collected by filtration without cooling and washed with hot toluene twice. The product, having the composition of 9,10-bis(diphenylphosphino)phenanthrene monosulfide, was obtained in a yield of 13%: mp 294.5–297.5 °C; ^{31}P NMR (tetrachloroethane) δ 40.3, 39.2, −13.0, −14.0. Anal. Calcd for $C_{38}H_{28}P_2S$: C, 78.87; H, 4.88; P, 10.71; S, 5.54. Found: C, 78.55; H, 4.98; P, 11.59; S, 5.56.

The phosphination was carried out with lithium diphenylphosphide as phosphinating reagent. After reflux for 12 h, the chloride ion released during the reaction was only 38.2%.

General Procedure for the Polymerization. To a resin flask were added 0.8169 g (2.000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**11**), 0.4577 g (1.800 mmol) of 4,4′-diacetyldiphenyl ether (**12**), 0.2000 mmol of the comonomer (**6** or **8**), 10 g of di-*m*-cresyl phosphate, and 4 g of *m*-cresol.[14] The flask was purged with nitrogen. The polymerization was carried out at 135–140 °C with mechanical stirring for 24 h. An additional portion of *m*-cresol was added when the mixture became too thick for stirring. The yellow-orange viscous solution was precipitated into 200 mL of ethanol containing 10% of triethylamine and chopped in a blender. The resultant yellow fibrous polymer was extracted with ethanol in a Soxhlet extractor for 24 h and dried at 100 °C under reduced pressure for 24 h (Table III).

General Procedure for Macromolecular Phosphination. To 20 mL of liquid ammonia was added 0.078 g (0.340 mmol) of sodium to afford a dark blue solution; then 0.63 g (0.34 mmol) of diphenylphosphine was added, followed by the addition of 20 mL of THF. An orange solution was generated in a few minutes. The ammonia was driven off as described above. The phosphide solution was added rapidly to the mixture of **13** in 30 mL of THF at room temperature with stirring overnight and then heated to reflux for 1 h. After the mixture cooled, the polymer was precipitated in ethanol, extracted with ethanol under nitrogen for 24 h, and dried at 100 °C under reduced pressure for 24 h (Table III).

General Procedure for the Catalytic Reactions. All catalytic reactions were carried out in a 100-mL stainless steel bomb with a glass cylinder and a glass cylinder lid. The catalyst, substrate, and solvent were charged into the cylinder. The bomb was purged with synthesis gas 3–5 times before heating. After the reaction, the bomb was cooled thoroughly by a dry ice/2-propanol bath, and then the pressure was released very slowly. The mixture was vacuum transferred and then examined by GLC and/or other means such as NMR or IR.

Acknowledgment. This research was supported in part by Grant No. DMR-8016503 from the National Science Foundation.

Registry No. **2**, 17219-94-2; **3**, 85565-99-7; **4**, 85566-00-3; **5**, 85566-01-4; **6**, 85565-95-3; **7**, 85566-02-5; **8**, 85565-97-5; **10**, 39705-76-5; **13**, 85565-96-4; **14**, 85565-98-6; phenanthrene, 85-01-8; ethylene glycol, 107-21-1; *o*-bis(diphenylphosphino)benzene, 13991-08-7; *o*-dichlorobenzene, 95-50-1; 1-pentene, 109-67-1; hexanal, 66-25-1; 2-methylpentanal, 123-15-9; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Rh(COD)_2Cl]_2$, 12092-47-6.

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Synthesis of High Molecular Weight Ring Polystyrenes†

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ABSTRACT: The reaction of two-ended living polystyrylsodium with dimethyldichlorosilane was used to prepare narrow molecular weight distribution ring polymers. The molecular weight of the samples ranged from 5×10^3 to 4.5×10^5. It was found that ring and linear polymers of the same molecular weight can be fractionally precipitated. Ultracentrifugation sedimentation and gel permeation chromatography were used to monitor the purity of the ring polymers.

Introduction

It was discovered in 1962 that certain DNA molecules occur in nature in a circular form.[1] DNA molecules, however, are complex molecules and their circularity imposes certain constraints on their conformations. A particularly illuminating introduction to the peculiar aspects of circular DNA conformations was written by Cantor and Schimmel.[2] It was soon recognized that it would be useful to study ring polymers that occur normally as flexible random coils,[3] but the challenge of their synthesis had to be rekindled.[4]

Ring polymers are formed in the polymerization of certain heterocyclics and during polycondensation reac-

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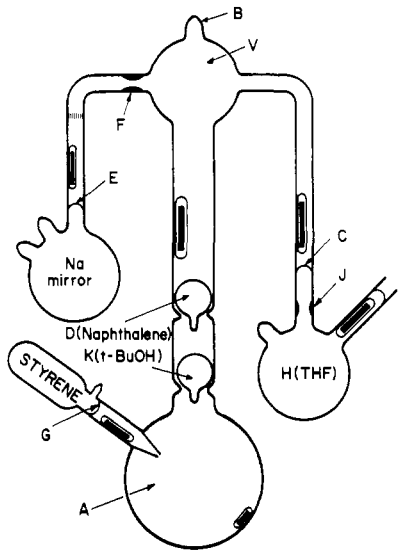


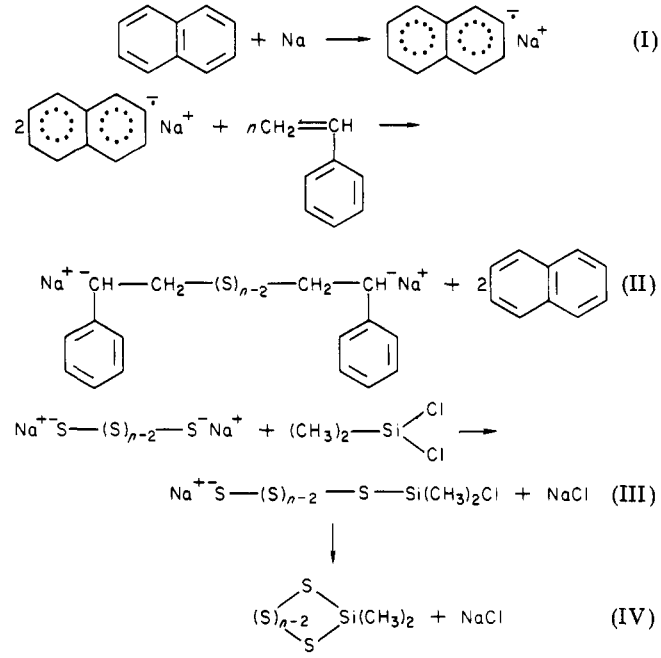
Figure 1. Apparatus for the synthesis of two-ended polystyrylsodium in benzene–THF.

tions (polyesters, polyamides). However, the ring polymers occur in equilibrium with linear species and have broad molecular weight distributions.[5] Cyclic poly(dimethylsiloxanes) were obtained by the equilibrium polymerization of octamethylcyclotetrasiloxane with KOH.[6] This procedure was improved and scaled up to yield gram quantities of cyclic poly(dimethylsiloxane) fractions with molecular weights up to 24000.[7] Milligram quantities of cyclics with molecular weights up to 74000 could be isolated with a preparative gel permeation chromatograph.[8] Low molecular weight cyclic poly(dimethylsiloxanes) are produced directly in the cationic polymerization of hexamethylcyclotrisiloxane.[9] Cyclic oligomers were found also in the metathesis polymerization, e.g., of cyclododecene. These oligomers were converted by hydrogenation to cycloalkanes with up to 96 carbon atoms.[10]

Recently, attempts have been made to synthesize ring polymers by anionic polymerization techniques. The basic strategy, suggested long ago,[3] is to form a narrow molecular weight distribution polymer with two carbanion end groups and to react the latter, under extreme dilution, with a difunctional electrophile. Rempp and collaborators used potassium naphthenide in a mixture of benzene and tetrahydrofuran (THF) to polymerize styrene and α,α'-dibromo-*p*-xylene as the cyclizing agent.[11] Their evidence for the formation of ring polymers was that the apparent molecular weights of the ring polymers in gel permeation chromatography (GPC) were about 20% lower than those of the parent linear polymers. Vollmert et al. used sodium naphthenide in THF to polymerize styrene and α,α'-dibromo-*p*-xylene to perform ring closure.[12] Some of the fractions had a low intrinsic viscosity compared with that calculated for the linear polymer of the same molecular weight. A rather complete analysis of eight ring polystyrenes, prepared with sodium naphthenide in tetrahydropyran and with α,α'-dichloro-*p*-xylene, was made by Geiser and Höcker.[13] Fetters et al. have since that time initiated work on ring polymers using dilithium compounds in hydrocarbon solvents.[14]

In these published studies, the molecular weight of the ring polymers was usually less than 25000. Unfortunately, at these low molecular weights the long-chain limit of the polymer properties are not fully reached. For establishing relations between the physical properties and molecular weights of ring polymers, it is desirable to have a larger range of high molecular weight samples.

In this paper we describe the synthesis of high molecular weight ring polystyrenes. The basic reactions used are schematically



An example of the intermolecular (poly)condensation is

$$Na^{+-}S\text{-}(S)_{n-2}\text{-}S\text{-}Si(CH_3)_2Cl + Na^{+-}S\text{-}(S)_{n-2}\text{-}S^{-}Na^{+} \longrightarrow Na^{+-}S\text{-}(S)_{n-2}\text{-}S\text{-}Si(CH_3)_2\text{-}S\text{-}(S)_{n-2}\text{-}S^{-}Na^{+} \quad (V)$$

We have developed methods to purify the ring polymers and to ascertain their structural purity. Some dilute solution properties are described because they verify the architecture of the polymers.

Experimental Section

A. Synthesis of Ring Polystyrenes. Materials. Naphthalene was purified by double sublimation and stored over P_2O_5. A single crystal was weighed into a fragile bulb and evacuated to high vacuum.

Dimethyldichlorosilane (Eastman) was distilled and a middle fraction degassed and stored under vacuum in *n*-BuLi–hexane-washed and -rinsed fragile bulbs. The content of one fragile bulb was diluted with *n*-hexane and divided over several ampules. The concentration of $(CH_3)_2SiCl_2$ was determined by titration with NaOH.

Tetrahydrofuran (THF, Fisher Certified) was distilled two or three times from K metal in the presence of benzophenone (blue benzophenone ketyl). A middle fraction was taken each time. The purified solvent was immediately degassed and stored on the vacuum line over fresh CaH_2 and distilled twice onto fresh sodium–potassium alloy. The characteristic blue color should form immediately. The quality of the THF was monitored by its UV spectrum as obtained in a 1-cm quartz cell (filled and kept under vacuum). The characteristic optical densities were 0.05 (220 nm), 0.10 (215 nm) and <0.80 (210 nm)[15]. THF that did not meet these specifications produced unstable sodium napththenide and polystyrylsodium solutions. Finally, THF was treated with polystyrylsodium prepared by the reaction of styrene with a sodium mirror and sealed into an ampule.

Benzene (Phillips 99%+) was stirred under argon with small batches of concentrated H_2SO_4 till no further color developed over 24 h. It was washed with water, KOH solution, and water and dried over Na_2SO_4. It was fractionally distilled from CaH_2 and stored on the vacuum line over *n*-BuLi.

Cyclohexane (Eastman) and *n*-hexane (Phillips) were passed through activated silica gel columns till aromatics were absent as monitored by their UV spectrum in the range 240–270 nm. These solvents were stored under vacuum over *n*-BuLi.

Styrene (Polysar) was fractionally distilled under reduced pressure. A middle cut was degassed, treated with CaH_2, and

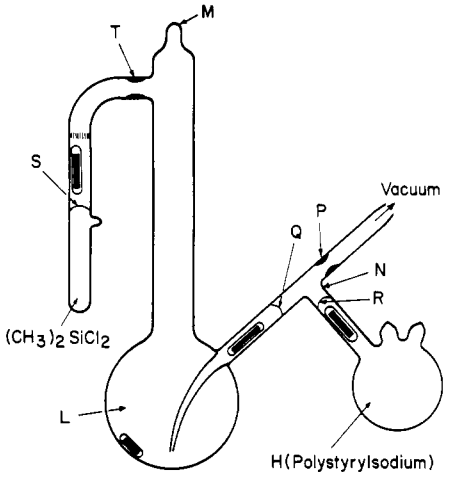


Figure 2. Apparatus for the cyclization of two-ended polystyrylsodium near Θ solvent conditions.

prepolymerized with *n*-BuLi (0 °C). It was stored on the vacuum line over CaH_2 and sealed in an ampule as a 30% solution in benzene just before use.

Preparation of Two-Ended Polystyrylsodium. Ring polymers were prepared in all-glass vessels provided with break seals and fragile bulbs for the addition of solvents and reagents and constrictions for removal of products.

The apparatus shown in Figure 1 was used to prepare two-ended polystyrylsodium. It was previously washed with a benzene solution of *n*-BuLi and repeatedly rinsed by refluxing benzene from a dumbbell attached at B (not shown; see ref 16). Typically, about 80 mL of benzene was condensed into A and the apparatus sealed at B. Break seal C was broken and about 100 mL of THF introduced into A. Fragile bulb D was broken and the naphthalene dissolved in the solvent mixture. The solution was brought into contact with the sodium mirror after E was broken. The green color of sodium naphthenide developed immediately. The solution was shaken on the Na mirror for 1–2 h, and then returned completely to A. The Na mirror was removed by sealing at F. The apparatus was then so tilted that the styrene inlet was straight above flask A. The sodium naphthenide solution was cooled to 0 °C and vigorously stirred with the glass-sealed magnet. G was then broken. The polymerization occurs almost instantaneously. The final polystyrene concentration never exceeded 0.04 g/mL. The polystyrylsodium solution was transferred to H, cooled, sealed at J, and immediately used in the cyclization step. A small amount of polystyrylsodium solution was retained in A. It was terminated with *t*-BuOH from bulb K and used as the linear parent polymer.

Cyclization Reaction. The cyclization reaction was performed in two different ways. The apparatus for the first method is shown in Figure 2. The whole apparatus was treated with a cyclohexane–THF (100:1) solution of polystyrylsodium and rinsed with the solvent mixture. About 500 mL of the solvent mixture was distilled into L and the apparatus sealed at M. The polystyrylsodium solution (in flask H) was attached at N and the connection between H and L evacuated and sealed at P. The cyclohexane in L was kept at room temperature and the polystyrylsodium solution in H at about 0–5 °C in order to equalize the vapor pressure in both parts of the apparatus when Q and R are broken. About 1–2-mL samples of polystyrylsodium solution were transferred from H to L by tilting the apparatus while the solution in L was vigorously stirred. Break seal S was broken and vapor from the 0 °C solution of $(CH_3)_2SiCl_2$ was allowed to slowly transfer to L. After almost all color had disappeared in L, new polystyrylsodium was added from H. It was ascertained that no $(CH_3)_2SiCl_2$ transferred to H by keeping the inlet in L under the solvent level. The cyclization reaction took from 1 to 5 h, depending on the amount of polymer. Excess $(CH_3)_2SiCl_2$ was removed at T before the apparatus was opened.

In the second method of cyclization no cyclohexane was used but rather an internal dilution was realized. The apparatus of Figure 1 was modified so that the polystyrylsodium solution could be concentrated in a side arm; the solvent was collected in A. The polystyrylsodium and solvent were separated by sealing the inlet to the side arm. The same system of stepwise adding the polystyrylsodium to flask A while slowly distilling $(CH_3)_2SiCl_2$ (attached at V) as in the first method was used. In this case it was difficult to obtain pure samples of the linear precursor.

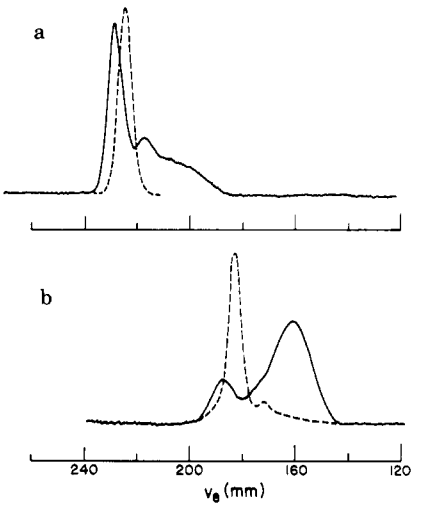


Figure 3. Chromatograms of the crude product of the cyclization reaction: (a) R16; (b) R15. The chromatogram of the parent linear polymer is indicated by the dashed line.

Fractionation. Figure 3 shows examples of the crude reaction product. The desired ring polymer is the low molecular weight species to the left of the chromatogram. The crude polymer was fractionally precipitated from benzene–methanol solution. The ring polymer is the most soluble fraction. The fractionation was monitored by GPC and by ultracentrifugation sedimentation.

B. Polymer Characterization. GPC was performed with five 30-cm μ-Styragel columns of nominal size 500, 1×10^3, 1×10^4, 1×10^5, and 1×10^6 at 35 °C. THF was the elution solvent and the flow rate was 1 mL/min. A standard sample injection contained 0.12 mg of polymer in 80 μL. The columns were calibrated with a set of linear narrow molecular weight polystyrenes. Elution volumes were reproducible to 0.5 mm.

Light scattering measurements were performed with a Fica 50 photogoniometer following procedures published previously.[17] Cyclohexane was fractionally distilled from CaH_2 to remove 2,4-dimethylpentane. The Rayleigh ratio of benzene at 35 °C was taken as 50.8×10^{-6}. The refractive index increment of polystyrene in cyclohexane at 35 °C is 0.181 mL/g.

Ultracentifugation sedimentations were performed in cyclohexane with a Beckmann Spinco Model E at 60 000 and 68 000 rpm (titanium rotor).[18] Schlieren optics were used to view the sedimentation patterns.

Results

Figure 3a shows GPC traces of the crude product R16 obtained with the cyclization in cyclohexane. Overlaid is the elution peak of the parent linear polymer. The material eluting between 186 and 218 mm is the high molecular weight polycondensation product formed by reactions of type V. Some of this material may be cyclic.[12] The polymer eluting at 230 mm is the desired ring polymer. The elution maximum of the parent linear polymer is at 225 mm. Figure 3b shows R15 cyclized by the internal dilution technique. The cyclic polymer elutes at 188 mm, and the parent linear polymer elutes at about 184 mm.

The fractionation of the crude polymer yielded ring polymer samples. Some GPC elution traces are shown in Figure 4. Care was taken to ensure that the peak width at half-height ($w_{h=h_{max}/2}$) is identical, to within 5%, with that of the parent linear polymer. It is found that broader peaks are caused by the presence of linear polymer of the same molecular weight as the ring polymer. Small amounts of linear polymer can be removed by careful fractionation at very low concentration. Examples are shown in Table I. Each ring polymer is numbered in the order of its

Table I
Fractionation of Ring from Linear Precursor Polymer

sample	M_w [a]	Θ_{A_2}, [b] °C	$[\eta]$, [a] dL/g	V_e^{max}, mm	$w_{h=h_{max}/2}$, [c] mm
R4P	52 500	35.0	0.190_5	211.2	5.8
R4D	51 900	31.2	0.128_5	214.2	6.5
R4DA				213.3	7.0
R4DB	48 000	28.2	0.123	215.0	6.0
R10P	205 000 [d]	35.0	0.365	191.9	6.0
R10D	204 000		0.265	195.1	7.8
R10DD	198 000	28.5	0.229	196.6	6.0

[a] Measured in cyclohexane at 35 °C. [b] In cyclohexane; temperature at which the apparent second virial coefficient is zero. [c] Width at half-height. [d] 195 000 by GPC.

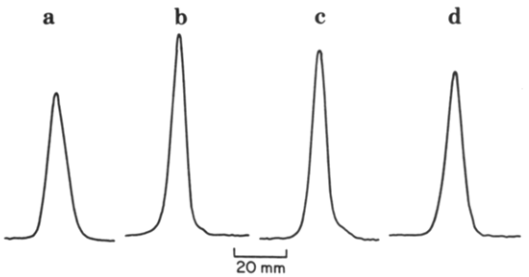


Figure 4. Chromatograms of the ring fractions: (a) R17H; (b) R9E; (c) R12D; (d) R15E.

preparation. The linear precursor is identified by the letter P. Each fraction is given a letter in alphabetical order. A refractionated fraction is identified by a second letter. It can be seen that fractionation and refractionation do not change the molecular weight from that of the linear precursor polymer. A narrowing of the GPC elution peak and a small shift to longer elution times are also observed. Moreover, the Θ_{A_2} temperature and the intrinsic viscosity measured in cyclohexane at 35 °C decrease slightly by removal of linear polymer. Obviously, the fractionation of ring from linear polymer is feasible because the polymers have different solubilities, as will be discussed later.

Evidence for the purity of the ring polymers can be obtained from their ultracentrifugation sedimentation pattern at long sedimentation times. This technique has been very useful in the case of regular star polymers.[19] In a Θ solvent and neglecting concentration effects, the sedimentation velocity coefficient (s) is given by

$$s = (K/h)M^{1/2}$$

where K depends on the polymer–solvent pair, $h = 1$ for a linear polymer but otherwise depends on the architecture of the polymer molecules, and M is the molecular weight. Since for a ring polymer $h < 1$, it is expected to sediment faster than the parent linear polymer. Figure 5a shows the sedimentation pattern of R13E, a ring fraction with $M_w = 5.5 \times 10^5$. Three sedimenting bands are seen, which are from left to right linear polymer with molecular weight equal to half that of the parent linear polymer, linear polymer with $M_w = 6.0 \times 10^5$, and ring polymer with the same molecular weight. The central species was identified by admixing a small amount of linear precursor as shown in Figure 5b. The slowest moving band was identified by its initial sedimentation coefficient, which is approximately $\sqrt{2}$ smaller than that of the linear polymer. A full analysis of the sedimentation pattern to eliminate the Johnston–Ogston effect observed with the Schlieren optics[20] indicated 17% linear with $M_w/2$ and 7% linear parent polymer.

Analysis of lower molecular weight ring polymers becomes increasingly more difficult as longer sedimentation times are required and diffusion of the boundary becomes more pronounced. Sedimentation patterns c and d of Figure 5 are those of R15E and R12D, respectively. No indication of linear material could be found. R8DC and R9E were investigated at 68 000 rpm. The Schlieren pattern of R9E is symmetrical, but that of R8DC shows a small shoulder where the linear parent polymer is expected. Admixture of the linear parent polymer to R9E only produced a broadening of the sedimentation pattern.

A low molecular weight linear polymer ($M_w/2$) found in the highest molecular weight rings, Figure 5a,c, arises during the anionic polymerization of styrene when one living end is accidentally terminated. In principle, such polymer should disappear by polycondensation with two-ended molecules, but nevertheless small amounts (<0.5% of total) are terminated before chain extension. Fractional precipitation proved extremely inefficient for the removal of this low molecular weight material from the ring. An attempt to fractionate R13E further on a set of Styragel GPC columns was unsuccessful.

The molecular weights of the ring polymer samples were measured by light scattering in cyclohexane at 35 °C. The data are collected in Table II. A comparison is made with the molecular weights of the linear parent polymers. These are determined by GPC using narrow molecular weight distribution linear polystyrenes as calibration standards and, where sufficient sample was available, by their intrinsic viscosity in cyclohexane at 35 °C using

$$[\eta] = 8.3 \times 10^{-4} M^{0.5}$$

Some linear polymer molecular weights were checked by light scattering.

In the course of the light scattering measurements it became apparent that the apparent second virial coefficient is positive for ring polymers at the Flory Θ temperature

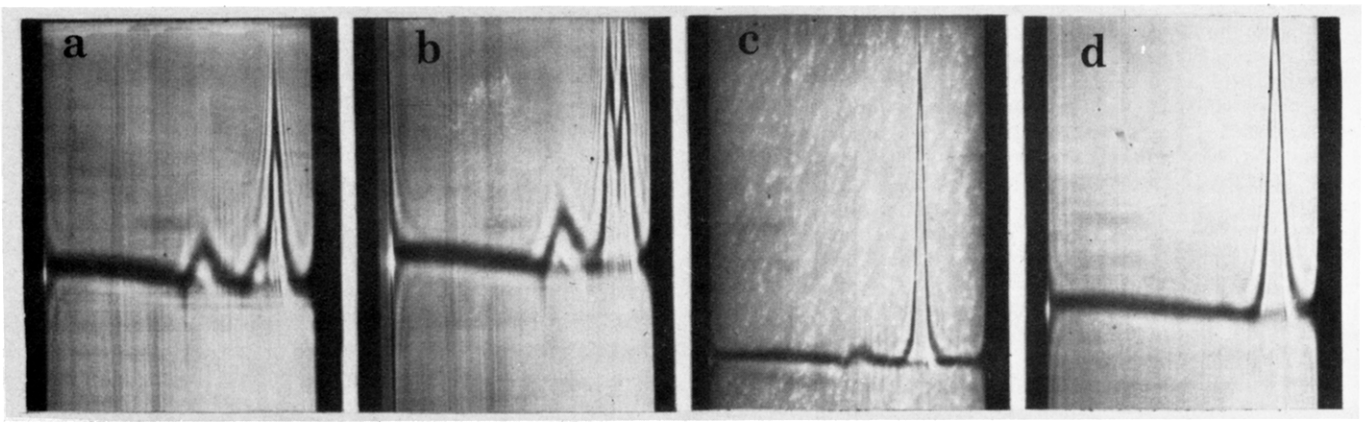


Figure 5. Ultracentrifugation patterns of ring polystyrenes in cyclohexane: (a) R13E; (b) R13E + parent linear polymer; (c) R15E; (d) R12D.

Table II
Synthesis and Molecular Weight Characteristics of Ring Polymers and Their Linear Precursors

			precursor		ring	
sample	method[a]	yield,[b] %	$M_{GPC} \times 10^{-4}$	$M_{[\eta]}$[d] $\times 10^{-4}$	M_w[e] $\times 10^{-4}$	A_2[e] $\times 10^{-5}$, cm³/g²
R17H	A	55	0.49	0.69		
R7F	B	19	1.21			
R16E	A	50	1.80	1.77		
R1F	A	35	2.31	2.27	2.34	5.2
R4DB	A	40	5.4_3	5.3	4.8	5.3
R8DC	A	19	7.4	7.0_3[f]	7.3_3	4.4
R9E	B	23	8.6_7	8.3_6[g]	8.6_9	5.0
R10DD	A	20	19.5	19.5[h]	19.8	4.2
R12D	B	15	23.8		25.8	4.2
R15E	B	18	44.0		43.9	3.5
R13E	B	9	60.5		55.0	

[a] A, dilution in cyclohexane; B, internal dilution. [b] Crude yield as measured by GPC. [c] Obtained from the maximum of the elution curve. GPC calibrated with standard linear polystyrenes. [d] From $[\eta]$ in cyclohexane at 35 °C with $[\eta] = 8.3 \times 10^{-4} M^{1/2}$. [e] Light scattering in cyclohexane at 35 °C. [f] 7.58 from $[\eta]$ in toluene; 7.43 from light scattering in cyclohexane. [g] 8.87 from $[\eta]$ in toluene. [h] 20.9 from $[\eta]$ in toluene; 20.5 from light scattering in cyclohexane.

for linear polystyrenes (34.5 °C)[14]. Measured values are given in Table II. The temperature at which $A_2 = 0$ is about 28.0 °C, independent of molecular weight in the range 20 000–450 000. The Θ_{A_2} of ring polymers seems to be quite sensitive to the presence of linear polymers; see, e.g., R4D in Table I.

The ring polymers were further characterized by their GPC elution volume. The results are shown in Figure 6. It can be seen that the elution of the ring polymers is delayed from that of a linear polymer with the same molecular weight. It appears that the log M vs. V_e lines for linear and cyclic polymers are practically parallel over the molecular weight range investigated. The apparent molecular weight of the rings based on the universal calibration is given by

$$(M_{ring})_{app} = 0.71 M_{ring}$$

Such parallel behavior of linear and ring polymers was observed previously over a smaller molecular weight range.[13,21]

The intrinsic viscosities of the ring polymers were measured in cyclohexane at 35 °C. Examples are given in Table II. The ratio of the intrinsic viscosity of a ring to that of the linear polymer with the same molecular weight, $g' = [\eta]_r/[\eta]_{lin}$, is found to be 0.66–0.68 at low molecular weight, in agreement with earlier determinations.[7,13] At high molecular weight g' decreases to 0.58–0.60. Therefore, g' is not a reliable characteristic for the evaluation of the purity of ring polymers.

Discussion

The synthesis of ring polymers is based on a favorable competition of an intramolecular reaction (between the two ends of one chain) over the intermolecular reaction (with the end of another chain). Since the intra- and intermolecular reactions are the same, they will have the same rate constant and the fraction of ring formation will only depend on the relative probability of finding the end of the chain (P_r) in the small reaction volume (v_s) over that of finding any other chain end (P_2), following Jacobson and Stockmayer[22]

$$P_r = \left(\frac{3}{2\pi}\right)^{3/2} \frac{v_s}{\langle r^2 \rangle^{3/2}} \quad (1)$$

$$P_2 = N\frac{v_s}{V} = \frac{N_A c}{M} v_s \quad (2)$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance of the chain, N is the number of living polymer molecules in the total volume V, N_A is Avogadro's number, and c is the concentration of polymer in g/mL. The right-hand side of eq 2 will have a factor 2 if both ends of the polymer can react. We will omit this case from the discussion. The concentration at which intramolecular reaction and intermolecular reaction are equally probable is given by

$$c_{eq} = \left(\frac{3}{2\pi\langle r^2 \rangle}\right)^{3/2} \frac{M}{N_A} \quad (3)$$

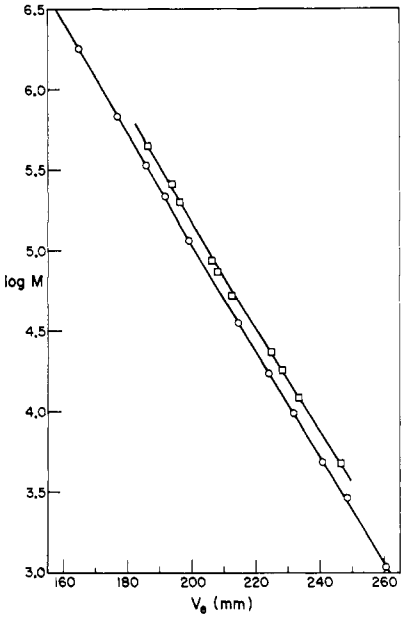


Figure 6. Comparison of the GPC elution volume of linear (○) and ring (□) polystyrenes.

In Figure 7, c_{eq} for polystyrene is plotted for the case of the Θ solvent and the good solvent. The living end concentration for equal ring formation and intermolecular condensation, $[LE]_{eq} = c_{eq}/M$, is also shown.

It can be seen that cyclization in a Θ solvent is to be preferred over cyclization in a good solvent, especially at high molecular weights. At high molecular weights extremely low living end concentrations have to be used. These are much lower than the lowest impurity levels that can be achieved by the best anionic polymerization techniques.[16]

Ideally, ring formation is performed well below c_{eq} or $[LE]_{eq}$ since the instantaneous fraction of ring polymer

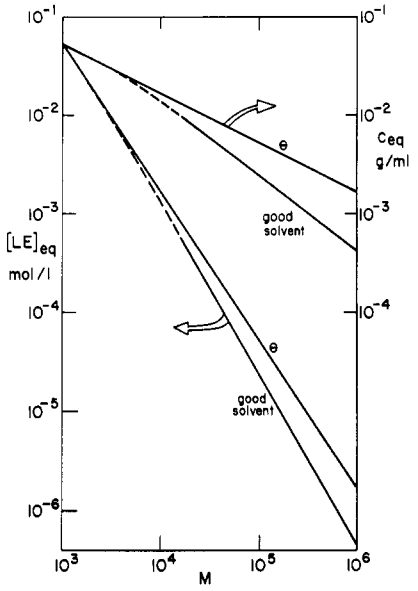


Figure 7. Polystyrene concentration for equal ring formation and intermolecular condensation, c_{eq} (eq 4), vs. molecular weight of the polymer [θ solvent: $\langle r^2\rangle = 6\langle s^2\rangle_\theta = 6 \times (7.9 \times 10^{-18}M)$ (ref 2); good solvent: $\langle r^2\rangle = (6 + 5\epsilon + \epsilon^2)\langle s^2\rangle = 6.88 \times (1.66 \times 10^{-18}M^{1.17})$ (ref 25)] and living end concentration for equal ring formation and intermolecular condensation, $[LE]_{eq}$, vs. molecular weight of the polymer.

formed is give by $c_{eq}/(c_{eq} + c)$, where c is the instantaneous concentration.

From Table II it can be seen that the yield of ring polymer decreases with increasing molecular weight of the ring. This reflects the fact that the low molecular weight polymers were prepared with an initial concentration (c_0) of polymer 20 times less than c_{eq}, but high molecular weight rings were formed at $c_0 \approx c_{eq}$.

The technique of adding small batches of two-ended living polymer and slowly distilling the electrophile into the solution leads to a decreasing yield of rings on successive additions. If we assume that all linear polymers are terminated by two Si–Cl groups and that, on addition of a new batch of living polymer, these groups will both react with living polymer, then the amount of ring polymer formed in the ith addition of living polymer is given by $\bar{f}c_0(2\bar{f} - 1)^{i-1}$, where $\bar{f}$ is the average fraction of ring polymer formed from a batch of living polymer with initial concentrations c_0. The overall fraction of monomeric ring polymer after n batches have been added is $\bar{f}/n\sum_{i=0}^{n-1}(2\bar{f} - 1)^i$. The last term is the sum of a geometric series. This scheme highly simplifies what happens in the complex reaction mixture and probably underestimates the yield of monomeric ring polymers because $\bar{f}$ is expected to rise slowly with successive additions of linear polymer, some linear polymer with S^-Na^+ end group will be terminated by impurities, and some high molecular weight linear polymer eventually disappears from the reaction mixture by ring formation. The latter can be shown to occur from the appearance in Figure 3a of a maximum at 219 mm, the location expected for a ring with twice the parent polymer molecular weight. The important fact is that the amount of ring polymer formed decreases asymptotically to zero as the number of additions of living polymer is increased. Of course, the formation of very high linear polymer facilitates the separation of the ring fraction during fractionation.

Another point to consider is the possible formation of knots in the rings. In linear chains knots may always be disentangled, but when the chain forms a ring, knots become permanent. A knot in a polymer chain is formed by a minimum of six entanglements of the chain with itself. The first three entanglements must be of the type underpass, overpass, and underpass or its inverse. Therefore, only one-fourth of all sets of three consecutive entanglements would lead to knots. The other three entanglements on the chain are the compliments of the first three. The number of self-entanglements in a polymer in a θ solvent can be estimated from its molecular weight and the molecular weight between entanglements (M_e) derived from the zero-shear recoverable compliance.[23] While in the bulk, the entanglements of a chain are mostly with neighboring molecules, a fraction $Mc^*/M_e\rho$ may be self-entanglements. Here, ρ is the bulk polymer density ($\approx$1) and c^* is the polymer concentration in the volume occupied by the coil. c^* can be estimated to be $c^* = M/(N_A\langle S^2\rangle_\theta^{3/2})$. In the case of polystyrene ($\langle S^2\rangle_\theta = 7.9 \times 10^{-18}M$ and $M_e = 18000$) the number of self-entanglements of the chains in the θ solvent is given by $0.004M^{1/2}$. Thus, a linear chain of $M = 1 \times 10^6$ would have an average of four self-entanglements. Therefore at $M = 1 \times 10^6$ the chance of forming a ring polymer with a knot is about 15%. A similar result was proposed previously.[24] It was also shown that a chain in a good solvent is much less likely to be entangled than in a θ solvent.[24] In agreement with these estimated, we have not found any evidence that the ring polymers contain knots. Rings R10DD and R12D with $R = 2 \times 10^5$ were prepared in a θ solvent and in a good solvent, respectively, but did not show different properties. Furthermore, the largest rings were prepared in a good solvent medium.

Finally, the ring formation was performed at such low total polymer concentration that the probability for catenation (two rings linked as in a chain) is very small. Catenation requires strong overlapping of a ring and a living polymer coil. The overlap concentration (g/mL) for a linear polymer in a θ solvent will be given by $c^\ddagger = M/(N_A(4\pi/3)\langle S^2\rangle_\theta^{3/2})$, which, in the case of polystyrene, leads to $c^\ddagger = 17.8M^{-1/2}$. Because $\langle S^2\rangle_{\theta,r}$ is calculated to be $^1/_2\langle S^2\rangle_{\theta,lin}$[26], the overlap concentration for two rings is estimated to be 2.8 times higher. The final total polymer concentration in the cyclization reaction never exceeded 0.01 g/mL (1%) and the ring polymer concentration was only a fraction of this concentration. Catenated molecules have probably not been produced. Any such molecules are expected to be removed in the high molecular weight fractions.

Conclusion

It has been shown that high molecular weight ring polymers can be prepared by anionic polymerization techniques. The solubility of ring and linear polymers is sufficiently different that a fractionation can be performed. Low molecular weight linear material proved to be difficult to remove. The purity of ring polymers can be checked by GPC, when the elution volume and the width of the eluding band are carefully considered. Ultracentrifugation sedimentation can be used to analyze high molecular weight ring polymers. The purity of the very dilute anionic polymerization systems at the point of the cyclization reaction seems to be the limiting factor for the preparation of high molecular weight rings.

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High Molecular Weight Linear Poly(ethylenimine) and Poly(*N*-methylethylenimine)

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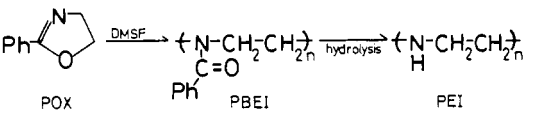
ABSTRACT: Linear poly(ethylenimine) (PEI) with high molecular weight was synthesized via acid-catalyzed debenzoylation of poly(*N*-benzoylethylenimine) (PBEI), which was obtained by cationic ring-opening polymerization of 2-phenyl-2-oxazoline (POX) at 140 °C with high monomer/initiator ratios up to 10^4. The anhydrous PEI crystals melted at 59–60 °C; the maximum weight-average molecular weight reached was estimated to be ca. 10^5. The presence of only a single ^{13}C NMR peak at δ 49.4 ($CDCl_3$) rules out the possibility of branching in the PEI chain. PEI was transformed into poly(*N*-methylethylenimine) (PMEI) by the Eschweiler–Clarke reductive N-methylation.

Introduction

It is a relatively easy task to attach a variety of organic groups to poly(ethylenimine) (PEI) and endue it with some desired functions.[1] This makes PEI one of the most convenient entrances to polymeric multifunctional catalysts or enzyme models.[2,3] Nevertheless, the usually available PEI is a highly branched polymer. Characterization of model catalysts or study of structure–activity relationships in such systems is rather complicated.[4] High molecular weight linear PEI, therefore, is desirable for such studies. In its original or chemically modified forms, it might give rise to some interesting chemical or physical properties distinct from those of highly branched PEI.

Recently, in collaboration with us, Chatani et al. determined the crystal structures of linear PEI, its sesquihydrate, and its dihydrate. The anhydrous PEI chains exist as double-stranded helices (a rare case for synthetic polymers); moreover, it undergoes peculiar morphological transformations during the course of hydration.[5,6] Preparation of a uniaxially oriented specimen of anhydrous PEI for such X-ray crystallographic study became possible only after linear PEI of sufficiently high molecular weight had been synthesized. The purpose of this paper is to disclose the details of the synthesis, to report a few interesting physical properties of the PEI, and to describe its derivatization to linear poly(*N*-methylethylenimine) (PMEI) by the Eschweiler–Clarke reaction.[7]

Scheme I



The conceptually simplest route to linear PEI, namely, cationic ring-opening polymerization of aziridine, usually suffers extensive branching.[8] Historically, the first synthesis of linear PEI was accomplished by Saegusa et al., who cationically polymerized 2-oxazoline or 2-methyloxazoline in dimethylformamide and hydrolyzed the product under alkaline conditions. To the best of our knowledge, the molecular weights of their crystalline PEI, which melted at 58.5 °C, did not exceed 10^4.[9,10]

In 1972, Gembitskii et al. polymerized aziridine in water at 0–20 °C using perchloric acid as an initiator and obtained precipitates of hydrated crystals of PEI in 5–15% yield.[11] The ^{13}C NMR of the dried PEI showed only a single peak, indicating the absence of branches. The maximum M_w value among the fractionated PEI was 2.5×10^4.[12] The Russian group also reported X-ray, infrared, DTA, and TGA data but gave no detailed structural analysis.[13,14]

Litt et al. obtained poly(*N*-benzoylethylenimine) (PBEI), which exhibited an extraordinarily high reduced viscosity (η_{sp}/c = 0.42 dm^3/g; 0.5% in *m*-cresol), by ring-

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