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SYNTHESIS OF RING-SHAPED MACROMOLECULES

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Abstract—Ring-shaped macromolecules have been synthesized by the reaction of a bifunctional "living" polystyrene with a stoichiometric amount of dibromo-*p*-xylene, at very low concentration. The reaction is carried out step by step, leading both to the expected cyclic polymer and to a "polycondensate". Fractionatal precipitation and one-step fractionation lead to well defined macrocycles of known size.

Ring-shaped macromolecules are of great interest to investigate the influence of cyclization [1, 2] on the size and shape of macromolecules. Statistical properties of such flexible ring polymers have been extensively studied [3, 4]. Two fundamental conditions are, at least, required to lead to conclusive evidence:

(i) the cyclic polymers obtained should be entirely free of linear homologues;
(ii) in a given sample, the range of the ring size should remain within well defined limits.

Only a few attempts have been made to synthesize well-defined ring shaped macromolecules [5, 6]. There are however a number of papers [7–11] and a review article [12] on ring-chain equilibria, based on backbiting reactions. Such equilibria have been studied extensively in the case of polydimethylsiloxanes [13, 14]. However they are not well suited to yield cyclic macromolecules of uniform size and free of linear homologues, although fractionation can help in that matter.

In the present investigation, we have sought a system which allows efficient control of the end-to-end cyclization. It occurred to us that anionic polymerization can be used for the purpose of synthesizing well defined cyclic polystyrenes of uniform size. Starting from a bifunctional "living" precursor chain and reacting it under *strictly stoichiometric conditions* with an efficient bifunctional electrophilic compound, at very low concentration, it is possible to obtain cyclic macromolecules. Simultaneously a linear "polycondensate" of *much higher molecular weight* is formed. Thus it is then possible to separate the former from the latter by an efficient fractionation.

METHOD USED

The clue to the success of the method proposed is the choice of a concentration as low as possible to increase the probability of intramolecular coupling. According to a calculation based on the work of Stockmayer [7], the concentration at which inter- and intramolecular reactions are equiprobable can be expressed as:

$$c_{eq} = \left(\frac{3}{2\pi}\right)^{3/2} \frac{1}{2\mathcal{N}} \cdot \frac{M}{\langle r^2 \rangle^{3/2}}$$

where $\mathcal{N}$ is Avogadro's number, M the molecular weight and $\langle r^2 \rangle$ the mean end-to-end distance of the "precursor" polymer in the solvent considered. Below c_{eq}, cyclisation is favoured; above c_{eq}, the yield of linear "polycondensate" should increase. For a polystyrene of molecular weight 10,000 in THF solution, c_{eq} is of the order of 0.4%. We have chosen to work at a concentration of 0.5%; obviously a lower value of c would have been better but experimental difficulties are involved.

We have chosen potassium naphthenide as initiator. It is fast and efficient and it exhibits a characteristic green colour. Styrene was used as the monomer: the "living" polystyrene solution is red. Dibromo-*p*-xylene was selected as the ring closing reagent. This bifunctional electrophilic compound reacts quickly, whereupon the solution becomes colourless again. If the temperature and the solvent are chosen carefully, side reactions can be disregarded. Potassium was chosen as counter-ion to avoid metal–halogen interchange reactions [15] which are rather frequent with lithium counter-ions.

EXPERIMENTAL PART

Materials

Styrene was purified according to standard procedures, solvents were distilled from dilute initiator solutions (sodium benzophenone for THF, butyllithium for benzene and cyclohexane) and recovered under dry argon in graduated dropping funnels. Dibromo-*p*-xylene was recrystallized twice from benzene. Potassium naphthenide was made from potassium and naphthalene in THF solution at room temperature under dry argon. It was titrated using the classical acetanilide method.

Reaction procedure

The experiments were carried out in a reactor subject to efficient stirring and temperature control, under a slight excess pressure of argon. A 1:1 mixture (by volume) of THF and benzene, or of THF and cyclohexane, was used as solvent. Styrene was placed in a graduated dropping funnel on top of the reactor. Another dropping funnel contained the dibromo-*p*-xylene as a 1% solution in benzene. These reagents were maintained under dry argon. The initiator solution was connected to the reactor by means of a graduated burette, allowing transfer without contact with the outside.

The reaction was carried out as a succession of individual steps, each of them involving the *same* amount of living sites, chosen beforehand.

To the solvent placed in the reactor, a given amount of initiator solution was added. Thereafter styrene was introduced drop-wise and the solution turned rapidly from green to red. The amount of styrene was determined by the molecular weight of the precursor polymer that was wanted. Next the dilute dibromo-*p*-xylene solution was added slowly until the red colour of the "living" precursor just vanished. This step was as sharp as a titration.

Immediately after decolouration, the next step was started by addition of the *same* amount of initiator solution as above. Attention is called to the fact that the first drop of potassium naphthenide solution should cause a green colour of the solution, thus confirming that no excess dibromo-*p*-xylene was involved in the previous step. Next styrene was added, and again dibromo-*p*-xylene solution, and so on.

The polymers were recovered by precipitation into methanol (containing 5% of water). The samples were filtered, washed and dried in vacuum.

Characterization and separation of the ring-shaped macromolecules

Gel permeation chromatography was performed using a Waters apparatus fitted with a set of six columns filled with styragel. Elution solvent was THF, at a flow rate of 1 ml/min. The calibration curve was obtained using standard polystyrene samples of low polydispersity.

Fractionatal precipitation was carried out using benzene as solvent and methanol as precipitant. Each fraction was characterized by its GPC diagram; from the overall fractionation data, it is easy to determine at which value of the precipitant content, γ, optimal separation between the linear "polycondensate" and the ring-shaped macromolecules is achieved.

Good results were obtained using a one-step fractionation. Methanol was added to a benzene solution of the sample, until the value of γ previously determined was reached. The whole of the linear polymer precipitated as a coacervate, and the supernatant contained the cyclic macromolecules. The yield of the fractionation can be increased (up to 95%) by repeating the process.

Light scattering measurements were carried out using a Fica apparatus.

RESULTS AND DISCUSSION

Cyclization yield

The coupling of two living sites by means of a xylene unit can occur intramolecularly to give cyclic macromolecules, or intermolecularly to yield a polycondensate, the molecular weight of which is much higher than that of the "precursor".

The gel permeation traces of the samples (Fig. 1) clearly show that both constituents are present; there

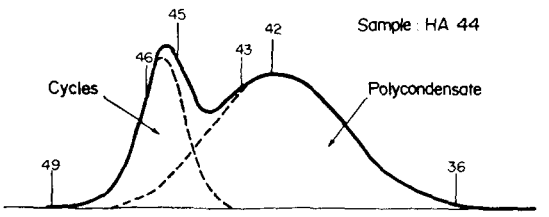

Fig. 1. Gel permeation chromatography diagram of sample HA 44.

is a low molecular weight peak of low polydispersity and also a high molecular weight constituent. The polydispersity ratio of the latter constituent, calculated from the GPC curves as shown on Fig. 1 using polystyrene calibration, is close to 2, as expected for a polycondensate.

The yields, R, of intramolecular coupling can be calculated from the areas of the peaks in the GPC trace of the raw samples. They are indicated on Table 1. The lower the molecular weight of the precursor, at constant concentration, the higher the probability of cyclization.

If the reaction is carried out in a THF/cyclohexane mixture, rather than THF/benzene, the yields are increased slightly. Cyclohexane is a bad solvent, the expansion of the polymer is reduced, thus favouring intramolecular coupling. Increase of the cyclohexane content beyond 50% by volume is however impossible as the initiator becomes unstable, and dibromo-*p*-xylene becomes insoluble.

If a precursor chain has reacted with two different dibromo-*p*-xylene molecules, this chain cannot cyclize any more. To prevent this as far as possible, the dibromo-*p*-xylene was added slowly as a very dilute solution.

Cyclic molecules of twice the expected size, that could be formed by double coupling between an α-ω-dibromobenzyl polymer chain and a living precursor, have never been detected. The probability of formation of such species is very low.

It should be pointed out that the yields of cyclization determined from the GPC traces are in good agreement with those originating from the fractionatal precipitations.

Characterization of the ring-shaped macromolecules

The molecular weights of the isolated ring-shaped macromolecules agree satisfactorily with the "theoretical" values of M_n, if account is taken of the fact that the weight-to-number average ratio is of the order of 1.1 for the precursor polymer. The fact that

Table 1. Yield and molecular weight of intramolecular coupling

Samples	Solvent	R% GPC	R% Fract	$\bar{M}_n\bar{M}_w$ theo.	$\bar{M}_w$ GPC	LS
HA 40	THF/benzene	10	—	18,000	17,000	—
HA 41	THF/benzene	15	—	20,000	15,000	—
HA 43	THF/benzene	30	36	10,000	7800	9800
HA 44	THF/toluene	35	36	5000	6200	7800
HA 45	THF/benzene	10	—	20,000	17,500	—
HA 46	THF/benzene	40	47	5000	4500	5800
HA 47	THF/cyclohexane	45	—	4500	4000	—

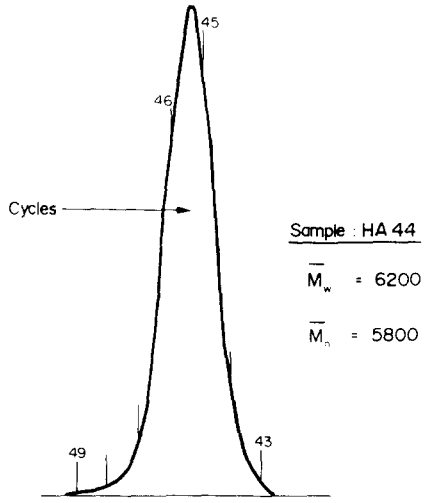

Fig. 2. Gel permeation chromatography of macrocycles (sample HA 44).

the molecular weight distribution of the ring-shaped macromolecules is a little broader is due to the step-by-step procedure, which introduces further fluctuations in molecular weight (Fig. 2).

We have also compared the retention volumes of cyclic and linear polystyrenes. It is well known that the parameter that determines GPC retention is the volume of the macromolecular coil [16]. Cyclization involves a decrease of molecular size, and consequently an increase of the retention volume. This explains why the molecular weights of the cyclic molecules are found to be about 20% lower than those determined by light scattering, the GPC molecular weights being obtained by interpolation on an accurately defined calibration curve established with narrow molecular weight linear polystyrenes.

More details about the synthesis and a precise characterization of the ring-shaped macromolecules will be published in the near future [17].

CONCLUSION

This anionic coupling method, carried out at low concentration, yielded cyclic macromolecules which could be separated quantitatively from the "polycondensate" of much higher molecular weight formed simultaneously. Thus ring-shaped macromolecules of known size, of rather narrow polydispersity, and free from linear homologues have been synthesized. These species can be regarded as model macromolecules and are well fitted for a detailed investigation of their solution properties.

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REFERENCES

1. M. Gordon, *Proc. R. Soc., Lond.* **A-272,** 240 (1962).
2. M. Gordon and G. N. Malcolm, *Proc. R. Soc., Lond.* **A-295,** 29 (1966).
3. E. F. Casassa, *J. Polym. Sci.* **A-3,** 605 (1965).
4. G. C. Berry and E. F. Casassa, *J. polym. Sci., D* **4,** 1 (1970).
5. H. Hocker, Private communication.
6. B. François, Private communication.
7. H. Jacobson and W. H. Stockmayer, *J. chem. Phys.* **18,** 1600 (1950).
8. K. Dodgson and J. A. Semlyen, *Polymer* **18,** 1265 (1977).
9. K. Dodgson, D. Sympson and J. A. Semlyen, *Polymer* **19,** 1285 (1978).
10. J. S. Higgins, K. Dodgson and J. A. Semlyen, *Polymer* **20,** 553 (1979).
11. J. Chojnowski, M. Scibiorek and J. Kowalski, *Makromolek. Chem.* **178,** 1351 (1977).
12. J. A. Semlyen, *Adv. Polym. Sci.* **21,** 41 (1976).
13. F. R. Jones, *Eur. Polym. J.* **10,** 249 (1974).
14. J. C. Saam, D. J. Gordon and S. Lindsey, *Macromolecules* **3,** 1 (1970).
15. F. Candau and E. Franta, *Makromolek. Chem.* **149,** 41 (1970).
16. Z. Gallot-Grubisic, P. Rempp and H. Benoit, *J. Polym. Sci.* **B5,** 753 (1967).
17. G. Hild and P. Rempp, To be published.

Résumé—La synthèse de macromolécules cycliques de dimensions connues a été mise au point par réaction entre un polystyrène "vivant" bifonctionnel et le dibromo-*p*-xylène. La réaction a lieu en solution diluée et s'effectue étape par étape. Des macrocycles ainsi qu'un "polycondensat" sont obtenus. Le produit de la réaction est soumis à un fractionnement ce qui permet d'obtenir des polymères cycliques bien définis.