike conformation has been extensively characterized by their behavior in dilute solutions. It has been reported in particular that the Θ temperature of the cyclic polystyrene molecules is slightly lower[22] than for the linear ones and that the limiting viscosity number $[\eta]$[21] as well as the size exclusion chromatography[22] are consistent with the expected[7-13] reduction of the radius of gyration and hydrodynamic radius of the macrocycles relative to their linear counterparts of the same contour length. Nevertheless, some important discrepancies in the intrinsic viscosity–molecular weight relationship have been reported by Roovers[26] for cyclic polystyrenes, some of which were synthesized below the Θ temperature.

In addition, some preliminary data have been reported[27-29] for the melt viscosities of PS macrocycles, extending in molecular weight up to about $10M_c$. In particular, Roovers[29] reports on the molecular weight dependence of the melt viscosities for cyclic PS fractions. His results are directly relevant to, though somewhat conflicting with, the present work. They will be discussed in some detail in the appropriate sections of this paper.

In addition to the data of Roovers,[29] other data on cyclic polystyrene fractions synthesized at the CRM[30-32] or the University of Akron[23,33] pertain to their creep behavior in the melt[30] or their diffusion behavior in melts[31] or solutions[32] of linear chains and have been or will be reported elsewhere.

In this paper, we *first* present a few salient features of the synthesis, fractionation, and dilute solution behavior of the PS cycles investigated in order to characterize their ringlike nature in a critical way. The *second* part of the paper is devoted to the zero-shear melt viscosity, η_0, of PS macrocycles, ranging in molecular weight from about 11×10^3 to 4×10^5, thus encompassing M_c ($\sim 3.5 \times 10^4$) for linear PS fractions,[25,34-39] to which the behavior of the cyclic fractions will be compared.

The essential results of these investigations show the following: (a) For all molecular weights the *temperature dependence* of η_0 of the macrocycles is virtually indistinguishable from that of linear polystyrenes of high molecular weight. Thus all the log $[\eta_0(T)]$ isobars display the classical WLF type temperature dependence[39,40] and they can be superimposed onto a single master curve by a shift along the log η_0 ordinate. (b) Over the range of molecular weights investigated and above M_c the viscosities of the cyclic molecules are slightly lower than those of their linear analogues and follow the classical 3.4 power law relationship with molecular weight similar to that of linear chains. (c) Below M_c the viscosity–molecular weight relation for the cyclic molecules is similar to that of the linear molecules when for the latter account is taken of the changing segmental mobility with decreasing molecular weight. (d) Finally, the critical molecular weight for entanglement coupling in the melt of PS macrocycles does not differ significantly from that of the linear chains, in spite of the fact that the cycles are expected to be appreciably more compact than their linear homologues.

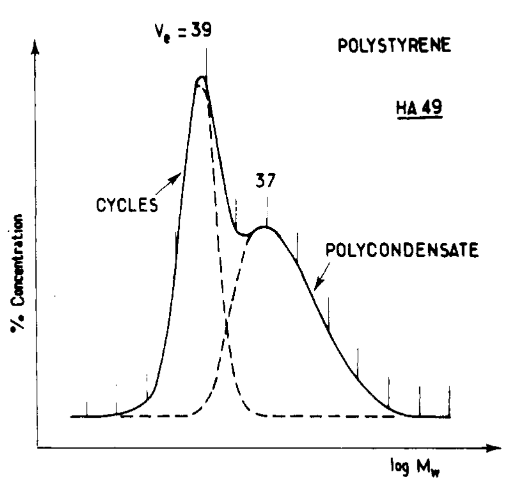

Figure 1. GPC chromatogram for cyclic polystyrene sample HA49 prior to fractionation.

These results will be critically compared with those recently reported by Roovers[29] on similar PS macrocycles and it will be suggested that the differences in results arise from two competing effects—i.e., an increased probability of knot formation for the Roovers rings and an increasing, although small, amount of linear contamination in these rings[29] with increasing molecular weight. Finally, the relevance of these data to the reptation models[1-5] will be briefly discussed.

Experimental Section

Materials. (1) Synthesis and Fractionation. The method of preparation of the cyclic PS fractions has been described in detail elsewhere.[20,21] Briefly, the uncatenated rings were synthesized by reacting bifunctional "living" polystyrene with α,α'-dibromo-*p*-xylene in very dilute tetrahydrofuran (THF) solution. The concentration at which the reaction was carried out was sufficiently low so that *ring closure* was favored over intermolecular "polycondensation". Nevertheless the raw product contains, in addition to the cycles, an important proportion of high molecular weight, linear polycondensate (Figure 1). Therefore, a careful fractionation of the raw material is required to separate the "macrocycles" from the polycondensate.

This separation was performed by fractionate precipitation in benzene solution, using methanol as precipitant. Each fraction was allowed to settle for 24 h to provide adequate sedimentation of the precipitate. The recovered fractions were characterized by size exclusion chromatography (SEC) and their M_w determined by light scattering. The efficiency of the fractionation procedure is satisfactory whenever the M_w of the polycondensate is much higher than that of the parent polymer. In this case one can show[21] that the amount of unreacted parent polymer left is vanishingly small. Due to the extremely low polymer concentration used in the cyclization procedure, however, this condition is not perfectly satisfied since some accidental deactivation of the living precursor cannot be completely prevented.

Figure 2a illustrates a suitable separation of the cycles (solid line) from the polycondensate represented by the right-hand shoulder of the chromatogram shown in Figure 1. The dashed line depicts the chromatogram of the parent linear polymer, which appears similar to that of the cycles, but shifted toward higher M_w values. The difference in M_w is nevertheless only apparent and reflects the smaller hydrodynamic volume of the rings relative to the parent linear polymer.[22]

Figure 2b shows a less satisfactory example of the separation of the cycles from the parent linear polymer. In fact, the respective chromatograms overlap and the width of the peak obtained with the cycles is slightly larger than that of the linear precursor polymer. Other characteristics of these two samples (HA49 and

Table I
Molecular Weights and Intrinsic Viscosities of Cyclic Polystyrenes and Their Linear Precursors (CRM Fractions)

sample		M_w LS	M_w/M_n GPC	$[\eta)_\Theta$, mL g^{-1} CHX, 35 °C	$[\eta]$, mL g^{-1} THF, 25 °C	$[\eta_c]_\Theta/[\eta_l]_\Theta$
PS2653	cyclic	11 100	1.09	5.55	7.0	0.68
	lin prec[a]	10 500	1.15	8.20[b]	10.3	
HA50	cyclic	12 500	1.30	5.65	8.1	0.66
	lin prec	11 200	1.55	8.6	10.7	
PS2857	cyclic	19 400	1.16	7.55	10.05	0.68
	c	19 400		11.14[b]	14.05[d]	
	lin prec	22 000	1.19	11.87[b]	15.34[d]	
PS2648	cyclic	27 000[e]		8.7		0.66
	lin prec	27 200	1.10	13.19[b]	19.5	
PS2654f[f]	cyclic	37 800	1.13	9.90		0.64
	c	37 800		15.55[b]	22.41[d]	
	lin prec	45 000	1.19	16.84	26.0	
HA49	cyclic	44 000	1.08	11.9	18.2	0.73
	lin prec	45 000	1.07	16.4	26.6	
HA51	cyclic	50 500	1.17	12.5	21.5	0.69
	lin prec	52 000	1.12	18.1	30.5	
PS2774	cyclic	79 400	1.12	15.9		0.70
	lin prec	79 500	1.10	22.56[b]		
PS2829	cyclic	106 000		17.8	35.5	0.68
	lin prec	107 000	1.16	26.0	46.42[d]	
PS2829f[f]	cyclic	106 000	1.13			
HA53	cyclic	117 000	1.12	22.1	41.0	0.83
	lin prec	111 000	1.08	26.7	48.5	
PS2780	cyclic	181 500	1.10	23.5	53.0	0.69
	lin prec	182 000	1.08	34.13[b]	67.33[d]	
PS2780f[f]	cyclic	185 000	1.12	23.0		0.67
	c	185 000		34.41[b]		
PS2590	cyclic	239 000	1.50	35.8		0.88
	lin prec	260 000	1.12	40.79[b]		
HA52	cyclic	276 000	1.35	40.8		1.04
	lin prec	237 000	1.13	39.2		

[a] Linear precursor. [b] Calculated from the equation $[\eta]_\Theta = 8.0 \times 10^{-2} M_w^{0.5}$. [c] Linear sample of the same M_w as the cycles. [d] Calculated from the equation $[\eta] = 14.0 \times 10^{-3} M_w^{0.7}$ (Strazielle, C.; Herz, J. *Eur. Polym. J.* **1977**, *13*, 223). [e] Determined by neutron scattering.[46] [f] Refractionated cycles.

HA53), to be discussed below, display more important differences. One can thus conclude that SEC does not provide a sensitive method for an accurate appreciation of the quality and purity of the cyclic fractions.

Here we note that the cyclic PS fractions of Roovers[22,26,29] were synthesized by essentially the same technique using dimethyldichlorosilane as the ring-closure agent. In contrast to the CRM procedure[20,21] (where ring closure occurred in good solvent), for eight of the Roovers samples the ring-closure reaction was performed in a dilute cyclohexane (CHX) solution below the Θ temperature. It is anticipated that such reaction conditions might favor a significantly higher probability of knot formation over that which would occur in good solvent conditions.[41] Also, four of the Roovers samples were cyclized in good solvent conditions. For these latter samples, however, no melt viscosity data were reported.[29]

In addition to the above materials, we report data on the zero-shear melt viscosity of three other cyclic PS fractions, synthesized by Fetters and Hostetter using dilithium compounds in hydrocarbon solvents for which ring closure took place in good solvent conditions.[23,33]

(2) Molecular Weight and Limiting Viscosity Numbers. The weight-average molecular weights, M_w, of the PS fractions (precursors and cycles) were determined by light scattering, using a laser-equipped FICA instrument at 632 nm.[42] The incident light was vertically polarized.

The molecular weight (MW) distribution, as characterized by the M_w/M_n ratio, was determined by size exclusion chromatography (SEC), using a standard Waters GPC apparatus fitted with a set of six columns filled with Styragel and another GPC device fitted with two columns filled with 10-μm (Shodex 80M) microbeads. The latter instrument improves the control of the homogeneity of the cyclic fractions. The columns were calibrated with a set of narrow molecular weight distribution linear PS fractions of known MW.

In principle, and often in practice, the apparent width of the chromatograms of the cycles is expected to be the same as that of the their precursors (cf. Figure 2a). In some cases, however, the chromatogram for the cycles had a slightly larger width than that for the parent linear polymer, due to some contamination by the unreacted precursor and/or by the polycondensate of double chain length left in the cyclic fraction (cf. Figure 2b). Their elimination by fractionation is favored since the Θ-point de-

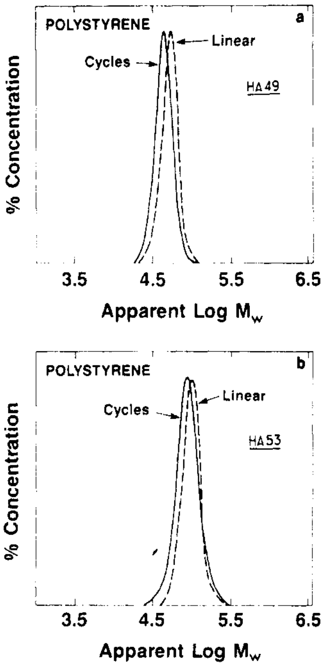

Figure 2. GPC chromatograms for cyclic polystyrenes after fractionation compared with their linear precursors: (a) fraction HA49, M_w = 44 000; (b) fraction HA53, M_w = 117 000.

pression[22] of the cyclic molecules favors the separation of the linear chains from the cycles. Also, the peak of the cyclic fraction appears at larger values of the eluted volume than for the linear precursor due to the more compact size of the cycles.[7,8]

Table I lists the characteristic parameters of the cyclic fractions and their linear precursors (or counterparts). The values of the M_w/M_n ratio have not been corrected for the instrumental lag. The limiting viscosity numbers $[\eta]$ were determined in both a Θ solvent at the Θ temperature of linear polystyrene (cyclohexane, CHX, at 35 °C) and a good solvent (THF at 25° C), using conventional capillary viscometers equipped with an automatic dilution device. The $[\eta]$ values listed in Table I correspond for each fraction to the average of the extrapolated plots to infinite dilution of the reduced $[c^{-1}(\eta - \eta_s)/\eta_s]$ and inherent $[c^{-1} \ln (\eta/\eta_s)]$ viscosities, where the concentration c is expressed in mL g^{-1} and η_s is the viscosity of the pure solvent. The $[\eta_c]/[\eta_l]$ ratios obtained in CHX at 35 °C, i.e., in the Θ condition of the linear polymer, are listed in the last column of Table I.

(3) Melt Viscosity Measurements. The zero-shear (rate) viscosities, η_0, were determined in the melt by using a cone-and-plate "microconsistometre" described by Kepes.[43] Shear rates as low as 2.7×10^{-4} s^{-1} could be applied to the molten fractions. With one exception (HA53 at $\eta_0 > 2 \times 10^8$ P) all values of η_0 reported hereafter were *measured* (as opposed to estimated) on the Newtonian plateau.

In addition to these data, we report here on data obtained with the Plazek[44] magnetic bearing torsional creep apparatus (MBTCA) on several cyclic fractions. In this case all the η_0 values reported are measured values of the zero-shear viscosity, obtained by one of us (G.B.McK.) as part of a study on the viscoelastic behavior of cyclic PS.[30]

The η_0 values measured between 104 and 220 °C by both techniques are collected in Table II. The temperature control for these measurements was estimated to be better than ±0.5 K. No degradation of the fractions during the experiments was detected by repeat measurements of η_0.

Freeze-dried powders of the cyclic and linear PS fractions were premolded into disks under vacuum. Subsequent molding into the appropriate geometry was performed under either a dry nitrogen atmosphere (microconsistometre)[43] or a sequence of vacuum and nitrogen (MBTCA).[44]

Results and Discussion

A. Dilute Solution Behavior. A valid comparison of the melt properties of the cyclic and linear molecules depends upon the certainty that the cyclic PS fractions investigated are in fact uncatenated ring-shaped macromolecules. One sensitive measure of the nature and the quality of these fractions is their limiting viscosity number in (or near to) Θ conditions. Theoretical calculations carried out by several authors[8-11] lead to the important conclusion that the ratio $g' = [\eta_c]_\Theta/[\eta_l]_\Theta$ should be 0.66 if the cycles are indeed uncatenated closed rings without knots. Therefore, measurements were made of the intrinsic viscosities of the cyclic polystyrenes and their linear precursors in cyclohexane at 35 °C (the Θ temperature for linear PS). The relevant $[\eta]$ values are listed in Table I, together with the values of $[\eta]$ obtained at 25 °C in THF, which is a good solvent.

The limiting viscosity numbers obtained with the cycles, $[\eta_c]$, and some of their linear precursors, $[\eta_l]$, in CHX at 35 °C are plotted against M_w in Figure 3 using a double-logarithmic scale. This figure also shows the $[\eta_c]$ values reported by Roovers[22,26] on similar PS cycles in the same conditions (triangles and dashed lines). They differ only slightly from our data (open circles).

Several important features emerge immediately from Figure 3. First, as expected, near the Θ condition the exponent a in the Mark–Houwink expression $[\eta] = KM^a$ is close to 0.5 for both series of cyclic fractions. Second, one can readily notice that the results for the two CRM fractions having molecular weights above 230 000 (designated as HA52 and PS2590) lie well above the least-squares line derived from the other $[\eta_c]$ values (except HA53; see below). Most likely, these two fractions, which have a large polydispersity, are heavily contaminated with the linear polycondensate and will not be considered in the melt viscosity investigations nor in the analysis of the $[\eta_c]$ values presented below. They are mentioned here because their melt viscosities were previously reported erroneously as being for cyclic fractions.[27]

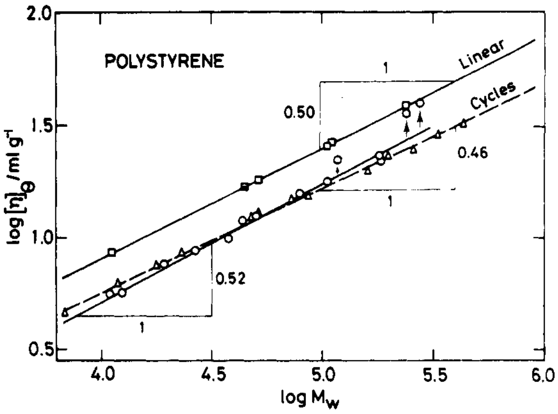

Figure 3. Logarithm of intrinsic viscosity vs. logarithm of molecular weight for cyclic and linear polystyrenes in cyclohexane at 35 °C. Squares are for linear precursors from this study. Open circles denote cyclic fractions used in this study. Heavy arrows denote samples which are heavily contaminated with linear chains; light arrow denotes sample HA53, which is marginal (see text). Triangles are data of Roovers[26] for cyclic polystyrenes. Solid lines represent least-squares fits to data from this study (not including arrowed points). Dashed line: least-squares fit to data of Roovers.[26]

Third, although the HA53 fraction has a rather narrow molecular weight distribution (see Table I and Figure 2b), its $[\eta_c]$ value lies in an intermediate position between the linear and cyclic fractions. Again, this discrepancy is attributed to some contamination with linear polymer. The melt viscosity data relevant to this fraction will be considered with caution and will not be included in the analyses of solution properties discussed below.

The other fractions have reasonably sharp molecular weight distributions and their g' values are close to the theoretical predictions.[7,12] One cannot completely exclude, however, the possibility of some contamination of the cyclic molecules by linear chains since the dilute solution behavior is relatively insensitive to small amounts of such contamination. Furthermore, rheological[30,45] measurements of the recoverable compliance of several fractions indicated that two of them (PS2829 and PS2780) were slightly contaminated either with high molecular weight cycles or by linear chains. Therefore, these samples were refractionated,[30,45] as indicated by the suffix f in Table I.

The slope of the least-squares solid line, as derived from the ten "best" cyclic fractions shown in Figure 3, is equal to 0.52 ± 0.03. This value of a suggests that the CRM cycles are actually slightly expanded at 35 °C in CHX, a suggestion which is consistent with the observations of Roovers et al.[22,26] and others[23,33,46] that the Θ temperature of these cycles lies below 35 °C.

One cannot a priori exclude, however, an alternative interpretation of the small excess of a relative to 0.5, by attributing it to the slight contamination of the cycles with linear polymer, since the $[\eta_l]_\Theta$ value of the linear analogue is about 1.5 times larger than $[\eta_c]_\Theta$ (cf. Table I). Owing to the rather moderate scatter of the $[\eta_c]_\Theta$ values, this interpretation would imply a regular increase of the concentration of the contaminant as MW increases. Such a regularity can be deemed, however, highly unlikely on the

Table II. Zero-Shear Viscosity (η_0) and Reduced Viscosity (η_0/β_η) Data for Cyclic Polystyrene Fractions

T, °C	log (η_0/P)	log (η_0/β_η)
	PS2653 (M_w = 11 100)	
124.6	6.286^a	7.495
130.1	5.600	6.809
134.5	5.202	6.411
137.4	4.883	6.092
142.0	4.496	5.705
146.9	4.122	5.331
151.2	3.797	5.006
156.8	3.434	4.643
164.4	3.029	4.238
164.4	2.968	4.177
168.8	2.791	4.000
173.6	2.531	3.740
184.0	2.017	3.280
192.4	1.796	3.005
200.5	1.562	2.771
	HA50 (M_w = 12 500)	
120.0	6.785^a	7.853
124.9	6.204	7.272
135.2	5.140	6.208
139.8	4.857	5.925
148.8	4.210	5.278
159.8	3.518	4.586
170.0	2.916	3.984
179.0	2.462	3.530
189.7	2.000	3.068
195.9	1.792	2.860
	PS2857 (M_w = 19 400)	
103.4	10.426^b	11.038
103.4	10.391	11.003
110.1	8.882	9.494
114.0	8.135	8.747
118.5	7.447	8.059
125.0	6.565	7.177
136.8	5.289	5.901
148.1	4.395	5.007
164.5	3.317	3.929
164.5	3.292	3.904
	PS2648 (M_w = 27 000)	
124.2	6.836^a	7.383
130.8	6.195	6.742
137.7	5.534	6.081
140.4	5.315	5.862
143.1	5.091	5.638
147.6	4.745	5.292
151.7	4.421	4.968
155.7	4.161	4.708
161.0	3.871	4.418
169.5	3.397	3.944
179.3	2.983	3.530
189.4	2.588	3.135
200.9	2.227	2.774
209.6	1.988	2.535
222.2	1.695	2.242
	PS2654 (M_w = 37 800)	
127.8	6.807^a	7.088
134.5	6.157	6.438
140.4	5.621	5.902
145.4	5.210	5.491
151.1	4.780	5.061
156.1	4.435	4.716
159.8	4.199	4.480
168.0	3.744	4.025
177.4	3.301	3.582
181.9	3.098	3.379
186.2	2.949	3.230
193.4	2.680	2.961
202.4	2.392	2.673
	HA49 (M_w = 44 000)	
109.2	9.326^b	9.498
120.6	7.656	7.828
130.5	6.448	6.620
142.4	5.452	5.624
	M_w = 44 000F	
109.2	9.458^b	9.458
120.7	7.751	7.751
140.2	5.834	5.834
170.2	3.932	3.932
	HA 51 (M_w = 50 500)	
120.1	7.829^a	7.730
129.0	6.982	6.883
135.0	6.332	6.233
139.0	6.021	5.922
144.2	5.643	5.544
154.0	5.061	4.962
154.0	4.978	4.879
164.0	4.380	4.281
	PS2774 (M_w = 79 400)	
137.0	6.818^a	6.174
139.4	6.566	5.922
145.1	6.118	5.474
150.0	5.777	5.133
156.8	5.345	4.701
164.1	4.891	4.247
169.9	4.546	3.902
174.7	4.376	3.732
184.8	3.982	3.338
193.1	3.671	3.027
204.0	3.307	2.663
211.4	3.140	2.496
217.6	2.975	2.331
	PS2829f (M_w = 106 000)	
113.7	9.621^b	8.756
121.3	8.549	7.684
126.2	8.030	7.165
131.8	7.447	6.582
142.4	6.498	5.633
161.5	5.223	4.358
	PS2829 (M_w = 106 000)	
104.4	11.579^b	10.354
105.5	11.142	9.917
121.4	8.957	7.732
140.3	7.110	5.885
141.3	6.999	5.774
153.8	6.129	4.904
154.0	6.064	4.839
175.7	4.925	3.700
185.0	4.544	3.319
209.1	3.828	2.603
	HA53 (M_w = 117 000)	
123.5	8.748^a	7.358
129.0	8.301	6.911
129.0	8.255	6.865
132.2	7.860	6.470
139.2	7.292	5.902
149.9	6.458	5.068
159.7	5.892	4.502
169.9	5.394	4.004
180.6	4.875	3.485
191.0	4.544	3.154
200.2	4.238	2.848
208.8	3.849	2.459
	PS2780 (M_w = 181 500)	
114.4	11.336^b	9.031
126.2	9.603	7.298
153.2	7.235	4.930
153.2	7.228	4.923
170.3	6.176	3.871
170.7	6.159	3.854
170.7	6.114	3.809
186.1	5.469	3.164
188.2	5.392	3.087
188.2	5.375	3.070

Table II (Continued)

T, °C	log (η_0/P)	log (η_0/β_η)	T, °C	log (η_0/P)	log (η_0/β_η)
	PS2780f (M_w = 185 000)			M_w = 390 000F	
124.0	9.289[b]	7.500	120.9	10.787[b]	7.776
130.2	8.555	6.766	134.9	9.202	6.191
154.4	6.635	4.846	148.3	8.293	5.282
165.2	5.928	4.139	154.8	7.880	4.869
188.4	4.864	3.075	170.3	6.910	3.899
			185.2	6.338	3.327
	M_w = 240 000F		185.2	6.300	3.289
125.1	9.628[b]	7.343	199.2	5.826	2.815
138.0	8.335	6.050	199.3	5.884	2.873
150.1	7.391	5.106			
153.8	7.132	4.847			
167.2	6.379	4.094			
192.1	5.321	3.036			
192.1	5.332	3.047			

[a] Viscosity measurements made with the Kepes[43] microconsistometre. [b] Viscosity measurements made with the Plazek[44] MBTCA.

basis of further analysis and additional data to be presented below.

On the other hand, the $[\eta_c]$ values in CHX at 35 °C reported by Roovers[26] display a least-squares slope of 0.46 in the double-logarithmic plot of Figure 3 (triangles). In the midrange of the data (MW ~ 50 000) the two sets of $[\eta_c]$ values are virtually indistinguishable. One can tentatively conjecture that the highest molecular weight rings investigated by Roovers are more compact in CHX at the Θ temperature for linear chains. This behavior becomes more surprising when one considers that the Θ_{A_2} temperature at which the second virial coefficient of the cycles vanishes has been reported by Roovers[26] to be 28.5 °C and independent of MW (Θ_{A_2} temperatures determined for a few cycles at the CRM yield virtually the same value).[47] It is consistent with the finding of Roovers[26] that the Mark–Houwink exponent a has a value of 0.4 at Θ_{A_2}, which is considerably smaller than that (0.5) characterizing the unperturbed chain dimensions, again revealing an unexpected compactness of the Roovers ring-shaped polymer fractions at high molecular weights.

It should be emphasized that this behavior cannot be attributed to some contamination of the cycles by linear chains unless this contamination decreases as M_w increases, which appears unrealistic. Actually Roovers' data suggest that the large rings are less expanded than their linear counterparts.[26] Such behavior is consistent with an increasing probability of knot formation in the rings as molecular weight increases.[41] We note, however, that the samples for which ring closure occurred in good solvent show the same behavior. This suggests the possibility that fractionation procedures may also play a role in the concentration of knotted rings in a given sample.[41]

Another way of determining the chain dimensions from intrinsic viscosity data is that proposed by Stockmayer and Fixman[48] based on the relationship they established for moderately high molecular weight chains, viz.

$$[\eta]M^{-1/2} = K_\Theta + bM^{1/2} \qquad (1)$$

Here K_Θ denotes the value of the factor K in the Mark–Houwink equation in Θ conditions and b is a parameter which depends upon the thermodynamic interactions between the polymer and the solvent.[48] At the Flory Θ temperature clearly $b \equiv 0$, and eq 1 reduces identically to the Mark–Houwink equation, whereas in a good solvent ($b > 0$) the chain is expanded. In the opposite case ($b < 0$) the chain is collapsed with respect to its unperturbed dimension. Equation 1 can thus be used for determining the value of K_Θ independently of the quality of the solvent, by simply plotting $[\eta]M^{-0.5}$ as a function of $M^{0.5}$ and extrapolating the actual data to zero molecular weight.

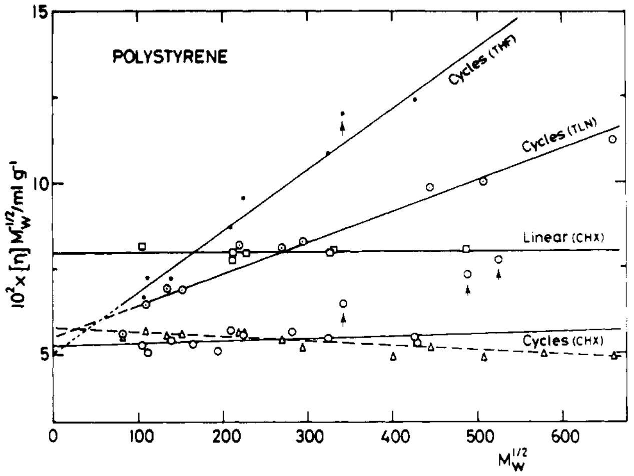

Figure 4. $[\eta_0]M_w^{-1/2}$ vs. $M_w^{1/2}$ for cyclic and linear polystyrenes in cyclohexane at 35 °C (CHX), toluene at 25 °C (TLN), and tetrahydrofuran at 25 °C (THF). Open circles, squares, triangles, and arrows have same meaning as in Figure 3. Filled circles are data from this study in THF. Circles with points are data from Roovers.[26] Lines represent least-squares fits to the data (see text for discussion).

Figure 4 depicts such plots obtained in CHX (both for the linear polymer and the cycles) and also in THF for the cyclic fractions listed in Table I. This Figure shows in addition the $[\eta_c]$ data reported by Roovers[26] in CHX and toluene (TLN) for his ring polymers.

The linear polymer in CHX at 35 °C yields, as expected, a virtually horizontal line (parallel to the abscissa), which extrapolates at $M_w = 0$ to a K_Θ value equal to 0.794×10^{-2} mL g^{-1}, which is only slightly lower than the best value derived from Figure 3 ($=8.04 \times 10^{-2}$ mL g^{-1}).[49] On the other hand, the cyclic fractions display a slightly positive slope for our samples and a negative slope for the ring polystyrenes of Roovers,[26] involving at $M_w = 0$, K_Θ values of 5.14×10^{-2} and 5.76×10^{-2} mL g^{-1}, respectively.

In the good solvents (THF and TLN), the least mean square lines display large positive slopes and extrapolate at $M_w = 0$ to K_Θ values which are in both cases slightly lower than those derived from the CHX data, i.e., $10^2K_\Theta = 5.02$ for the CRM cycles and 5.5_1 for those of Roovers et al.[22,26]

Although eq 1 has been derived by Stockmayer and Fixman[48] for linear chains, it appears also to apply for the cyclic PS fractions. Furthermore, the slopes obtained for the CHX solutions (b in eq 1) are fully consistent with a slight chain expansion for the CRM cycles and with a slight chain contraction for those of Roovers et al.[22] (with respect to the unperturbed chain dimension) as already noted

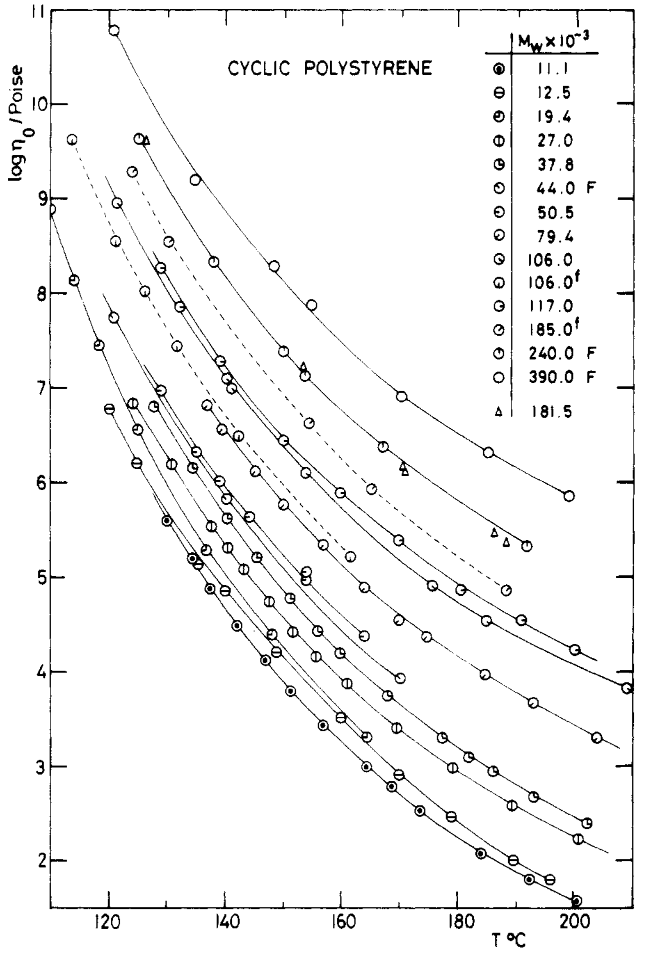

Figure 5. Logarithm of zero-shear viscosity vs. temperature for cyclic polystyrene fractions of different molecular weights.

above. Moreover, the differences between the respective K_Θ values given above amount to about the same value in the good solvents as in CHX. The difference in the K_Θ values derived from the two series of cyclic fractions (i.e., Roovers and CRM), albeit small, appears to be significant. Nevertheless its exact origin cannot be specified presently and needs further investigation.

One can also calculate the average g' values referring to the different pairs of K_Θ values derived from the plots shown in Figure 4 and those of their linear counterparts. In fact, according to the definitions of the various parameters given above, one has

$$g' = [\eta_c]_\Theta / [\eta_l]_\Theta = K_{\Theta,\mathrm{cyc}} / K_{\Theta,\mathrm{lin}} \qquad (2)$$

Adopting the K_Θ values given above for the linear polymer[49] and those derived from Figure 4, eq 2 yields for the CRM cycles $g' = 0.65$ in CHX at 35 °C and $g' = 0.63$ in THF at 25 °C. On the other hand, for the ring polystyrenes of Roovers, one obtains $g' = 0.69$ in CHX and $g' = 0.66$ in TLN. These values are all in reasonable agreement with the theoretical value of 0.66.[8-11,49] One may thus raise the question whether the different values of K_Θ and g' do not just reflect the inherent experimental scatter of the data obtained independently in two different laboratories. Because this suggestion contradicts the conclusion reached above, it should be noted that the values of $K_{\Theta,\mathrm{cyc}}$ will be strongly influenced by the results for the lowest MW fractions, which would be expected to have the fewest knots.[41]

B. Zero-Shear Melt Viscosity Data. The logarithms of the zero-shear melt viscosities (η_0) of the cyclic PS fractions investigated at various temperatures (T) are listed in Table II. This table includes in addition to the CRM cycles (see Table I) three cyclic fractions prepared by Fetters et al.[23,33] (referred to hereafter by the code F). The corresponding temperature dependence of the log η_0 for the different MW fractions is depicted in Figure 5, from which one fraction listed in Table I has been omitted for clarity (M_w = 44 000). Also, another fraction (M_w = 181 500) is only represented by the data points.

Table III
Zero-Shear Viscosity (η_0) and Reduced Viscosity (η_0/β_η) Data for Linear Polystyrene Fractions from This Work

T, °C	log (η_0/P)	log (η_0/β_η)
	PS2654 (M_w = 45 000)	
128.8	6.866^a	6.866
137.6	6.061	6.061
143.0	5.617	5.617
150.9	5.051	5.051
159.5	4.507	4.507
167.9	4.065	4.065
176.4	3.671	3.671
187.3	3.261	3.261
193.4	3.037	3.037
202.5	2.775	2.775
210.9	2.549	2.549
	HA51 (M_w = 52 000)	
131.0	6.898^a	6.641
141.2	6.047	5.790
150.1	5.369	5.112
	PS2774 (M_w = 79 500)	
136.7	6.945^a	6.168
143.2	6.401	5.624
149.6	5.962	5.185
155.2	5.566	4.789
159.0	5.318	4.541
171.6	4.650	3.873
176.0	4.464	3.687
183.5	4.153	3.376
191.7	3.852	3.075
202.2	3.560	2.783
209.9	3.335	2.558
217.3	3.120	2.343
	PS2558 (M_w = 92 000)	
129.0	7.748^a	6.818
140.0	6.778	5.848
158.0	5.591	4.661
	HA53 (M_w = 111 000)	
129.0	8.114^a	6.854
139.0	7.146	5.886
158.0	5.924	4.664

Following the same procedure, the zero-shear melt viscosities of five linear PS fractions (precursors) determined in the present work are listed in Table III. In addition, Table IV lists a great number of other linear fractions with their molecular weights and the relevant η_0–T ranges. They have been taken from the unpublished theses of Pierson[34] and Suzuki,[35] obtained at the CRM using the Kepes microconsistometre,[43] from results of Plazek and O'Rourke[36] using the MBTCA,[44], and from η_0 data reported by Marin[37] and Montfort et al.,[38] evaluated from dynamic shear investigations. All of the η_0 data selected here refer exclusively to linear fractions of high molecular weight, where entanglement coupling prevails, i.e., $M_w > M_c$ (~35 000).[25,39] The relevant temperature dependences of log η_0 are depicted in Figure 6, in which some of the data summarized in Table IV have been omitted for clarity.

(1) Temperature Dependence of η_0. Three simple features emerge immediately from Figures 5 and 6. *First,* for each set of log η_0 vs. T curves (referred to hereafter as log η_0 thermograms) one can superimpose, within experimental uncertainty, any thermogram upon any other by merely shifting it along the log η_0 axis without modification

Table IV
Summary of Range of Molecular Weights and Temperatures of Zero-Shear Viscosity Data for Linear Polystyrene Fractions Analyzed in This Study[a]

authors	M_w	M_w/M_n	no. of measurements	temp range, °C	log (η_0/P) range
Pierson[34]	47 500	1.30	7	120.0–200.0	8.059–2.909
	51 400	1.23	7	120.0–217.0	8.265–2.613
	82 500	1.05	5	130.0–200.0	7.675–3.720
	125 000	1.07	8	130.0–217.0	8.312–3.846
	267 000	1.08	5	140.0–190.0	8.505–5.727
	570 000	1.10	5	160.0–200.0	8.380–6.748
Suzuki[35]	125 000	1.07	8	129.9–210.2	8.190–3.932
	190 000		5	147.6–199.0	7.328–4.925
	267 000	1.08	7	139.7–210.1	8.415–5.065
	570 000		6	147.8–210.3	8.947–6.191
	1 190 000	1.19	5	173.5–210.4	8.645–7.392
Plazek et al.[36]	46 900	1.05	8	104.5–160.0	10.499–4.506
	94 000	1.08	5	113.4–180.0	10.088–4.668
	189 000	1.02	5	113.7–180.3	11.085–5.665
	592 000	1.06	4	119.4–180.0	12.077–7.386
	800 000		2	160.0–180.0	8.706–7.666
Marin[37]	125 000	1.2	6	146.5–209.0	6.796–3.949
	110 000	≈1.05	6	140.9–207.5	6.996–3.782
	160 000	≈1.05	6	141.4–208.3	7.459–4.322
	390 000	1.10	2	178.8–188.3	6.681–6.290
	670 000	≈1.10	2	179.6–188.7	7.380–7.021
Montfort et al. [38]	110 000	1.05	9	154.5–198.5	6.244–4.28
	200 000	1.06	4	143.4–206.4	7.95–4.88
	900 000	1.12	3	189.8–247.0	7.60–6.46

[a] These data are available upon request.

of the temperature scale. *Second*, for the cyclic fractions such superposition can be successfully achieved in the whole range of M_w investigated. *Third*, the temperature dependence of the viscosities of the cyclic and linear (M_w > 40 000) fractions appears to be virtually the same.

(a) Construction of Master Curves. As noted above, one can empirically shift each thermogram along the ordinate to superpose to a conveniently chosen reference curve (denoted by $M_{w,ref}$) to obtain a single *master curve.* Since no specific assumption is made about the temperature dependence of log η_0, this simple procedure implies only that all of the log η_0 curves have the same shape within experimental error for each class of PS fractions (linear or cyclic). Hence the magnitude of the vertical shift is

$$\log \beta_\eta = \log [\eta_{0,M}(T)/\eta_{0,M_{ref}}(T)] \qquad (3)$$

After evaluation of the log β_η shifts required for superimposing the log η_0 thermograms of the linear fractions, the relevant composite master curve is depicted in Figure 7. The reference M_w chosen here is 45 000 (see HA49 in Table I), which was nevertheless complemented by M_w = 46 900, a fraction investigated by Plazek et al.,[36] the pertaining η_0 values of which extend up to 10^{12} P. Although these two $M_{w,ref}$ values differ slightly, the relevant log η_0 plots virtually merge without any vertical shift, as can be seen in Figure 6. The master curve log (η_0/β_η) obtained with the 29 linear PS fractions is depicted in Figure 7. When two or more data overlapped, which is often the case, only one of them was represented. Therefore, Figure 7 dipicts only 64 data points over a total of 162 η_0/β_η values. Hence the superposability of the log η_0 curves can be qualified as excellent for the linear PS fractions, provided that their molecular weight is larger than 40 000.

Figure 8 depicts in a similar way the master curve of log (η_0/β_η) vs. T for the cyclic polystyrene data shown in Figure 5 and listed in Table II. (For clarity Figure 8 shows only 91 data points of the 151 measured ones.) The reference M_w chosen in this case was the 44 000 fraction synthesized by Fetters et al.,[23,33] complemented by the superposition of the PS2774 cycles of molecular weight 79 400. The log

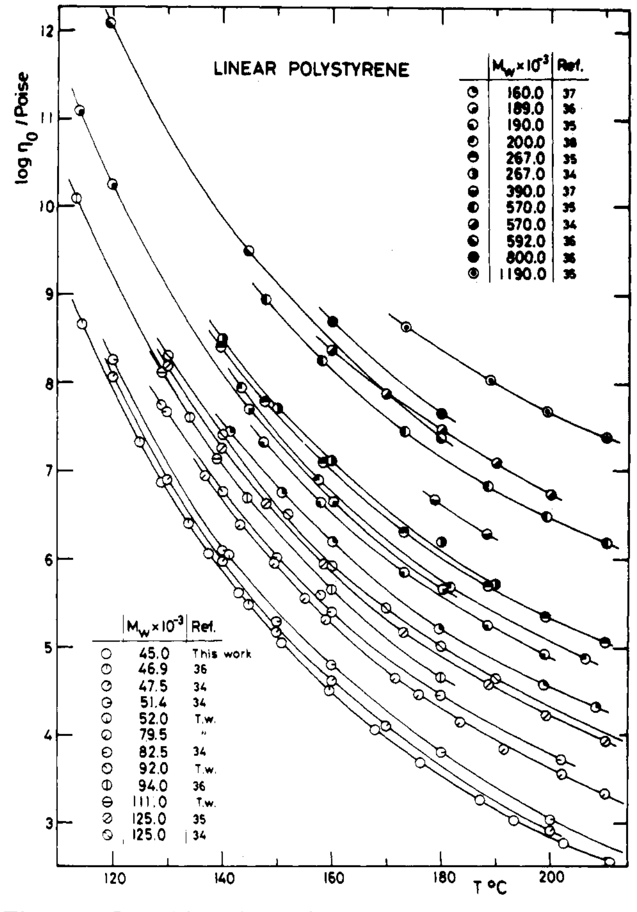

Figure 6. Logarithm of zero-shear viscosity vs. temperature for linear polystyrene fractions of various molecular weights. Data from this study and literature sources as indicated by the reference numbers.

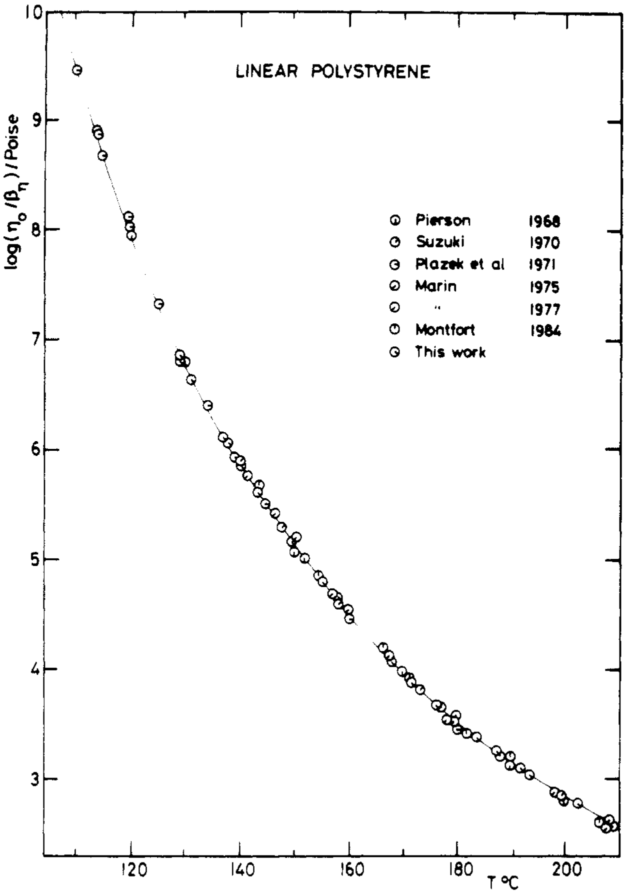

Figure 7. Viscosity data points and the resulting master curve: log (η_0/β_η) vs. T for linear polystyrene fractions as indicated.

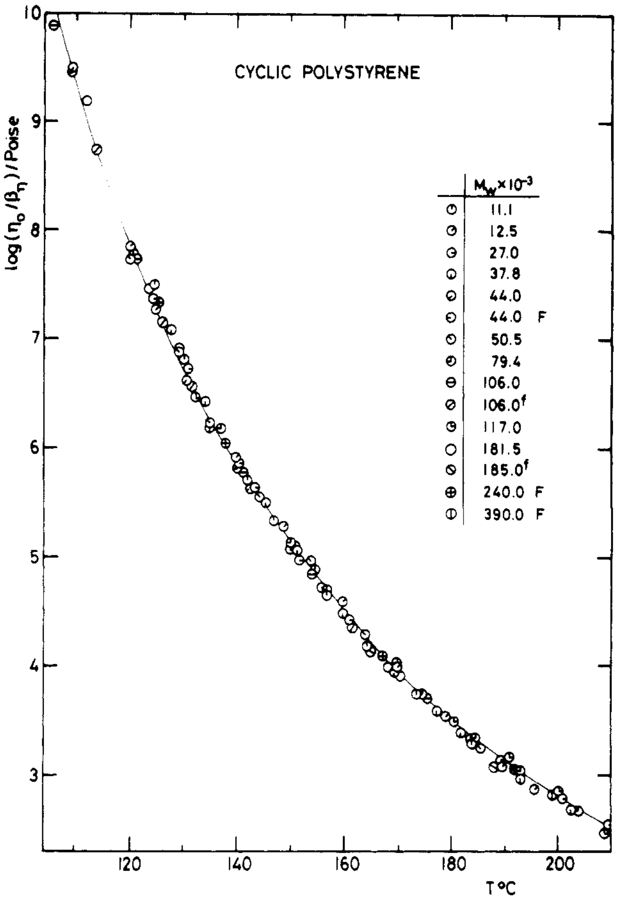

Figure 8. Viscosity–temperature data points and master curve: log (η_0/β_η) vs. T for cyclic polystyrene fractions as indicated.

η_0 thermogram of the latter was shifted toward lower η_0 values by log β_η = 0.644. The scatter displayed by this master curve is approximately 2 times greater than for the linear fractions in Figure 7.

The increased scatter of the log (η_0/β_η) master curves obtained with the cyclic fractions results clearly from the lack of parallelism of a few of the log η_0 thermograms shown in Figure 5. For example, to obtain acceptable superposition of the thermogram of the PS2780 cycles (M_w = 181 500), it was necessary to shift it toward lower temperatures by ΔT = −2.5 K, whereas the curve for the refractionated PS2780f cycles superposes onto the reference curve without any adjustment of the temperature scale (cf. Figure 6). Fortunately, the original sample PS2780, although only slightly contaminated according to its g' value (0.69; see Table I), was unique among the high molecular weight fractions requiring a substantial ΔT correction. Hence data obtained with this sample will be considered with caution.

Superposition of the log η_0 thermogram of the cyclic PS2857 (M_w = 19 400) fraction to the reference curve is also quite poor (see Figure 5), though again the relevant value of g' = 0.68 is quite close to its theoretical value. Superposition can be, however, greatly improved by shifting the relevant thermogram (again) toward *lower* temperatures by ΔT = −4.0 K. It should be emphasized that none of the negative ΔT shifts can be attributed to some contamination of these cycles by their linear precursor, and thus to the effect of chain ends. The latter would give rise to increased mobility, resulting in a shift of the log η_0 thermogram toward *higher* temperatures in order to maintain the constant-mobility criterion.[25] The actual situation reflects the opposite effect and these cycles will be considered with reservation. The relevant data will be analyzed both by accounting for and by neglecting the ΔT shifts given above.

(b) Comparison of the Master Curves. The master curves obtained with the linear and cyclic PS fractions (cf. Figures 7 and 8) can be easily compared with each other, since $M_{w,ref}$ has been chosen to be almost the same for both (i.e., 45 000 for the linear materials and 44 000 for the cyclic materials). In order to give a clear picture to this comparison, Figure 9 compares the master curve for the linear fractions (solid line) with the reduced data (circles) for the cyclic polystyrenes. In spite of a small difference appearing above 160 °C, this figure shows a rather good agreement between the log (η_0/β_η) master curves of the two types of PS fractions investigated. One can thus conclude that the temperature dependences of the zero-shear viscosities of the linear and cyclic fractions are nearly identical, the difference being of the order of the experimental uncertainty.

Actually, this result is not surprising since the temperature dependence of η_0 is essentially controlled by the monomeric friction coefficient,[25,39] which should be independent of the architecture of the chain, provided that the effect of chain ends can be neglected, which is in fact the case for the materials compared in this section.

(c) Numerical Analysis of the Master Curves. The slight differences between the master curves of the linear and cyclic fractions can also be evaluated in a quantitative manner by a statistical analysis of all of the data points (i.e., even those not shown in Figures 7 and 8), by assuming a *specific relationship* between η_0 and T. Although a great number of models have been proposed for describing the temperature dependence of the melt viscosity of amorphous polymers (and other glass-forming liquids),[25,34–36,39] we restrict ourselves here to the empirical relationship put

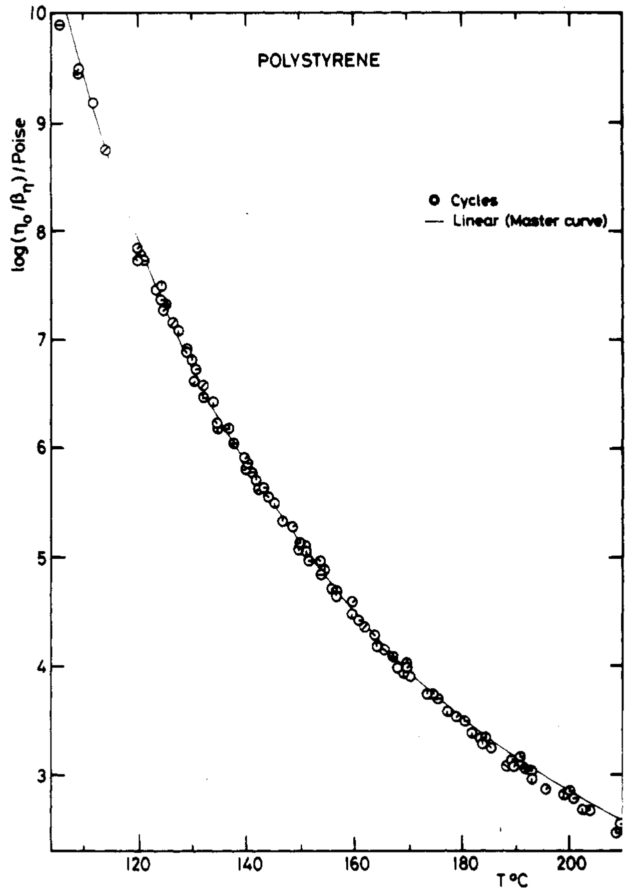

Figure 9. Comparison of reduced viscosity–temperature data for cyclic polystyrene fractions (points) with the master curve for linear polystyrene fractions (solid line).

Table V
Parameters from Nonlinear Least-Squares Fit of Viscosity–Temperature Master Curves to Eq 4

parameter	linear ($M_w \geq 40\,000$)	cycles
$\log A'$	−2.14 ± 0.10	−2.15 ± 0.10
B, K	779 ± 21.9	771 ± 19.7
T_∞, °C	42.8 ± 1.42	43.5 ± 1.20

forward by Vogel,[51] which can also be interpreted in terms of free volume.[39,40]

One can write accordingly

$$\log (\eta_0/\beta_\eta) = \log A' + B/(T - T_\infty) \qquad (4)$$

where A' and B are constants and T_∞ is the temperature at which η_0/β_η approaches infinity. For polymers[39,40] this temperature is located about 50 °C below the glass transition temperature.

Assuming the Vogel equation to hold in the entire temperature interval investigated (which has been shown, however, to be an oversimplification[35,36]), one can determine the values of the parameters $\log A'$, B, and T_∞ using a *nonlinear* least-squares analysis[52] of all the data points. This yields the values listed in Table V.

These values confirm that the temperature dependence of the linear and cyclic PS fractions is the same within experimental uncertainty. In addition, the values of B and T_∞ are of comparable magnitude to those previously reported for linear PS fractions ($M \geq M_c$).[25,34-39]

(2) Molecular Weight Dependence of η_0. Quantitative analysis of the data depicted in Figures 5 and 6 leading to the molecular weight dependence of η_0 can be carried out in three different manners, which will be described in this section.

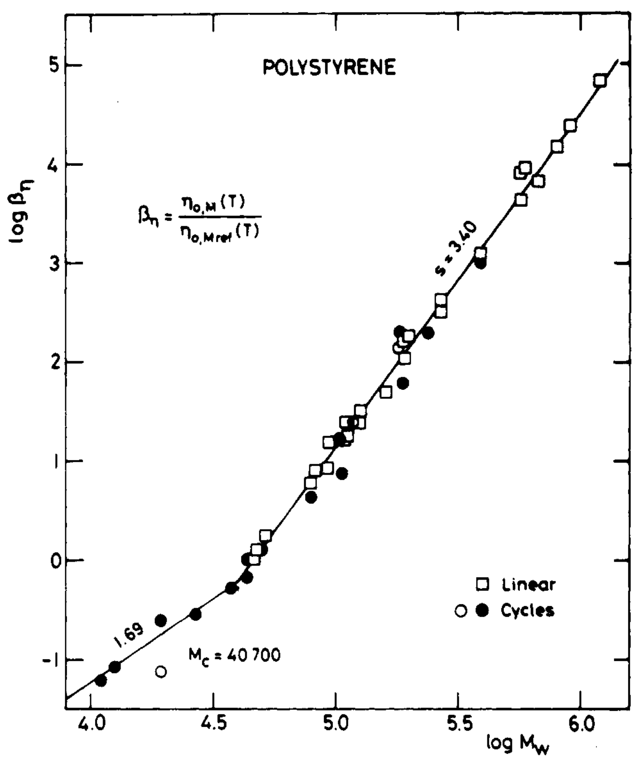

Figure 10. Logarithm of viscosity shift factor, β_η, vs. logarithm of molecular weight for cyclic and linear polystyrenes. The open circles are for fractions PS2857 corrected for ΔT = −4.0 °C and PS2780 corrected for ΔT = −2.5 °C. Solid lines represent least-squares fits to data above M = 40 000 (s = 3.40) and below M = 40 000 (s = 1.69).

(a) Analysis from the Master Curve. As above, the molecular weight dependence of the zero-shear viscosity for both the linear and cyclic fractions can be obtained from the variation of $\log \beta_\eta$ (cf. eq 3) with M_w. The relevant data are plotted double logarithmically in Figure 10, where the ordinate zero refers to both values of $M_{w,ref}$, i.e., 45 000 for the linear fraction and 44 000 for the cyclic fraction.

Several features emerge immediately from Figure 10. First, there is much more scatter than observed in producing the master curves. For the linear fractions this can be attributed to various causes: the determinations of η_0 have been performed in different laboratories, using different instruments and methods. In addition, and more importantly, the determination of M_w and molecular weight distribution give rise to additional uncertainties. For the cyclic fractions this situation is worse since in addition to the above error sources, the contamination of the cycles by a small amount of linear chains may introduce other uncertainities which are difficult to estimate, although they can be quite important as discussed subsequently.

With this in mind, Figure 10 shows that the differences in the molecular weight dependence of the cyclic and linear fractions ($M_w > 44\,000$) is of the order of the experimental scatter. Accordingly, the solid line depicts the least mean square average by accounting for *all* the data (a few of which are not shown in Figure 10). Interestingly, the slope of the line $d \log \beta_\eta / d \log M_w \equiv s$ = 3.40.

One must, nevertheless, question whether the same situation would prevail if the linear and cyclic fractions were compared separately. The relevant calculations yield for the 29 linear fractions almost the same value of s (3.39) as above, whereas for the 11 cycles s slightly decreases to 3.31 ± 0.02. There is, however, some hint that over the range of molecular weights investigated, the $\log \beta_\eta$ values

Table VI
Summary of Viscosity–Molecular Weight Dependences for Cyclic and Linear Polystyrenes

	s[a]			$\Delta \log (\eta_0/\mathrm{P})$[b]		
	$M > 44\,000$		$M < 44\,000$			
T, °C	linear	cyclic	cyclic	$M = 44\,000$	$M = 400\,000$	M_c[c]
130	3.38	3.37	1.82	0.075	0.085	46700
140	3.42	3.37	1.75	0.069	0.113	43300
150	3.45	3.31	1.66	0.030	0.162	38700
160	3.39	3.37	1.60	0.108	0.128	39200
169.5	3.37	3.32	1.62	0.097	0.146	37400
200	3.40	3.33	1.65	0.086	0.151	39600

[a] $\eta_0 = AM^s$. [b] $\Delta \log \eta_0 = \log \eta_{0,\mathrm{lin}} - \log \eta_{0,\mathrm{cyc}}$. [c] M_c = critical molecular weight for entanglements for the cyclic fractions from the abscissa at the point of intersection of the lines below and above $M_w = 44\,000$.

are about 10% lower for the cycles than for the linear fractions, rather than being greater. This trend is made more evident if one omits the β_η values obtained with the presumably contaminated cycles. (This is discussed below.)

Figure 10 also shows the data obtained with the five low molecular weight cyclic fractions ($M_w < 40\,000$), which yield a much lower value for the slope $s = 1.69$, albeit considerably higher than that predicted by the classical theory,[25,39,53] leading to $s = 1.0$. By accounting for the temperature shift ($\Delta T = -4$ K) for the PS2857 cycles discussed above, we find that the value of s remains 1.69, but the average line is shifted toward lower values by $\Delta \log \beta_\eta = 0.11$.

Intersection of the least mean square lines obtained with the cyclic fractions yields the value of their critical molecular weight $M_c = 42\,000$ without adjustment of the temperature scale. When the latter is taken into account (for the PS2857 cycles), the value of M_c decreases slightly to 36 200. These values are both within the usual range reported by most authors for linear PS fractions.[34-39] One can thus conclude that the molecular parameters (s and M_c) describing the variations of η_0 for the macrocycles barely differ from those of their linear homologues, a conclusion which will be further refined below.

(b) Comparison of the Raw η_0 Data. Another, more direct evaluation of the molecular weight dependence of η_0 can be achieved by plotting at fixed temperatures the η_0 values vs. M_w. Individual η_0 values are thus obtained at each value of T from the set of thermograms. (Note that interpolation or extrapolation was limited to ±10 K.) This procedure only assumes that there is no singularity in the temperature dependence of η_0.

Figure 11 depicts such η_0 plots for both the linear and the cyclic fractions at four temperatures within the T interval investigated. This plot displays a considerable scatter originating from the same error sources as those specified above, the major ones being uncertainties in the values of M_w, errors in the instrument calibration, and the lack of perfect superposition of the thermograms. These uncertainties are enhanced for the cycles by their possible contamination. This method of comparison, therefore, does not improve upon the previous analysis in which effective averages (i.e., $\log \beta_\eta$) rather than individual values were analyzed.

Consequently, for the high molecular weight materials there is no major difference between the molecular weight dependence of η_0 for the cyclic and linear polymers (although the relative positions of the individual η_0 values may vary somewhat from one temperature to another). For this reason Figure 11 shows only the average 3.4 slope for $M \geq M_c$, which appears consistent with both types of fractions. Separate least mean squares analysis of these data shows, however, that the slope s is again slightly greater for the linear fractions than for the cycles (the s values of the latter being quite sensitive to the presence or the omission of the η_0 value of the PS2780 cycles).

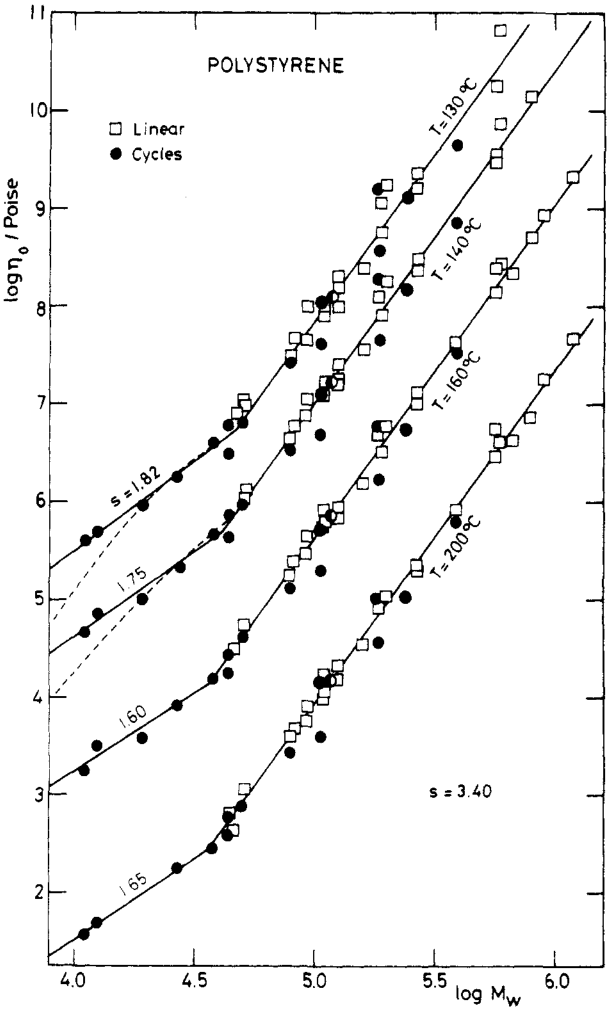

Figure 11. Logarithm of zero-shear viscosity vs. logarithm of molecular weight for cyclic (●) and linear (□) polystyrene fractions at four temperatures as indicated. Half-filled circles are data for the HA53 sample, which was probably contaminated by linear chains (see text for discussion).

The relevant numerical data obtained at six temperatures are listed in Table VI, which also indicates the difference $\Delta \log \eta_0 = \log \eta_{0,\mathrm{lin}} - \log \eta_{0,\mathrm{cyc}}$ at both limits of the M_w range of the cycles, i.e., at 44 000 and 390 000, in order to show the reduction of their η_0 with respect to that of their linear homologues. Due to the larger s values of the latter, the $|\Delta\eta_0|$ difference apparently increases with M_w, a presumably fortuitous result difficult to rationalize on the basis of reptation theories,[1-3] which would predict the opposite trend.[4,5,50]

Figure 11 also shows the average slopes for the five low molecular weight cyclic fractions ($M_w < 44\,000$), obtained

Table VII
Parameters for a Nonlinear Least-Squares Fit to Eq 5 for Cyclic and Linear Polystyrene Fractions

parameter	linear ($M_w > 40\,000$)	cycles ($M_w > 40\,000$)	cycles ($M_w < 40\,000$)
log A	−18.1 ± 0.35	−17.8 ± 0.46	−10.04 ± 0.19
B, K	759 ± 49	765 ± 54	689 ± 16
T_∞, °C	43.9 ± 3.2	42.9 ± 3.4	50.1 ± 0.95
s	3.45 ± 0.044	3.36 ± 0.072	1.74 ± 0.037

without a ΔT correction for the PS2857 fraction. Due to the rather large scatter of the η_0 values of these cycles, the value of s varies erratically with T but displays a tendency to decrease as the temperature increases. In any case it is always much larger than unity. On the other hand, the corresponding M_c values remain relatively insensitive to temperature and are located quite close to the M_c values obtained from Figure 10 (cf. Table VI) and those reported in the literature.[34-39]

At the two lowest temperatures the dashed lines represent the actual variation of η_0 for the linear fractions as determined from data reported by Suzuki.[35] These η_0 values do not obey a linear relationship in the double-logarithmic plot of Figure 11; rather they curve toward smaller η_0 values as M_w decreases. This well-known effect is usually attributed to the increase of the molecular mobility as the concentration of chain ends increases with decreasing M_n[25,39] in a way parallel to the depression of their T_g value. One can correct for this effect in various manners.[34-39] An easy way for achieving this compensation is to evaluate η_0 at constant $T - T_g$, in order to obtain values of η_0 at constant segmental mobility.

T_g values investigated by DSC with the low molecular weight CRM cycles[54] indicated that within experimental uncertainty (±1 K) they display the same value as the high molecular weight fractions (except PS2857, which was not investigated). In other words, chain-end effects were virtually absent from the low-MW cycles investigated. Although indirect, this result confirms the predominantly ringlike conformation of these fractions. The rather high value of the slope s thus appears to be incompatible with the theoretical value of 1.0.[25,39,53] Note that in most investigations performed with low molecular weight linear PS fractions, the value of s appears always significantly larger than unity.[25,34-39] Suzuki, using another, more sophisticated approach, reports independently of T that s = 1.5, in a wide range of M_w extending below M_c to about 550, i.e., to about five monomer repeat units. This result will be further discussed subsequently.

(c) Statistical Analysis of the Raw Experimental Data. One can analyze the data by assuming, as above, a specific relationship between η_0 and T, e.g., the Vogel equation (eq 4), complemented by a power law dependence of the viscosity on molecular weight. Limiting ourselves to $M_w \geq M_c$, we can write

$$\log \eta_0 = \log A + B/(T - T_\infty) + s \log M_w \tag{5}$$

where A is a constant, B and T_∞ have the same meanings as in eq 4, and s is the molecular weight exponent. The four parameters A, B, T_∞, and s were determined from a nonlinear least mean square analysis[52] for both the linear and cyclic PS fractions ($M_w \geq 40\,000$), taking into account *all* the relevant data used in this work. Similarly, the cycles have also been analyzed for $M_w < 40\,000$. The values of these parameters and their standard deviations are listed in Table VII and it can be seen that the results are similar to those obtained from the previous analysis. That is, the temperature dependences and molecular weight dependences of the cyclic and linear polystyrenes are approximately the same. Below M_c, the slope s is greater than unity and the absolute values of the viscosities of the cyclic polymers as revealed by the differences in the values of A are about 2 times lower than their linear counterparts. The high value of T_∞ for the cycles with $M_w < M_c$ is presumably biased by the PS2857 fraction (see the above discussion).

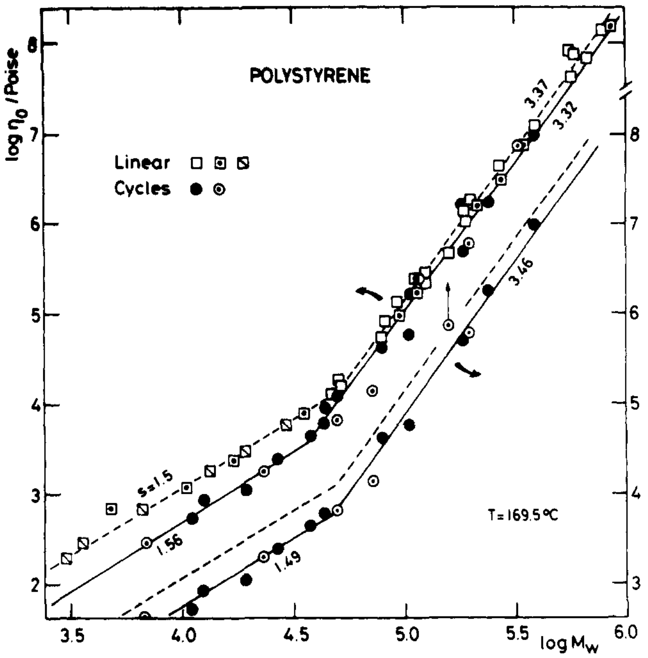

Figure 12. Dependence of the zero-shear viscosity on weight-average molecular weight for cyclic and linear polystyrenes at 169.5 °C. Closed circle and half-circle are data for cyclic fractions and have the same meaning as in Figure 11. Circled points are data of Roovers[29] on cyclic polystyrene. Squares with diagonal lines are literature data for linear fractions for which changing T_g has been taken into account below M_w = 40 000. Square points are data of Roovers[29] for linear polystyrenes. Dashed lines represent least-square fits to linear polystyrene data above and below M_c. Arrow points to data for Roovers' R18D cyclic fraction, for which the viscosity is extremely low. Lower data set is selected "best" cycles (see text for discussion).

(d) Comparison with Roovers' Data. To our knowledge the only other data available for the zero-shear melt viscosity of polystyrene macrocycles of high molecular weight are those recently reported by Roovers.[29] The molecular weights of the seven cyclic PS fractions, to be referred to hereafter as RT cycles,[22] ranged from 7000 to 334 000, five of which are located above M_c. As noted previously, for all of those fractions the ring-closure step took place in poor solvent conditions.

The relevant η_0 values were determined from the frequency (ω) dependence of the shear storage and loss moduli (G' and G'')[39] rather than directly measured as in the present investigations. Although a classical procedure, it may be recalled that such evaluation of η_0 from dynamic mechanical investigation involves for each fraction several independent steps to obtain the value of η_0 at a reference temperature, which in the present case was 169.5 °C. The η_0 values reported by Roovers[29] for the cyclic fractions (circled points) together with our data (filled circles) are shown in the upper part of Figure 12. Also shown are Roovers' data for his linear PS fractions (squared points), together with similar data discussed in this work (open squares). For the low molecular weight linear fractions all the η_0 values have been corrected for chain-end effects, either by the depression of T_g[29] or by the appropriate ΔT shift for superposing the log η_0 thermograms as reported by Suzuki[35] (diagonalized squares).

Table VIII
Parameters for a Nonlinear Least-Squares Analysis of Viscosity-Molecular Weight Data at 169.5 °C for Cyclic and Linear Polystyrenes Fit to Eq 7

parameter	linear data	data selection: all cycles	data selection: "good" CRM cycles	data selection: "good" CRM + RT cycles
A	0.112 ± 0.01	0.060 ± 0.016	0.059 ± 0.082	0.062 ± 0.067
C^a	8.84×10^{-13}	4.26×10^{-14}	4.40×10^{-14}	8.08×10^{-15}
s	3.43 ± 0.06	3.64 ± 0.26	3.63 ± 0.16	3.76 ± 0.15

[a] The uncertainties in C are unrealistic because C is a number very close to zero and the values of C depend very much on the value of and uncertainty is s. They are therefore not reported here.

This comparison of the different sets of data displays a series of interesting features.

(1) Starting with the linear fractions, one can notice that below M_c the two sets of data follow virtually the same line, the slope of which is 1.5. For $M > M_c$ the RT fractions have systematically slightly lower η_0 values than those defined by the least-squares line of the 29 other fractions. Although the difference is small and appears to be compatible with the scatter, its systematic occurrence indicates a nonrandom origin.

(2) For the low molecular weight cycles, the agreement between the RT and CRM fractions is excellent. Actually by accounting for the data points of both origins, the least-squares line defines virtually the same line, the slope of which ($s = 1.56$) is only slightly smaller than that defined by the CRM fractions alone (see Table VI).

(3) Significant discrepancies occur, however, with two RT fractions (R8DC, $M_w = 73000$, and R18D, $M_w = 160000$), which appear to have η_0 values that are much too low with respect to those of the CRM fractions. Although the first of these (R8DC) is still compatible with the large scatter displayed by the CRM cycles, the η_0 value of the second (R18D) appears unreasonably low, even with respect to those displayed by the two refractionated samples PS2829f and PS2780f, which encompass R18D. Actually, PS2780f displays an η_0 value that is quite close to that shown by the R10DD ($M_w = 198000$) fraction of Roovers. On the basis of these arguments we consider the η_0 value of the R18D cycles with great reservation, and in any case, it is incompatible with our data.[55]

(4) The highest molecular weight sample R19D ($M_w = 336000$) has a viscosity quite close to that of the average linear fractions. Although Roovers states that the viscosity of this fraction is too low, the fact that he is unable to measure its steady-state recoverable compliance is indicative of contamination by linear chains.[30,45] In addition, its η_0 value appears to be a little too high, relative to that of our highest molecular weight fraction ($M_w = 390000$).

Also we remind the reader that the Roovers molecules for which melt viscosity data were reported[29] were cyclized in cyclohexane below the Θ temperature, which implies the increased possibility for trapped knot formation in the rings.[41] This possibility when combined with the apparent contamination by linear chains of his highest molecular weight fractions would explain his viscosity data as being too low in the intermediate molecular weight range and increasing with M_w due to linear contamination.[30,45] The combination of these two effects could result in an apparently exponential increase in viscosity with molecular weight, which is the interpretation that Roovers[29] gives to his results.[55]

We thus adopt here another viewpoint, which has the advantage of reconciling three η_0 values of the RT cycles with those of our six presumably less knotted and less contaminated cyclic fractions in the range $M_w \geq 40000$. The molecular weight dependence of the selection of nine "best" cyclic fractions is depicted in the lower part of Figure 12, together with all the low molecular weight cycles, but allowing here for a slight correction of η_0 due to a change in T_g[29] for two RT cycles.

This admittedly arbitrary data selection leads to an interesting set of results, i.e., $s(M_w \leq 49800) = 1.49$ and $s(M \geq 49800) = 3.46$. Also $M_c = 49800$, which is somewhat greater than the previously obtained values. We note that this makes the M_c value for the cycles somewhat more consistent with the M_e (the molecular weight between entanglements) obtained from measurements of the plateau modulus, $G_N{}^\circ$, the value of which for the cyclic molecules is about half that of their linear counterparts (i.e., $G_N{}^\circ]_{cyc} \approx {}^1/_2 G_N{}^\circ]_{lin}$ (ref 29)). Other more detailed investigations of the rheological properties of polystyrene macrocycles will be reported elsewhere.[30]

(e) Alternative Interpretation of the Molecular Weight Dependence of η_0 below M_c. As demonstrated above, for molecular weights below M_c, for both the cycles and the linear chains (when corrected for changing segmental mobility), the slope of the log η_0 vs. log M_w lines is greater than unity; i.e., $s \approx 1.5$. As noted, such behavior can be attributed to a failure of these melts to behave in a Rouse-like way.[53] Such a finding is not necessarily surprising, given that the Rouse[53] analysis is for a single chain in dilute solution. However, it has become common to treat the viscosity–molecular weight dependence at low molecular weights as Rouse-like[25,39] in both concentration, ϕ, and molecular weight, M; i.e., $\eta_0 \propto \phi^{1.0} M^{1.0}$. We, therefore, present in the following paragraphs an analysis that allows one to keep the Rouse-like behavior at low molecular weights, while still fitting the data below M_c which displays a slope greater than 1.

The approach we take is similar to one used by Graessley et al.[57] to explain the concentration dependence of the viscosity, where we now substitute molecular weight for concentration. Here we assume that at constant monomeric friction coefficient[39] the viscosity of polymer melts as a function of molecular weight is governed by two distinct mechanisms which are additive, one being the Rouse-like mechanism and the other, the power law mechanism.

At constant segmental mobility, such behavior may be described as

$$\eta_0 = AM + CM^s \tag{6}$$

or

$$\log \eta_0 = \log [AM + CM^s] \tag{7}$$

where A defines the prefactor for Rouse-like behavior at low MW (i.e., first power in molecular weight) and the values of C and s pertain to the power law dependent mechanism at high MW.

The data of Figure 12 for both the linear and the cyclic polystyrenes have been treated by using a nonlinear least-squares procedure[52] to fit the data to eq 7. The results are summarized in Table VIII, where values of A,

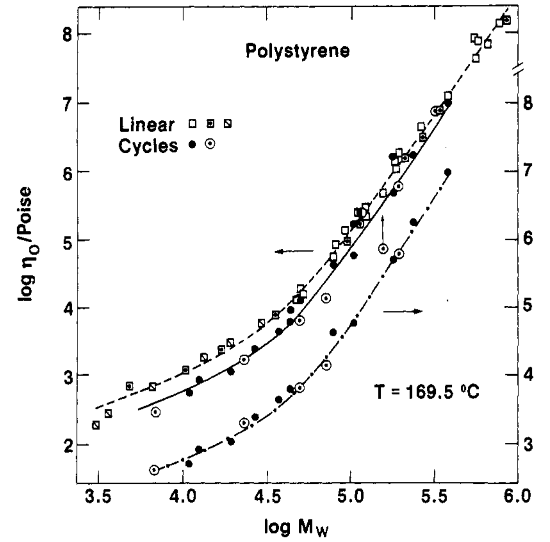

Figure 13. Same data as Figure 12 but with curves representing nonlinear least-squares fits to eq 7 passing through the data (see text and Table VIII).

C, and s are presented for the linear data and all of the cyclic data (from both this study and RT samples) depicted in Figure 12. Two selections were also made for the cyclic data—the "good" fractions from this work and the "combined" good fractions from this work and the RT samples. In Figure 13 the fits are compared with the data, where the dashed line represents the fit to the linear data, the solid line, the fit to all of the cyclic data, and the dashed-dotted line, the fit to the selection of combined "good" cyclic fractions.

We can see from Figure 13 that the fits are quite reasonable for both the linear and cyclic fractions. Interestingly, the power law dependence at high molecular weights for the macrocycles appears to be somewhat higher than for the linear molecules regardless of the data selection made.

If the analyses presented in the preceding sections represent the actual behavior of unknotted, uncatenated ring molecules in the melt (and we do not see any serious argument why they do not, at least to a reasonable approximation), their interpretation must be quite different from that put forward by Roovers.[29] The result that nonreptating macrocycles show very similar behavior to presumably reptating linear chains suggests a serious difficulty with the reptation[1-5,50] theories.

Summary and Conclusions

Narrow fractions of polystyrene molecules in the form of uncatenated rings were synthesized by reacting bifunctional living precursors with an appropriate coupling agent in dilute solution. Molecular weights ranged from 11 100 (below the critical molecular weight for entanglement coupling, M_c) to 185 000 (above M_c). The results of measurements of the dilute solution viscosities of these CRM fractions in both good and poor solvents were analyzed and compared with the results by Roovers[22,26] on nominally similar polystyrene fractions. The differences in the molecular weight dependences of the intrinsic viscosities both in cyclohexane at 35 °C (near the Θ temperature) and in good solvents for the CRM cycles and those of Roovers suggest that the latter have a more compact conformation than the former. This suggests that the Roovers macrocycles contain a significant fraction of permanently knotted chains.[41,56] Nevertheless, the reasons for this remain unclear as the dilute solution behavior of the Roovers[22,26] macrocycles for which ring closure occurred in good solvent conditions was the same as for those for which ring closure occurred below Θ conditions.

The zero-shear viscosities of the CRM cyclic fractions and several others synthesized at the University of Akron[23,33] were measured in the melt at temperatures ranging from 105 to 220 °C. The Akron fractions extended the molecular weight range to 390 000. The results were compared with the melt behavior of narrow fractions of linear polystyrenes and with the reported zero-shear viscosities of the Roovers[29] samples (cyclic and linear).

There are five key findings from these investigations:

(1) For all molecular weights, the temperature dependence of η_0 for the cyclic polystyrenes is virtually indistinguishible from that of linear polystyrenes of high molecular weight. Thus all the log $[\eta_0(T)]$ isobars display the classical WLF[39,40] or Vogel[51] type temperature dependence and they can be superimposed onto a single master curve by a shift along the log η_0 ordinate. The fact that this holds even for the lowest molecular weight macrocycles is consistent with the independence of the glass transition temperature on molecular weight over the range studied.

(2) For molecular weights above M_c (~35 000) the viscosities of the cyclic molecules have lower values than those of their linear analogues. They follow, however, a power law relationship with molecular weight similar to that of the linear chains, i.e., $\eta_0 \propto M^s$, where $s \approx 3.4$ for both the cyclic and linear fractions.

(3) Below M_c the viscosity–molecular weight relationship for the cyclic molecules is again similar to that of the linear molecules when in the latter case account is taken of the changing segmental mobility of the chains due to the increasing concentration of chain ends as the molecular weight decreases. However, the values of the viscosities of the cyclic molecules are a factor of 2 lower than for the linear chains. The fact that the apparent slope is greater (i.e., $s > 1$) than that predicted for a Rouse-like behavior ($s = 1$) is interpreted in two ways. Either the chains do not reach the Rouse limit for the viscosity–molecular weight behavior and s is always greater than unity or, even at low molecular weights, there is a contribution from the 3.4 power law mechanism to the viscosity.

(4) The critical molecular weight for entanglement coupling of melts of polystyrene rings does not differ appreciably from that of linear chains, in spite of the fact that the cycles are expected to be more compact[7-11,46] than their linear analogues.

(5) The comparison of our results with those of Roovers[29] suggests that there are significant differences between the CRM cycles and those of Roovers. The differences in results suggest that the Roovers cycles may contain a significantly greater fraction of knotted rings[41] than those produced by the CRM or Akron groups. This would lead to more compact cycles and, presumably, to fractions which have lower melt viscosities, although the dilute solution properties in near-Θ conditions are not greatly different. It should be noted that the Roovers cycles for which melt viscosities have been reported[29] have all been cyclized in cyclohexane below their Θ temperature. Under such conditions these fractions would be expected to contain a significant amount of permanently knotted[41] rings, presumably resulting in depression of the zero-shear melt viscosity.

While this accounts for the lower viscosities of the Roovers samples of intermediate molecular weight, it does not explain the rapid increase of the viscosity of these cycles in the high molecular weight range, since the probability of knotting increases with increasing molecular weight.[41,56] The explanation may come from the rheological data reported by Roovers,;[29] i.e., the steady-state recoverable compliance ($J_e{}^\circ$) is larger by nearly 1 order of magnitude than that reported by McKenna and Plazek[30,45] for the refractionated CRM cycles. This increase is consistent with a high molecular weight (presumably linear) contaminant, since small amounts of linear chains can greatly increase the viscosity of the cycles.[45] In fact, the combined effects of knotting and an increasing amount of linear contamination with increasing molecular weight would account for an apparently exponential molecular weight dependence of the viscosity of the cyclic fractions of Roovers.

The results presented in this paper thus raise some important questions about the motion of uncatenated rings in a matrix made of similar rings. The close similarities in the viscosity–molecular weight relations of the nonreptating cyclic molecules and the presumably reptating linear ones are surprising. The lack of a large difference in the behaviors of these systems strongly suggests that the contributions of reptation to the shear flow of macromolecular melts (and more generally to their chain dynamics) may be much less important than assumed in recent theories.[1-5,50]

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