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Preparation of Macrocyclic Polystyrene

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Prof. Dr. Dr. h. c. mult. Hermann Mark dedicated on the occasion of his 85th birthday

SUMMARY

A method for the preparation of cyclic polystyrene is described. Bifunctionally growing living polystyrene is terminated by addition of equimolar amounts of α,α'-dichloro-p-xylene under conditions of high dilution.

1. INTRODUCTION

A number of natural macromolecules, mostly deoxyribonucleic acids, e.g. from the bacteriophage ΦX 174 (1), from a polyoma virus (2), or viroids (3) themselves are long-chain ring polymers. Examples for synthetic macrocyclic molecules are very rare although they are of high interest as model compounds to compare theoretical calculations of configurational and thermodynamic properties with experimental results.

In 1965 Casassa (4) suggested already the preparation of synthetic long-chain ring polymers by anionic polymerization and termination with a difunctional reagent. In 1969 we (5) started experimental work in this field, which eventually lead to a method for the preparation of macrocyclic polystyrene (6,7). This method is described in the present paper while the properties of the macrocycles in comparison with linear chain

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molecules are discussed elsewhere (8).

2. SYNTHETIC PATHWAY

The basic ideas realized in the present work for the macrocyclization reaction are:

(i) The preparation of a bifunctional living polystyrene using sodium naphthalene as an initiator.

(ii) The reaction of the bifunctional living polystyrene with an equimolar amount of a bifunctional halide, e.g., α,α'-dichloro-p-xylene under dilution conditions (cyclization reaction) providing an excess of dihalide at the end of the reaction.

(iii) Preparation of very high molecular weight living polystyrene and reaction with the noncyclic material present after the cyclization reaction and carrying halogen endgroups (cyclic compounds are "inert" in this step).

(iv) The fractionation of very high molecular weight acyclic material and ring polymers.

Every step is followed and controlled by gpc. After the first step, part of the solution with living polystyrene is protonated and the molecular weight is determined by gpc. To perform the cyclization reaction nearly equimolar amounts of the bifunctional living polystyrene and of the dihalide - both in tetrahydropyran (THP)-solution - are added dropwise over a period of 3 - 4 hrs to a large volume of pure THP. The concentration of functional groups, i.e. chlorine

groups and carbanions during the entire period of reaction is very small - in the ideal case equal to zero - since the volume of the solvent is large and since the reaction between functional groups is fast. Consequently, quantitative conversion to cyclic macromolecules is expected under ideal conditions (equimolar addition of reactants to a large volume of solvent under efficient mixing allowing for long enough time of reaction). Deviations from quantitative ring formation are in the first place due to non-compliance with ideal conditions.

When the cyclization is accomplished the entire polymer is isolated, re-precipated, and freeze-dried. In gpc most of the material (main peak) is eluted at higher elution volume as compared with the starting material, i.e. acyclic polystyrene of approximately the same molecular weight[+)].

Besides the basic cycle, the higher multiples ($n > 1$) are observed in small and decreasing amounts. Moreover it is expected that the material is contaminated with acyclic polymer chains carrying Cl-endgroups.

The acyclic material is removed in the following step by reaction with very high molecular weight living polystyrene being used as a soluble carrier polymer. Subsequently a fractionation is easily accomplished yielding the high molecular weight polystyrene to which the acyclic fraction is attached and the cyclic material, i.e. basic cycle and higher multiples.

+) The molecular weight of the ring polymer is larger than that of the acyclic polymer by the molecular weight of the coupling unit (-CH_2-C$_6$H$_4$-CH_2-, M = 104).

The yield of cyclic polymers observed in different reactions is shown in Tab. 1.

Tab. 1 Relative amount of total cyclic polymers, C_{tot} and of the basic cycle, C_1 as determined from gpc elution curves (in % with respect to the amount of monomer used).

Exp. Nr.	M_1 [a)]	C_{tot} %	C_1 %
1	3150	58	21
2	11000	96	63
3	12000	93	62
4	13200	84	65
5	14600	79	55
6	17500	59	46
7	19700	74	58
8	24300	78	55

a) determined from gpc using a calibration curve for linear polystyrene

It is clearly seen that no dependency on molecular weight is found. Differences in yield are - as mentioned above - in the first place due to deviations from ideal conditions during the cyclization reaction; conditions in all reactions were slightly different.

3. GEL PERMEATION CHROMATOGRAPHY

The most evident property of cyclic macromolecules is their larger elution volume (due to smaller molecular dimensions) as compared with linear macromolecules with identical molecular weight (Fig. 1).

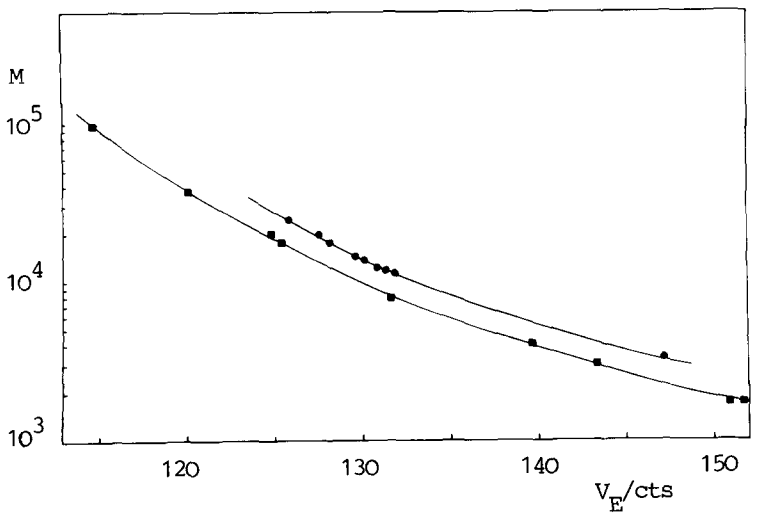

Fig. 1 Log M - V_E - relationships for linear ■ and cyclic • polystyrene

The elution volumes of a series of polystyrene samples are shown in Tab. 2 in conjunction with their real and apparent molecular weights. The apparent values were taken from the calibration curve for linear polystyrene, shown in Fig. 1. The ratio between real and apparant molecular weights is remarkably constant at 1.43 $\pm$ 0.05 indicating a relation between the hydrodynamic dimensions of cyclic and linear polymers which to a first approximation is independent of molecular weight. A more detailed discussion is presented elsewhere (8).

Tab. 2 Elution volume $V_{E,r}$, molecular weight M_r and apparent molecular weight M_r^* of cyclic polystyrene

Eluent: THF, Temp. 25°C

Exp.Nr.	$V_{E,r}$	M_r a)	M_r^* b)	M_r/M_r^*
1	147.2	3250	2200	1.48
2	131.8	11100	7900	1.41
3	130.8	12100	8800	1.38
4	130.1	13300	9600	1.39
5	129.6	14700	10300	1.43
6	128.1	17600	12300	1.43
7	127.5	19800	13500	1.47
8	125.8	24400	16600	1.47

a) determined from the molecular weight of the linear polystyrene sample (before cyclization) by adding the molecular weight of the coupling group (-CH_2-C$_6$H$_4$-CH_2-).

b) apparent molecular weight as determined from the calibration curve for linear polystyrene.

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