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Synthesis and Investigation of Macrocyclic Polystyrene[‡]

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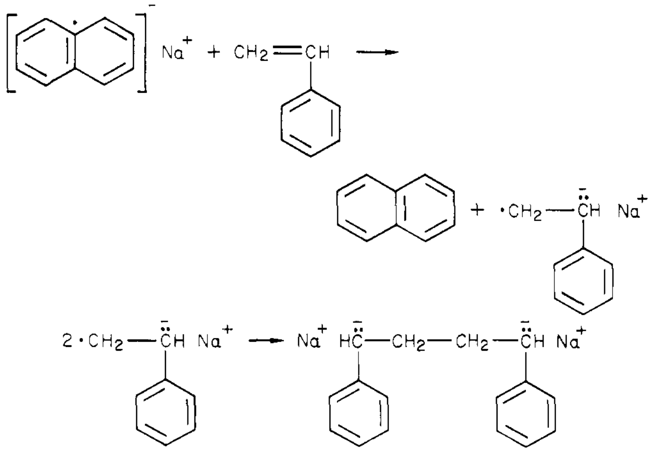
ABSTRACT: Macrocyclic polystyrene samples ($30 < DP < 250$) with narrow molecular weight distribution have been prepared by living bifunctional anionic polymerization and by coupling with α,α′-dichloro-*p*-xylene. The polymers have been investigated by gel permeation chromatography and viscosity measurements. The GPC data of both cyclic and acyclic polymers fulfill the Benoit relationship. The ratio of the intrinsic viscosity of ring and linear polymer chains was found to be close to 0.65 in cyclohexane at 34.5 °C. In toluene at 25 °C it is a function of the molecular weight ($0.56 < [\eta]_r/[\eta]_l < 0.76$).

A broad variety of circular DNA has been observed in the past,[1-3] proving the high biological importance of ring-shaped molecules.

On the other hand a number of theoretical studies have appeared treating the hydrodynamic properties of cyclic macromolecules in comparison with linear molecules of the same molecular weight.

Reports on synthetic cyclic polymers occur only sporadically in the literature. Semlyen et al.[4] described the preparation and characterization of cyclic poly(dimethylsiloxane) $[(CH_3)_2SiO]_x$ and Jones[5] reported on cyclics in styrene-dimethylsiloxane block copolymers.

In the present paper we describe a method for the preparation of cyclic polystyrene by anionic polymerization using sodium naphthalene as an initiator[6] which generates a bifunctional "living" chain and α,α′-dichloro-*p*-xylene as a bifunctional terminating agent. Linear and cyclic molecules were separated by fractionation after reaction of the linear molecules having chlorine end groups with high molecular weight living polystyrene.



The cyclic polymers with narrow (nearly Poisson) molecular weight distribution have been characterized by gel permeation chromatography and by viscosity.

Experimental Section

1. Materials. Inert gases (N_2, Ar) were purified by passing them through columns filled with Al_2O_3 as a support for metallic potassium and bubbling them through a solution of α-methylstyrylsodium.

Tetrahydropyran was refluxed over K and fractionated. Then it was stored over potassium benzophenone ketyl and distilled off before use.

Naphthalene was purified by sublimation.

α,α′-Dichloro-*p*-xylene (Schuchardt, Munich) was recrystallized from ethanol and sublimated in N_2 atmosphere. The melting point of the pure product was 100 °C.

Styrene was purified in the usual manner. Before use it was distilled from $LiAlH_4$.

2. Preparation of Polystyrene and Cyclization. The apparatus for polymerization and cyclization reactions is shown in Figure 1. It was heated in vacuo with a flame and then filled with Ar. From the 2-L flask A containing tetrahydropyran (THP) as a solvent and the tetrameric dianion of α-methylstyrene with Na^+ as the gegenion, THP was distilled into the 2-L flask B in vacuo. Via tube k all flasks can be filled with pure THP. In flask C the initiator, sodium naphthalene, was prepared in THP. From flask F containing styrene and $LiAlH_4$, styrene was distilled in vacuo into flask E. In flask D the polymerization of styrene (0.07 mol, dissolved in 500 mL of THP) initiated by sodium naphthalene (the amount calculated to achieve a certain degree of polymerization) took place. Half of the living solution was taken off via tube l and protonated by means of methanol to yield an acyclic polystyrene sample. The other half was added dropwise and simultaneously with an equimolar amount of α,α′-dichloro-*p*-xylene dissolved in 250 mL of THP (flask H) to 1 L of pure THP (flask G) where cyclization took place. At the end of the reaction an excess of dichloro compound was added to provide all residual open chain species to carry Cl end groups.

3. Separation of Macrocycles and Acyclic Material. The material obtained after the cyclization reaction was freeze-dried, dissolved in 100 mL of THP, and reacted with high molecular weight ($50000 < M < 200000$) living polystyrene prepared with a bifunctional initiator in THP solution which was added dropwise

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[†] Part of her Ph.D. Thesis.

[‡] Dedicated to Professor P. J. Flory on the occasion of his 70th birthday with very best wishes.

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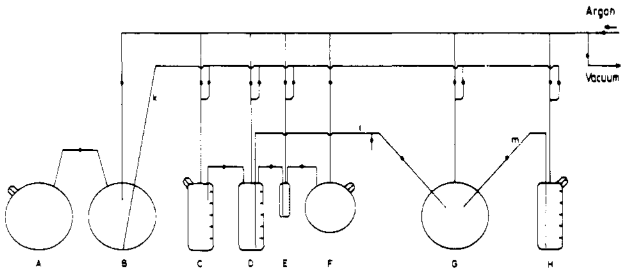

Figure 1. Apparatus used for the polymerization reaction of styrene and for the cyclization reaction.

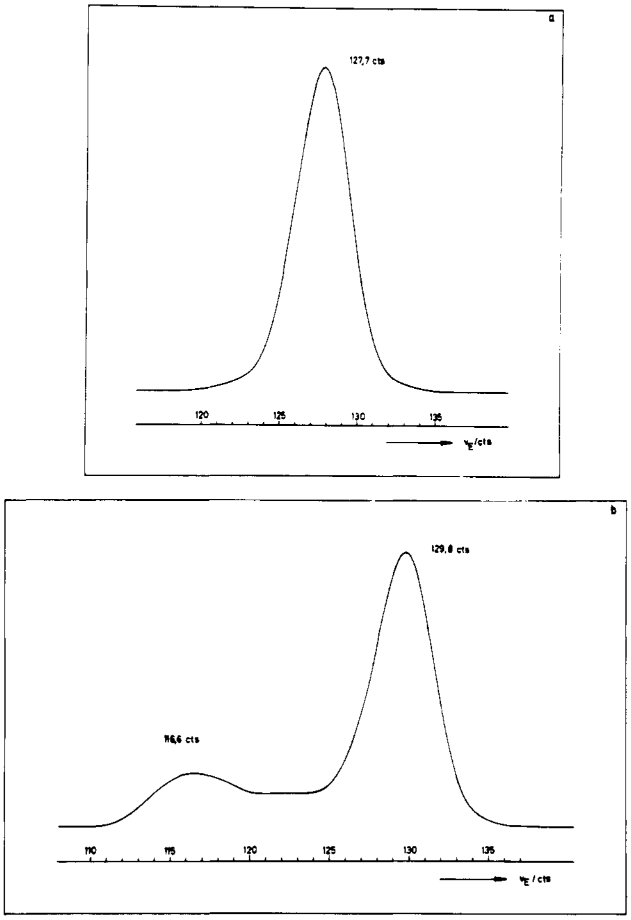

Figure 2. (a) Polystyrene sample prepared with sodium naphthalene as an initiator (sample 28). (b) Cyclization product.

until an excess of the living high molecular weight polystyrene (as seen from the red color of the solution) was achieved.

This procedure provides the reaction of all acyclic molecules carrying Cl end groups with the high molecular weight living polystyrene while the cyclic chains are "inert" and hence maintain their molecular weight. Then a small amount of methanol was added to the solution to protonate excess carbanions.

The resulting product was precipitated and dissolved in toluene (1% solution). Then methanol was added until the solution turned turbid. The gel phase was separated from the solution phase by centrifugation and the procedure was repeated until no more polymer precipitated upon the addition of methanol to the solution phase. The fractions were investigated by gel permeation chromatography.

4. Methods of Characterization. GPC was performed by using a set of nine Waters columns (1 m each) filled with Styragel and Poragel (class B), respectively, with the following specification: 10000, 3000, 2000, 700, 2 × 500, 350, 2 × 200 Å.

For calibration narrowly distributed polystyrene samples prepared by anionic polymerization were used.

Viscometry was performed in a Micro-KPG-Ubbelohde Viscosimeter, diameter of the capillary 0.42 mm (Schott-Geräte, Hofheim/Taunus).

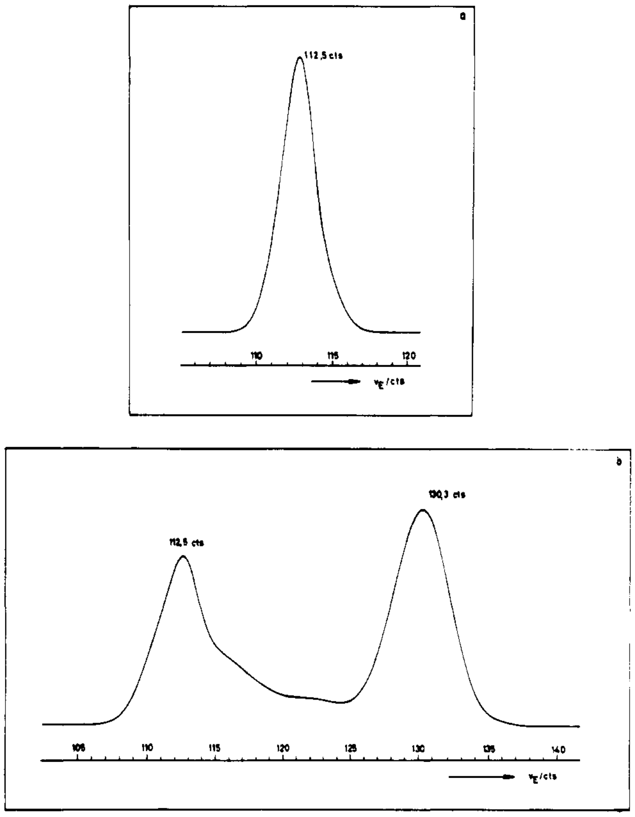

Figure 3. (a) High molecular weight polystyrene sample. (b) Coupling product of the high molecular weight polystyrene sample with the cyclization product.

5. Control of Reactions by GPC. Figure 2a shows the GPC of an acyclic polystyrene sample (experiment No. 28) prepared with sodium naphthalene as an initiator. The molecular weight is 13000, and the distribution is narrow. The Wesslau relationship yields a value of $M_w/M_n = 1.03$. The maximum of the GPC elution curve appears at 127.7 counts. After the cyclization procedure, some material at smaller elution volume, i.e., with higher molecular weight, occurs while the maximum of the main peak is shifted to $v_E = 129.8$ counts (Figure 2b). The latter effect is due to cyclization of the linear chains. The cycles formed exhibit a larger elution volume than the corresponding linear chains although their molecular weight is increased by the molecular weight of the coupling segment ($-CH_2-C_6H_4-CH_2-$, $M = 104$).

The higher molecular weight material originates from multiple coupling and may be either cyclic or acyclic.

After reaction with high molecular weight living polystyrene the acyclic material should be incorporated in the high molecular weight fraction while the low molecular weight fraction should consist of cyclic material. Figure 3a shows the GPC of the high molecular weight polystyrene ($v_E = 112.5$ counts) used for the coupling reaction while Figure 3b shows the result of the coupling reaction before fractionation. The material within the peak at $v_E = 130.3$ counts represents the basic cycle; cyclic multiples appear in the region $115 < v_E/\text{counts} < 125$.

Since the reaction of a carbanion with an alkyl chloride is fast and quantitative (and irreversible),[7] the concentration of reactive groups in the cyclization vessel is close to zero at any time provided the addition of the reaction components to the solvent is slow enough. Consequently the fraction of cyclic material theoretically to be expected is 100%. Experimentally, fractions between 50 and more than 90% are observed; these numbers, however, are not dependent on the molecular weight of the polystyrene sample subjected to cyclization. They rather depend on trivial experimental conditions which result in a deviation from the ideal situation outlined above.

The fraction of cycles with molecular weight M in most cases is between 70 and 80% of the total cyclic material. GPC, however, clearly indicates the formation of higher multiples, such as $2M$, $3M$, etc., as well (Figure 3b). These were removed by fractionation

Table I
Molecular Weight, Intrinsic Viscosity, and Ratio of Intrinsic Viscosities of Linear (l) and Cyclic (r) Polystyrene Determined in Cyclohexane at 34.5 °C and in Toluene at 25 °C

			cyclohexane			toluene		
expt no.	M_l	M_r	$[\eta]_l$, mL/g	$[\eta]_r$, mL/g	$[\eta]_r/[\eta]_l$	$[\eta]_l$, mL/g	$[\eta]_r$, mL/g	$[\eta]_r/[\eta]_l$
32	3 900	4 000	5.33	3.75	0.70_4	5.20	3.95	0.76_0
12/14	12 100	12 200	9.35	6.07	0.64_9	9.86	6.43	0.65_2
28	12 500	12 600	9.52	6.17	0.64_8	11.41	7.03	0.61_6
30	14 000	14 100	10.07	6.57	0.65_2	11.81	7.21	0.61_0
26	15 400	15 500	10.56	7.00	0.66_3	11.96	7.49	0.62_6
24	18 100	18 200	11.44	7.60	0.66_4	13.11	7.78	0.59_3
20	19 000	19 100	11.73	7.69	0.65_6	14.43	8.13	0.56_3
22	24 200	24 300	13.23	8.62	0.65_1	15.71	9.13	0.58_1

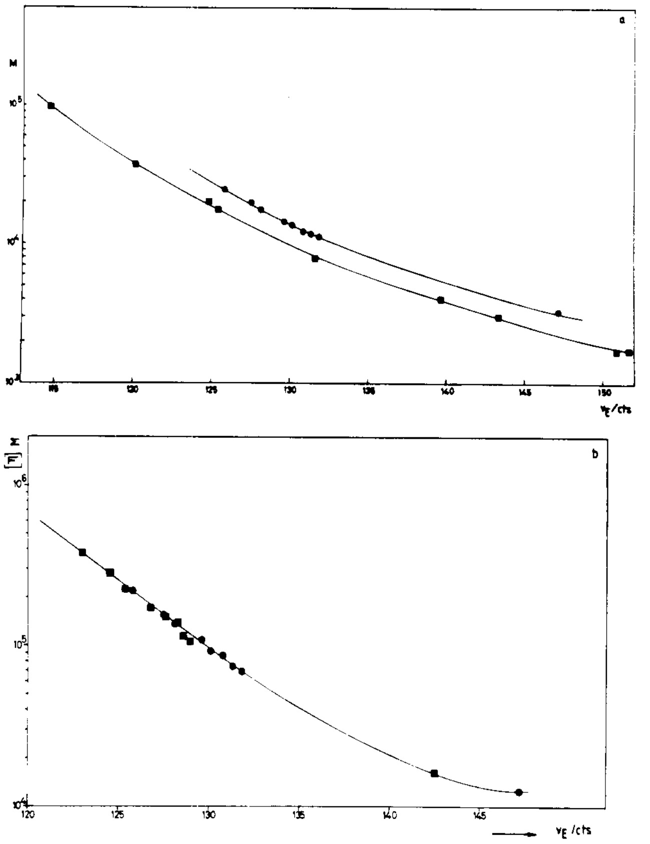

Figure 4. GPC calibration curves for cyclic (●) and linear (■) polystyrene: (a) conventional plot of log M vs. v_E; and (b) Benoit plot of log $[\eta]M$ vs. v_E.

since for the present purpose narrowly distributed cyclic polystyrene samples were striven for.

From a theoretical as well as an experimental point of view regarding the methods of investigation of macrocycles, those with higher molecular weights than achieved so far are of particular interest. The preparation and particularly the fractionation, however, become more difficult with increasing molecular weight of the macrocyclic polymers. Experiments in this direction are underway, though.

Results and Discussion

1. Gel Permeation Chromatography. It is well known that cyclic molecules exhibit a larger elution volume v_E than linear ones. This is generally attributed to the smaller molecular dimensions of cyclic chains as compared with the linear chains.

In order to receive a "universal" calibration curve at least for polymers consisting of the same monomer units but exhibiting different structures (linear, comb-shaped, star-shaped), different approaches have been reported. According to Benoit,[8] a plot of log $[\eta]$ M vs. v_E results in a "universal" curve in the sense described above. This also applies for linear and cyclic macromolecules. Figure 4a shows the conventional plot and Figure 4b the Benoit plot for linear and cyclic polystyrene.

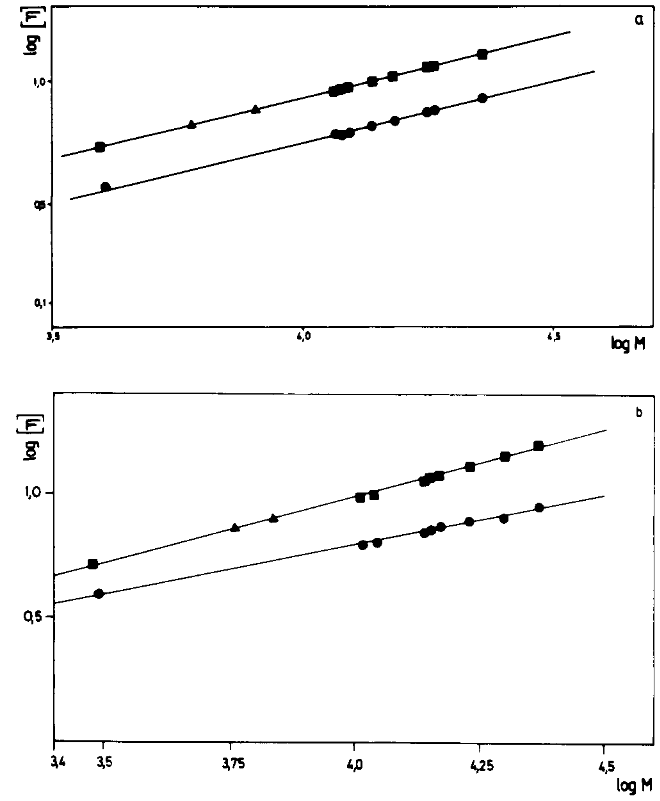

Figure 5. Intrinsic viscosity–molecular weight relationships for (●) cyclic polystyrene and (▲, ■) linear polystyrene in (a) cyclohexane at 34.5 °C and (b) toluene at 25 °C.

2. Viscosities. The molecular weights of the linear polystyrene samples prepared in the present paper have been determined by gel permeation chromatography by using a calibration curve and by viscosity measurements. The ratio M_w/M_n of the samples as determined from GPC by using the Wesslau relationship[18] is between 1.03 and 1.09 (in sample 32 it is clearly larger, i.e., 1.33).

The intrinsic viscosity[19]/molecular weight relationships are shown in Figure 5 for both linear and cyclic polystyrene as observed in cyclohexane and in toluene. For cyclohexane solutions the molecular weights of acyclic polystyrene have been calculated from the measured intrinsic viscosities by using the relation[9] $[\eta]_l = 0.085M^{0.5}$. Molecular weights of cyclic polystyrene result from those of the corresponding acyclic ones by adding 104.

For toluene solutions the intrinsic viscosity/molecular weight relationship in a double logarithmic plot is not linear over a wide range of molecular weights.[10-12]

3. Limiting Viscosity Ratios. As seen from Table I, the ratio of $[\eta]_r/[\eta]_l$ for cyclohexane as a solvent is between

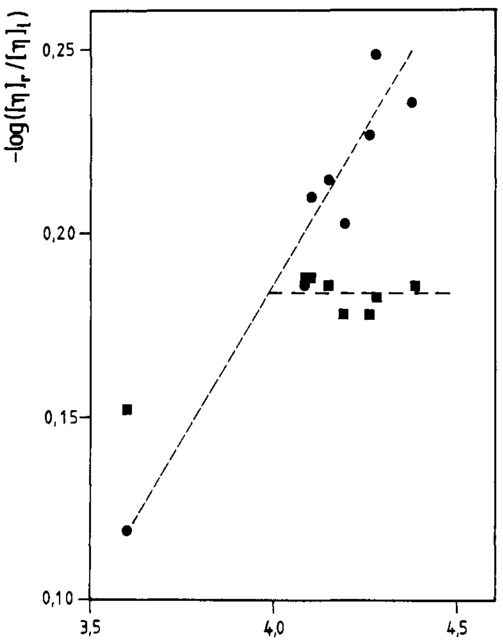

Figure 6. Molecular weight dependence of log $[\eta]_l/[\eta]_r$ for (■) cyclohexane and (●) toluene.

0.64_8 and 0.66_4, neglecting the lowest molecular weight sample (0.70_4). These values are in good agreement with values predicted by Bloomfield and Zimm[13] (0.658), Fukatsu and Kurata[14] (0.645), and Berry and Casassa[15] (0.66) for Θ conditions.

Moving from a Θ solvent (cyclohexane) to a thermodynamically good solvent such as toluene, we find that the ratio $[\eta]_r/[\eta]_l$ decreases and, in contrast to a Θ solvent, shows a significant dependency on the molecular weight of the macrocyclic polymer (Figure 6). These results indicate that the volume effect on $[\eta]$ in ring chains is *smaller* than that in the corresponding linear chains. This behavior has been predicted by Bloomfield and Zimm[13] ($0.1 < \epsilon < 0.3$). According to the relation given by Fukatsu and Kurata[14] the ratio $[\eta]_r/[\eta]_l$ is an increasing function of z.

A more recent approach of Fujita et al.[16] which was corrected by Shimada and Yamakawa[17] yields ${R_\eta}^3 = {\alpha_{\eta,r}}^3/{\alpha_{\eta,l}}^3 = 1 + 0.038z + \ldots$, where ${\alpha_\eta}^3 = [\eta]/[\eta]_\Theta$, and is compatible with Fukatsu's prediction with respect to the sign of the coefficient of z (first order perturbation coefficient). These theories consequently predict the volume effect on $[\eta]$ in ring chains to be *larger* than that in the respective linear chains and hence are in contrast to the experimental results.

To evaluate the radii of gyration of linear and cyclic polystyrenes, neutron scattering measurements are in progress. The results will be published elsewhere.

Acknowledgment. This work has been performed at the Sonderforschungsbereich 41 "Makromoleküle", Darmstadt/Mainz. Financial support of the Fonds der Chemischen Industrie is greatly acknowledged.

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(18) $M_w/M_n = e^{(B\sigma)^2}$, where B is the slope of the GPC calibration curve, $\ln M = A - Bv_E$, and σ^2 is the variance of the elution curve.
(19) The intrinsic viscosities have been determined by extrapolation of plots η_{sp}/c vs. c, η_{sp}/c vs. η_{sp}, and $\ln \eta_{rel}/c$ vs. c. Deviations between the three methods generally are in the range of ±1% and are not dependent on the molecular weight of the samples.