Macromolecular Cavities of Controlled Size. 1. Synthesis of Macrotricyclic Poly(chloroethyl vinyl ether)s by Living Cationic Polymerization

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ABSTRACT: The preparation of macrotricyclic poly(vinyl ether)s of controlled molar masses and MWD is described. The procedure consists of the synthesis in a first step of a three-arm star-shaped poly(vinyl ether) from a diheterohexafunctional precursor by living cationic polymerization. The cyclization of each star arm is then achieved under highly diluted conditions by the promoted intramolecular addition of the active end groups onto the three remaining head functions. High cyclization yields are obtained without the detectable formation of polycondensates resulting from intermolecular reaction. A series of head functional star-shaped and macrotricyclic poly(chloroethyl vinyl ether)s of various molecular weights was prepared and characterized. The effect of the cyclization on the apparent molar mass and on the glass transition temperature of the macromolecules has been examined by GPC and DSC, respectively. These derivatives can be considered as the first elements of a new family of macromolecules with potential host–guest properties.

Introduction

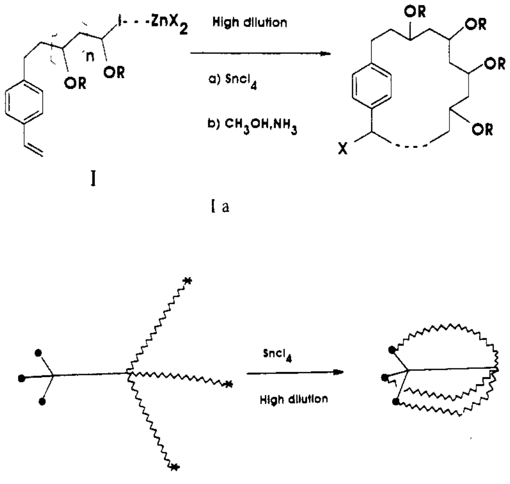
The preparation of polymers with special and well-defined architecture is an extremely active research area in macromolecular synthesis. Besides fundamental aspects, one main reason is that some physicochemical properties of macromolecules can be strongly influenced, or even directly determined, by their chain architecture. Among these tailor-made materials, macrocyclic polymers, with controlled size, are of great interest both for academic and finalized research.

Two main approaches have been developed to obtain well-defined macrocycles.[1]

(a) The first is use of fractionation procedures allowing the separation of cyclics and linears from polymerization systems exhibiting ring–chain equilibrium. This mainly concerns polycondensates or polymeric chains containing in their backbone reactive links subject to either intra- or intermolecular attacks.[2]

(b) The second is end-to-end cyclization of monodisperse α–ω difunctional polymeric precursors. The latter are obtained by a living polymerization technique. The coupling process must be carried out at high dilution, to favor intramolecular cyclization over intermolecular chain reaction which yields polycondensates.[3] Though this last approach has been restricted for a long time to a few anionic polymerization systems, recent progress in cationic polymerization of vinyl monomers has opened new opportunities in the preparation of α–ω difunctional linear precursors. This is the case, in particular, for vinyl ethers whose living cationic polymerization has been extensively studied.[4,5] The synthesis of macrocyclic poly(vinyl ether)s of controlled size, involving a different end-to-end closure procedure, has recently been described.[6]

Scheme I



I b

The principle of this new method is shown in Scheme Ia. It involves, in a first step, the synthesis of an α,ω-heterofunctional linear polymer of general formula I. The cyclization is then achieved, under high dilution conditions, by activation of the α-iodo ether end group by a strong Lewis acid, in order to allow its addition onto the styrenyl head group; high cyclization yields (>90%) are obtained with this technique. The reasons for such high cyclization efficiency, compared to the previously used end-to-end coupling procedure, will be discussed in detail in a forthcoming paper: the basic reason is that our cyclization procedure is a one-step process which involves a monomolecular reaction.

The selectivity of this intramolecular coupling process, encouraged us to investigate the possibility of preparing pluricyclic macromolecules, with controlled molecular weight.

We report in this paper the synthesis and the characterization of macrotricyclic poly(chloroethyl vinyl ether)s of controlled size; they are obtained from plurifunctional three-arm star polymer precursors, upon using a cyclization procedure derived from the previous one and presented in Scheme Ib.

Results and Discussion

The general strategy followed for the synthesis of poly(chloroethyl vinyl ether)s macrotricycles involves the following steps: (a) preparation of a diheterotrifunctional polymerization initiator; (b) initiation and living cationic polymerization of chloroethyl vinyl ether by this initiator, in order to form a living star polymer bearing functional head groups in the α position; (c) intramolecular coupling, under high dilution, of the active ends carried by each arm with a functional head group of the same precursor macromolecule.

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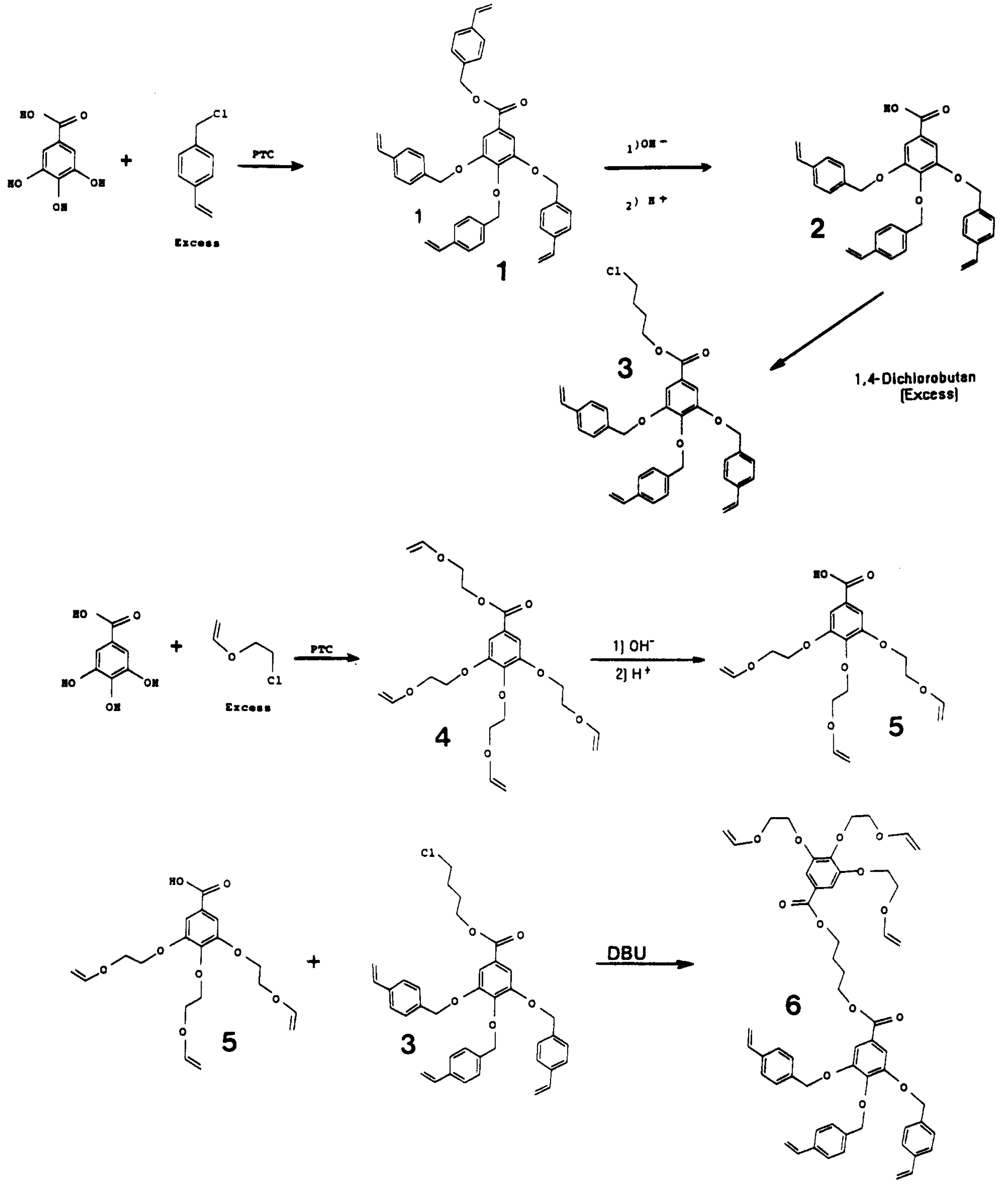
Scheme II



The different steps of the synthesis and the structure and the characteristics of the chain precursor as well as those of the star and the multicyclic polymers will be successively examined.

(1) Synthesis of the Functional Polymerization Initiator. 1-[[[3,4,5-Tris[((vinyloxy)ethyl)oxy]phenyl]carbonyl]oxy]but-4-yl 3,4,5-tris[((*o*,*m*,*p*-vinylphenyl)methyl)oxy]benzoate, noted **6**, which was used as functional chain initiator, was obtained according to the reaction pathway presented in Scheme II. There are two main steps of synthesis.

(a) Preparation of the Tristyrenyl Functional Fragment. (*o*,*m*,*p*-Vinylphenyl)methyl-3,4,5-tris[((*o*,*m*,*p*-vinylphenyl)methyl)oxy]benzoate, compound **1**, was synthesized upon reacting 3,4,5-trihydroxybenzoic acid with (chloromethyl)styrene (mixture of ortho, meta, and para isomers). The ester bond of **1** was then hydrolyzed in basic medium, yielding 3,4,5-tris[((*o*,*m*,*p*-vinylphenyl)methyl)oxy]benzoic acid (**2**). The ^{1}H NMR spectrum of **2** is shown in Figure 1.

The latter compound was then reacted with a large excess of 1,4-dichlorobutane, in order to form the ester derivative, 1-chlorobut-4-yl 3,4,5-tris[((*o*,*m*,*p*-vinylphenyl)methyl)oxy]benzoate (**3**).

(b) Preparation of the Trivinyl Ether Functional Fragment. 3,4,5-Tris[(oxyethyl vinyl ether)ethyl vinyl ether]benzoate (**4**) was prepared in a similar way to compound **1**, by reaction of 3,4,5-trihydroxybenzoic acid

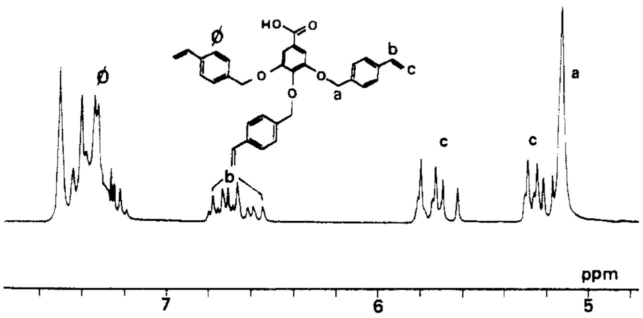


Figure 1. 250-MHz ^{1}H NMR spectrum in $CDCl_3$ and peak assignment of 2.

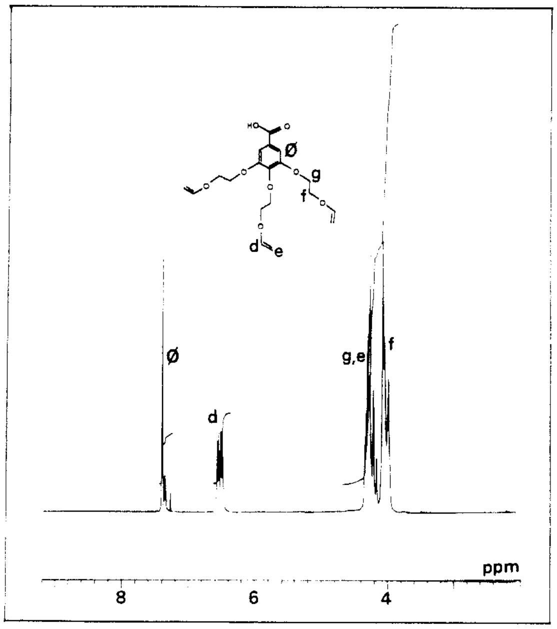


Figure 2. 250-MHz ^{1}H NMR spectrum in $CDCl_3$ and peak assignment of 5.

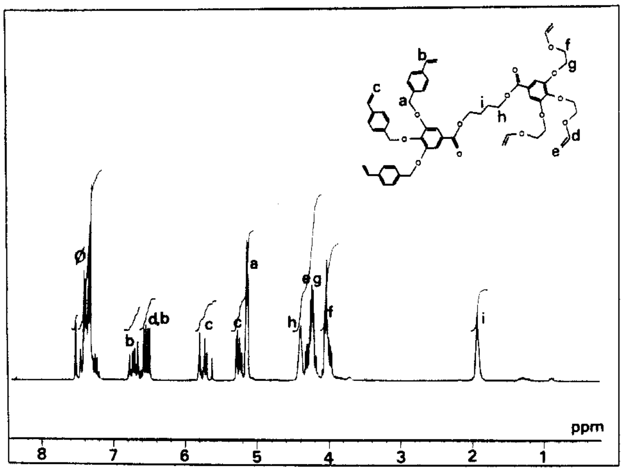


Figure 3. 250-MHz NMR spectrum in $CDCl_3$ and peak assignment of the functional polymerization precursor 6.

with an excess of chloroethyl vinyl ether. The ester bond of 4 was then hydrolyzed, to yield 3,4,5-tris[((vinyloxy)ethyl)oxy]benzoic acid (5). The ^{1}H NMR spectrum of 5 is given in Figure 2.

Finally, the polymerization initiator 6 was obtained by ester-type condensation between 3 and 5. The ^{1}H NMR spectrum of 6, bearing both three styrenyl and three vinyl ether functional groups, is given in Figure 3.

(2) Preparation of Three Styrenyl Head Functional, Three-Arm Poly(chloroethyl vinyl ether)s. The approach developed for the synthesis of functional star poly(CEVE)s from 6 is based on the selective use of vinyl ether groups, as the chain initiator of CEVE polymerization. To that purpose, vinyl ether functions were first derivatized, as illustrated in Scheme III, into α-iodo ethers, from which a clean and complete polymerization of CEVE can be initiated. The selective addition of HI onto the vinyl ether double bonds of a precursor, bearing a styrenyl function, has been already described in a previous publication.[6]

Polymerization experiments were carried out under dry nitrogen, under pressure in toluene, at −60 °C, according to the following procedure.

(a) Formation of a Tri-α-iodo Ether Derivative (6-I). To allow the selective addition of HI on the vinyl ether unsaturations, compound 6 and the protonic acid (~3.1 equiv with respect to 6) were reacted, at low temperature, −60 °C, yielding the tri-α-iodo ether polymerization initiator, 6-I (Scheme III). To avoid the presence of any unreacted vinyl ether groups on 6-I, which might lead to chain branching or cross-linking during propagation of CEVE polymerization, HI was introduced in slight excess with respect to the required stoichiometry.

(b) Polymerization of CEVE. After the monomer was introduced into the initiator solution, the polymerization was triggered by adding a small amount of $ZnCl_2$, dissolved in diethyl ether (mole ratio $ZnCl_2/HI = 0.05$). The polymer solution remained colorless during the whole polymerization, and then it slowly turned yellow as soon as the monomer had been totally consumed; this color change was taken as an indicator of the completeness of the polymerization. Then, the polymer mixture was split into two fractions: (a) the first one, about two-thirds of the total volume of the solution, was used as starting material for the synthesis of cyclic polymers (vide infra); (b) characterization of the three-arm star poly(CEVE) was performed on the second one, after deactivation of the iodo ether polymer end groups by mixture of methanol and ammonia.

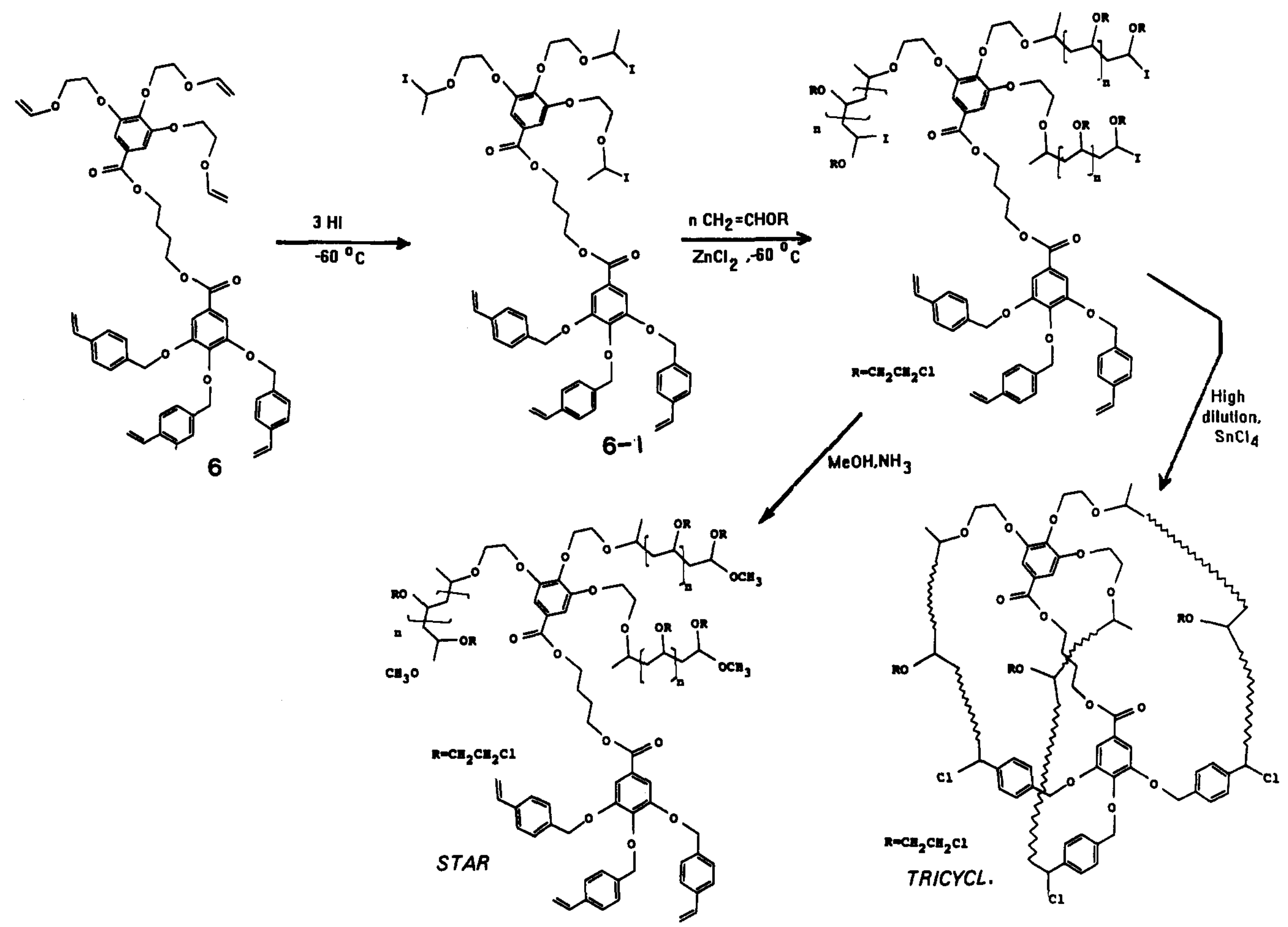
The ^{1}H NMR spectrum of a three-arm head functional poly(CEVE) is presented in Figure 4. Signals 1 and 2 can be attributed respectively to the resonances of the main-chain methylene and to those arising from both the methine and the two pendant methylenes of the CEVE units. In addition to these main peaks, resonances of the functional head group (signals ϕ, a–c and g and h) and of the terminal acetal units (signals j and k) are also seen in the spectrum. Peak attribution, as well as relative proton signal integrations, are indicated in Figure 4.

The resonance of the vinyl protons of the styrenyl groups, multiplets b and c, can be clearly identified in the spectrum of poly(CEVE), whereas those corresponding to the vinyl ether unsaturation, denoted d and e in preceding Figures 2 and 3, are not observed. Because of partial overlapping of d and e with other polymer proton signals, the complete disappearance of the methylene ($\delta = 86.9$ ppm) and methine carbons ($\delta = 151$ ppm) of vinyl ether unsaturations was checked and confirmed by ^{13}C NMR analysis.

The relative proton intensities of aromatic (ϕ), methine (b) and methylene (c) groups arising from the styrene unsaturations and of the terminal methine acetal (g) are collected in Table I in the case of two samples. Relatives intensities of proton signals are in good agreement with the polymer architecture drawn in Scheme III.

Typical GPC chromatograms are presented in Figure 5. In addition to the main polymer population, the presence of a small peak or shoulder in the low molar mass domain corresponding to monofunctional chain growth, $M_n = [M]_0$ $106/[HI]_0$, is observed. Formation of this fraction can be

Scheme III



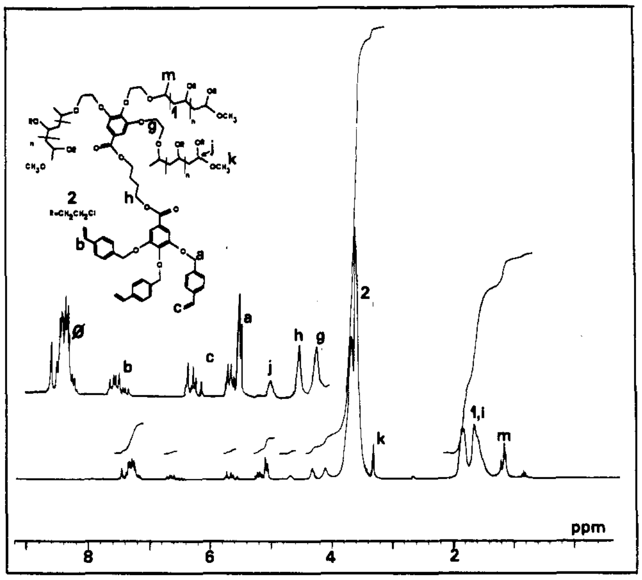


Figure 4. 250-MHz ^{1}H NMR spectrum in $CDCl_3$ and peak assignment of a head functional star poly(CEVE) ($\overline{\mathrm{DP}}_{n\,\mathrm{th}} = 14.9$).

attributed to a direct initiation by HI, introduced in slight excess with respect to the stoichiometry required by 6. This hypothesis is further supported by the absence of any UV absorbance arising from these polymer chains, contrary to the main fraction which exhibits an UV signal due to the head aromatic group (see Figure 6). If we neglect this side contribution, the MMD's of the polymers can be considered as monomodal and narrow (<1.25), as in the case of monofunctional "living" polymerization.

Experimental molar masses of the star polymers, i.e., the main poly(CEVE)s population, were tentatively determined by GPC on the basis of a polystyrene calibration which has been proved to be well suited for linear poly(CEVE).[7] It is much more uncertain that such calibration will be relevant to the characterization of star-shaped poly(CEVE). However, in recent studies on linear and three-arm star polymers, namely poly(isobutyl vinyl ether)[8] and poly(2-vinylpyridine),[9] it has been observed that GPC elution volumes are not very significantly affected by the chain architecture ($V_{el}/V_{es} \sim 0.97$), suggesting a close hydrodynamic volume for the two types of polymer. Other authors[10] have on the contrary noticed a strong effect of the chain structure.

The results that we have obtained for poly(CEVE) star-shaped molecules (Table II) are quite similar to those reported by Higashimura.[8] Indeed, the experimental $\bar{M}_n$ values—determined on one hand by NMR and on the other hand by GPC with a linear sample based calibration—and the theoretical M_n's calculated, upon assuming a trifunctional initiation, by the expression (1), fall within the same range. C% is the conversion and E is the total molar mass of the incorporated precursor fragment and of the terminal methoxy end groups.

$$\bar{M}_n = C\%\,[M]_0 106.3/[\mathrm{HI}]_0 + E \qquad (1)$$

In addition, the absence of any detectable cross-linked materials or of macromolecules with molar masses higher than those theoretically calculated by eq 1 indicates that the styrenyl functions of the precursor do not participate, in the present conditions, in the initiation and propagation

Table I
^{1}H Relative Intensities of Head and Terminal Groups of Star Poly(CEVE)[a]

	nature of ^{1}H	aromatics	=CH (b + c/2)	=CH + CH$_2$ (c/2) (a)	CH$_2$ (h)	CH$_2$ (g)	CH (j)
	theor no. of ^{1}H nH[b]	16	3	9	4	6	3
sample 1	integration value I	41.5	7.5	23	10	15	5
	ratio I/nH	2.6	2.5	2.55	2.5	2.5	1.7
sample 2	integration value I	55	8.5	26.5	9.9	12.4	7.6
	ratio I/nH	3.4	2.8	2.9	2.5	2.1	2.5

[a] See Scheme III and Figure 4 for attributions. [b] Assuming a three-arm chain architecture.

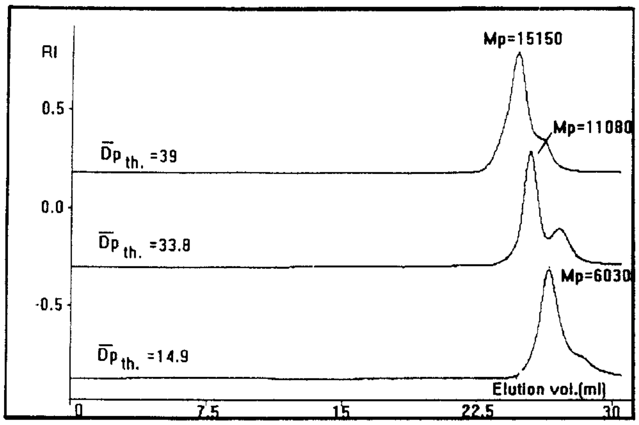


Figure 5. GPC chromatograms of head functional star poly(CEVE)s in THF by refractive index detection. M_p: peak molecular weight determined on the basis of linear polystyrene standards.

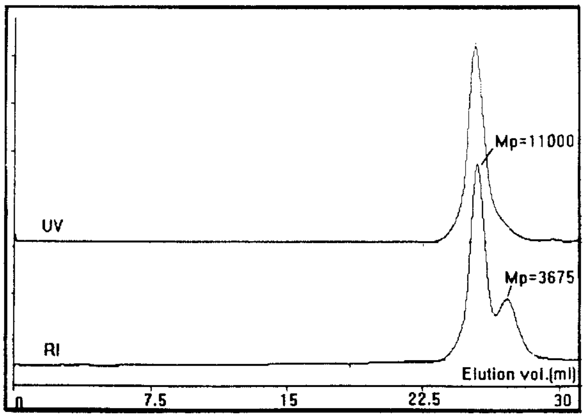


Figure 6. GPC chromatograms of head functional star poly(CEVE)s in THF. ($\overline{DP}_{n\,th}$ = 33.8) comparing the refractive index and UV detections.

reactions and are not incorporated into the growing poly(vinyl ether) chains.

On the basis of both these NMR and GPC observations, it can be reasonably concluded that the synthetized poly(vinyl ether)s exhibit a three-arm chain architecture, as represented in Scheme III.

(3) Cyclization Reaction: Preparation of Tricyclic Poly(chloroethyl vinyl ether). As it was already discussed for monocyclic poly(CEVE)[6] and as it may also be inferred from the above results, the terminal iodo ether groups of poly(CEVE) do not significantly react with the styrene double bonds, in the CEVE polymerization conditions when ZnCl$_2$ is used as polymerization activator. However, it has been previously shown, that the introduction of a stronger Lewis acid, such as SnCl$_4$, into the living polymer solution allows their quantitative addition onto the vinyl aromatic double bonds.

A similar activation procedure was applied in the present case. The reaction was performed in high dilution conditions so as to favor the intramolecular cyclization process; the latter would involve the preferential addition of an α-iodo ether function onto a styrenyl unsaturation located at the head of its own chain. Intermolecular reaction, on the contrary, would lead to polycondensation and, due to high functionality of the star polymer, very likely, to cross-linked materials.

High dilution reaction conditions were obtained by the slow addition of the living polymerization solution, typically 8–12 h, into a large volume of dried toluene containing a small amount of SnCl$_4$ ([SnCl$_4$]/[α-iodo ether] = 10). Under the assumption of a fast reaction with respect to the addition rate, the instantaneous concentration of iodo ether ends in the toluene is in the range of 10^{-7} mol/L. In order to preserve the livingness of the polymer ends during the whole addition step, the star polymer containing solution was maintained at −60 °C. After it had been completely introduced and allowed to react for an additional ca. 15 min, a solution of methanol and ammonia was added to deactivate the system. After concentration of the polymer solution, the polymer was precipitated into methanol. Its structural and physicochemical characteristics were then investigated.

^{1}H NMR spectra of cyclized samples exhibit a poor resolution compared to the corresponding star ones: the low resolution may be attributed to important restrictions in the chain segments mobility particularly in the vicinity of the polyaromatic linking unit. A typical spectrum of a cyclized poly(CEVE) of low $\overline{DP}_n$, sample 1, is presented in Figure 7. Interesting information can however be gathered from the presence or the disappearance of characteristic resonances of the star poly(CEVE) (see Figure 4). The proton resonances which are common to both star and cyclized samples are identified by the same letters.

The main differences observed in the spectra of cyclics are (1) the absence of vinyl protons due to styrene groups (b, c), indicating the complete consumption—within the accuracy of the measurement—of the vinyl aromatic unsaturations during the reaction with SnCl$_4$, and (2) the absence of methoxy (k) and α-hydrogen (j) resonances of the acetal termini, therefore suggesting that noncyclized poly(CEVE) segments (dangling end-free arms) are in low proportion compared to those linked to styrenyl groups.

These observations are therefore consistent with an almost quantitative addition reaction of the α-iodo ether end groups onto the styrenyl functions.

Moreover, the presence of two broad signals of low intensity (x, y), centered at 6.1 and 5.7 ppm, which are not observed on the star polymer, can be attributed to the side formation of ethylene unsaturations along the poly(CEVE) backbone, due to acid-catalyzed elimination of chloroethanol, as proposed by Higashimura.[11]

The nature of the linking bond formed by addition of the iodo ether onto the styrenyl double bond cannot be identified in the spectra. This may be due to overlapping with other signals of the polymer. On the basis of a study

Table II
Synthesis and Characterization of Head Functional Star Poly(CEVE)s[a]

exp no.	10^3[6], M	10^3[HI], M	10^3[CEVE], M	DP_{theor}[b]	DP_{exp} NMR[b]	DP_{exp} GPC[c]	$M_{n\ theor}$[d]	$M_{n\ exp}$[e]	M_w/M_n[e]
1	2.3	7.1	106	14.9	14.5	15.7	5 805	6 080	1.25
2	2.1	7.5	253	33.8	33	30.4	11 820	10 760	1.07
3	1.1	3.6	113	31.4		34	11 070	11 950	1.12
4	1.1	3.6	141	39		45.4	13 540	15 550	1.16

[a] All polymerizations were performed up to complete monomer conversion. Solvent, toluene; $ZnCl_2$/HI ~0.05; $T = -60$ °C. [b] DP_n corresponding to one star arm. [c] $DP_{n\ GPC} = {}^1/_3(M_{n\ exp} - E)$, where E is the sum of the precursor and methoxy end groups ($E = 1045$). [d] Calculated using equation I, at complete conversion. [e] Based on GPC, calibrated with linear polystyrene standards.

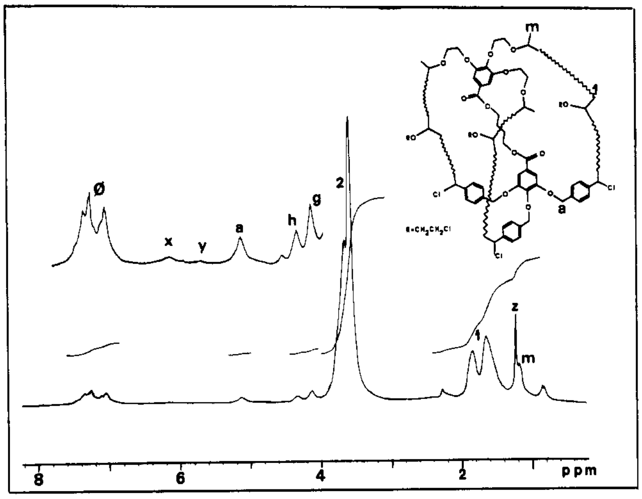


Figure 7. 250-MHz ^1H NMR spectrum in $CDCl_3$ of a cyclized star poly(CEVE) recovered by precitation into methanol ($\overline{DP}_{n\ th} = 14.9$). See Fig 4 for peak assignment. Peak z might correspond to residual organic solvent.

on models, a $-CH_2-CHX-Ph-$linkage might be formed in the majority.[12]

The apparent predominance of the intramolecular cyclization process versus the intermolecular condensation was further confirmed by analysis of the polymer dimensions.

The GPC curves of the poly(CEVE) samples, collected before (stars) and after introduction into the $SnCl_4$ solution (cyclics) and obtained from the same polymerization experiment, are shown in Figure 8. As it can be seen, the cyclization process leads to an important shift of the GPC traces to higher elution volumes, corresponding to apparent lower molar masses. This is in agreement with what is generally observed after cyclization of linear polymers,[1-3,13] as a result of a decrease of the hydrodynamic volume of the macromolecule. This is also what could be expected between opened and cyclized arms of star polymers.

The ratio between the elution time of cyclized and star polymers $M_{p\ cycl}/M_{p\ star}$ (see Table III) ranges from 0.75 to about 0.8. Note that the ratio observed between linear and monocyclic poly(CEVE) $M_{p\ cycl}/M_{p\ lin}$ varied from 0.85 to 0.88.[6]

Interestingly, it was observed that the small peak located in the low molar mass domain (see Figures 5 and 6) and attributed to side initiation by HI in excess remained at the same elution volume, after the treatment with $SnCl_4$. This indicates that the chain dimensions and architecture of this linear polymer fraction which is not end-fitted with styrene moieties are unchanged during the cyclization procedure, despite the presence of active chain termini; the livingness of this polymer population was confirmed by molar mass increase, upon adding a new monomer feed to the polymer solution (see Figure 9). Since monofunctional α-iodo ether polymer chains can only react with styrene entities by bimolecular addition, their apparently low reactivity observed in the highly diluted conditions of cyclization can be interpreted as resulting from the predominance of unimolecular processes corresponding to intramolecular reactions over the bimolecular ones.

The effect of polymer architecture on some other physicochemical characteristics of poly(CEVE)s has also

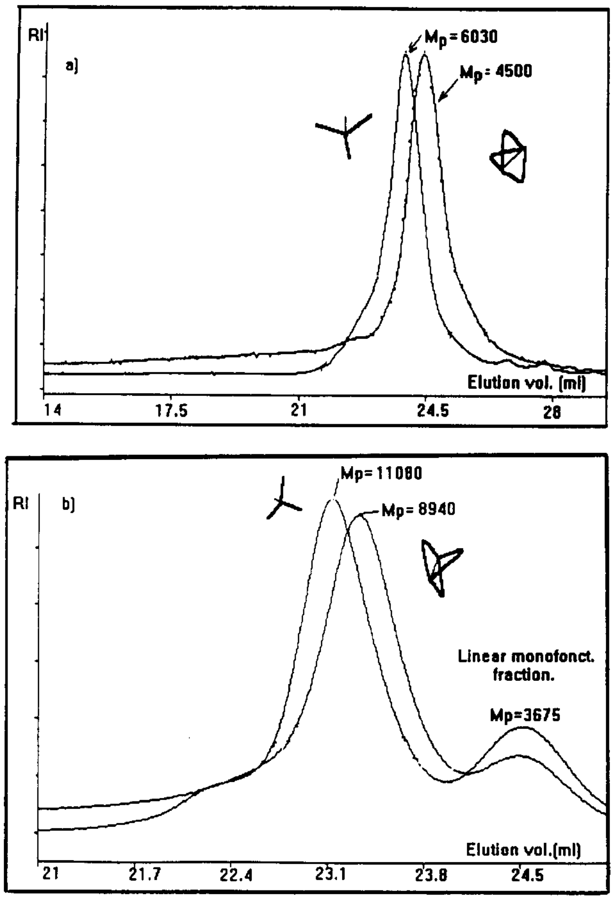


Figure 8. GPC chromatograms of star and cyclized star poly(CEVE): (a) $\overline{DP}_{n\ th} = 14.9$; (b) $\overline{DP}_{n\ th} = 33.8$. Toluene was used as the internal reference for volume elution calibration.

Table III
Characteristics of Star and Macrotricyclic Poly(CEVE)s[a]

exp no.	chain arch.	DP_{exp}[b]	M_p[c]	M_n[c]	M_w/M_n	$M_{p\ cycl}/M_{p\ lin}$	T_g, °C[e]
1	star[d]	15.7	6 030	6 080	1.25		−19.8
	tricycl		4 500	3 490	1.25	0.75	−10
2	star[d]	30.4	11 080	10 760	1.07		−16.2
	tricycl		8 940	9 330	1.18	0.8	−2.4
3	star[d]	45.4	15 150	15 550	1.16		−15.1
	tricycl		11 350	14 000	1.3	0.75	−5.5

[a] Cyclization conditions: living star polymer solution added whitin 7–8 h into 1 L of a $SnCl_4$ solution at −10 °C. [b] See Table II. [c] Apparent peak molecular weight determined by GPC using linear polystyrene standard. [d] Isolated before cyclization with $SnCl_4$. [e] Determined on fractionated samples (elimination of the linear monofunctional fraction if any).

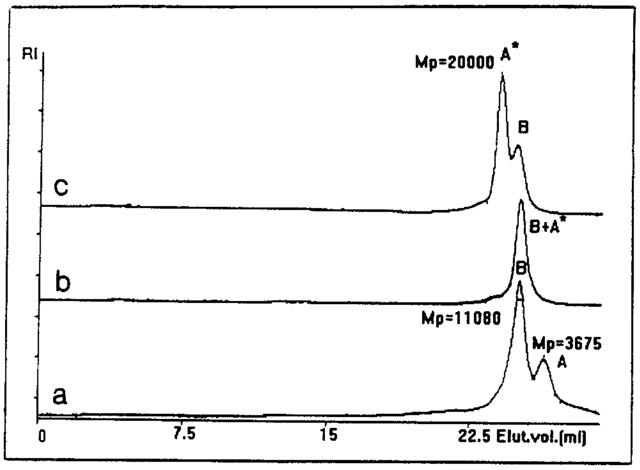


Figure 9. Effect of the addition of a new monomer feed on a cyclized star poly(CEVE) containing a linear monofunctional fraction (sample 2): peak B, cyclic; peak A, linear; (a) before addition; (b) after monomer addition, 60-min reaction; (c) after monomer addition, 180-min reaction.

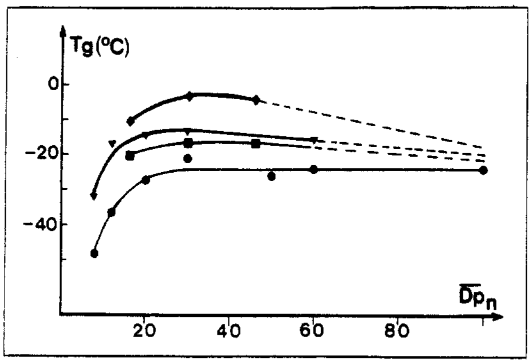


Figure 10. Dependence of glass transition temperatures of poly(CEVE) of various architecture with the $\overline{DP}_n$: linears (●); monocyclics (▼); stars (■); tricyclics (◆). The $\overline{DP}_n$ values refer to one arm for stars and one cycle for tricyclics.

been examined. The glass transition temperatures of star and macrotricyclic poly(CEVE) of different molar masses are compared in Table III. Higher T_g's are observed for tricyclics in agreement with the lower flexibility of their main chain. These T_g values can also be compared (Figure 10) with those determined for the corresponding linear and monocyclic poly(CEVE):[6] For a given $\overline{DP}_n$, corresponding to one arm for the stars and to one cycle for the tricyclic derivatives, the T_g's increase in the following order:

$$\text{linear} < \text{star} < \text{monocyclic} < \text{tricyclic}$$

The relative contribution of the incorporated aromatic structure in the determined T_g values is however difficult to evaluate.

For each polymer series, T_g increases from low oligomers, up to a given DP_n, in the 20–30 range. There is then the plateau value for linear poly(CEVE). In the case of mono- and tricyclics, and likely for star polymers, which all exhibit higher glass transition temperatures than the corresponding linear ones, T_g's reach a maximum and then tend to decrease, presumably to reach the plateau value observed for very high molar mass linear molecules.

Though it was first generally assumed[14] that the T_g of the cyclic polymers would increase for decreasing $\overline{DP}_n$, recent publications[15-17] have shown that this tendency cannot be generalized to all polymers. Several cyclic polymer series exhibiting almost a plateau or even a decrease of T_g for polymers of low $\overline{DP}_n$, as observed for vinyl ethers, have been recently reported.

Finally, we have presented in this first report, a series of structural and physicochemical data which support the synthesis of macromulticyclic poly(chloroethyl vinyl ether)s of controlled dimensions. It is believed, on the basis of structural analysis, that the tricyclic macromolecular derivatives are formed in the majority during the synthesis. It is however difficult to know at this stage the exact yield in tricyclic poly(CEVE); indeed it remains questionable whether monocyclic and bicyclic polymers with dangling arms can be accurately distinguished from the tricyclic one, particularly when they are in low proportion. Further studies focused both on the physicochemical characterization and on the properties of this new macromolecular structure need to be done and are in progress.

Among the different potential properties and applications of these macromolecules, we will investigate them as prototypes of new macromolecular cavities possessing (a) a controlled size (this may be determined by the polymerization degree and therefore may cover a relatively broad range of molecular dimensions) and (b) a surface, mainly constituted of the polymerized monomer units, whose nature may be varied at will, depending upon the vinyl ether chosen.

Therefore, it will become theoretically possible to adjust both the size and the nature of the surface of the cavity for a given solvent/substrate couple in order to develop interactions leading to the preferential binding of the substrate inside the cavity.

On the basis of solubility criteria and spectrospic analysis, preliminary experiments performed with various large organic molecules such as dyes and porphyrins tend to show that some of these compounds form stable complexes with these polymacrocycles. These results will be reported in a following paper.

Experimental Section

Procedures. (1) Preparation of 1-[[[3,4,5-Tris[((vinyloxy)ethyl)oxy]phenyl]carbonyl]oxy]but-4-yl 3,4,-Tris[((*o,m,p*-vinylphenyl)methyl)oxy]benzoate (6). (a) Synthesis of (*o,m,p*-Vinylphenyl)methyl 3,4,5-Tris[((*o,m,p*-vinylphenyl)methyl)oxy]benzoate (1). Into a 300-mL round-bottom flask fitted with a mechanical stirrer and a reflux condenser were successively introduced 3,4,5-trihydroxybenzoic acid (2 g, 0.0117 mol), *o,m,p*-(chloromethyl)styrene (8 g, 52.46 mmol), potassium carbonate (8 g), tetrabutylammonium bromide (5.3 g), and dimethylformamide (150 mL) and the mixture was heated at 85–90 °C for 48 h. After cooling, 300 mL of CH_2Cl_2 was added and the organic phase was washed with water (4 × 500 mL) and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure led to a yellowish oil which was recrystallized from a CH_2Cl_2/*n*-hexane mixture, yielding 1 as a white powder. Yield: 6.3 g, 84.4%. ^{1}H NMR ($CDCl_3$), δ: 7.5–7.6 (arom protons), 6.8–6.5 ($=CH$), 5.8–5.63 ($=CH_2$), 5.35–5.15 ($=CH_2$), 5.1 ($O-CH_2-Ph$).

(b) Preparation of 3,4,5-Tris[((*o,m,p*-vinylphenyl)methyl)oxy]benzoic acid (2). A 4-g sample of 1 (6.3 mmol) was dissolved in 20 mL of DMF in a 100-mL round-bottom flask, and a solution of KOH (1 g in 3 mL of water) was added. The mixture was then heated at 80 °C for 18 h. After cooling, it was then poored into 300 mL of a water–ice mixture from which the benzoic acid derivative was precipited by the slow addition, up to pH 7, of a 0.1 N CH_3COOH solution. The obtained white powder was washed with NaCl-saturated water (100 mL) and the product finally purified by chromatography (silica gel, $CHCl_3$/EtOH (3/1). Yield: 2.45 g, 75%. ^{1}H NMR ($CDCl_3$), δ: 7.5 5–7.2 (arom), 6.8–6.53 ($=CH$), 5.85–5.6 ($=CH_2$), 5.34–5.18 ($=CH_2$), 5.14 ($O-CH_2-Ph$).

(c) Preparation of 1-Chlorobut-4-yl 3,4,5-Tris[((*o,m,p*-vinylphenyl)methyl)oxy]benzoate. Into a 250-mL round-bottom flask were charged successively acid 2 (4 g, 7.7 mmol), freshly distilled 1,4-dichlorobutane (80 g, 0.63 mol), cesium carbonate (3.2 g, 10 mmol), and 80 mL of distilled DMF. The reaction mixture was kept at 85–90 °C for 18 h under argon. After cooling, 150 mL of CH_2Cl_2 was added and the organic phase was washed with water (4 × 300 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, toluene). Yield: 3.60 g, 77%. ^{1}H NMR ($CDCl_3$), δ: 5.7–7 (arom), 7.7–7.45 ($=\mathrm{C}H$), 5.75–5.5 ($=\mathrm{C}H_2$), 5.25–5.1 ($=\mathrm{C}H_2$), 5.05 ($\mathrm{O{-}C}H_2\mathrm{{-}Ph}$), 4.25 ($\mathrm{O{-}C}H_2\mathrm{{-}CH_2}$), 3.5 ($\mathrm{C}H_2\mathrm{{-}Cl}$), 1.8 ($\mathrm{C}H_2\mathrm{{-}C}H_2$).

(d) Preparation of 3,4,5-Tris[((vinyloxy)ethyl)oxy]benzoic Acid (5). The tetravinyl ether **4** was prepared from 3,4,5-trihydroxybenzoic acid (2 g, 11.7 mmol) and chloroethyl vinyl ether (8 g, 75 mmol) in a manner similar to **1**. It was then recrystallized from A CH_2Cl_2/ether mixture. Yield: 4.7 g, 90%. ^{1}H NMR ($CDCl_3$), δ: 7.2 (aromatic), 6.46–6.3 ($=\mathrm{C}H$), 4.4 ($\mathrm{C}H_2\mathrm{{-}O{-}C{=}O}$), 4.2–4.09 ($\mathrm{C}H_2\mathrm{{=}CH_2{-}O{-}Ph}$), 4–3.8 ($\mathrm{C}H_2\mathrm{{-}O{-}C{=}C}$).

(e) Preparation of 3,4,5-Tris[((vinyloxy)ethyl)oxy]benzoic Acid (5). The trivinyl ether benzoic acid **5** was prepared from **4** (4 g, 8.88 mmol) by a similar procedure as **2**. The product was recrystallized from an ether pentane mixture (1/2 v/v): Yield: 3 g, 90%. ^{1}H NMR ($CDCl_3$), δ: 7.4 (aromatic), 6.6–6.45 ($=\mathrm{C}H$), 4.4–4.15 ($=\mathrm{C}H_2$, $\mathrm{C}H_2\mathrm{{-}O{-}Ph}$), 4.15–3.9 ($\mathrm{C}H\mathrm{{-}O{-}}$).

(f) Preparation of 1-[[[3,4,5-Tris[((vinyloxy)ethyl)oxy]phenyl]carbonyl]oxy]but-4-yl 3,4,5-Tris[((*o*,*m*,*p*-vinylphenyl)methyl)oxy]benzoate. Into a 250-mL round-bottom flask were charged 100 mL of freshly distilled DMF, **3** (2.5 g, 4.1 mol), **5** (1.72 g, 4.5 mmol), and 1.8-diazabicyclo[5.4.0]undec-7-ene [DBU] (0.8 g, 5.25 mmol). The reaction mixture was maintained at 90 °C for 18 h. After cooling, 150 mL of CH_2Cl_2 was added. The organic phase was washed with water (4 × 30 mL), dried over Mg SO_4, and evaporated. **6** was finally purified by chromatography (basic alumina, CH_2Cl_2/tol (3/1, v/v). Yield: 2.5 g (64%). **6** is a solid melting at −4 °C, purity >98% determined by TLC and ^{1}H NMR (see Figure 3).

(2) Polymerizations. (a) Synthesis of Three-Arm Star Poly(CEVE): Typical Conditions. The living cationic polymerization of chloroethyl vinyl ether initiated by the HI adduct of vinyl ethers in the presence of zinc salts has already been described.[18] In the present case, the solvent (toluene, 100 mL), **6** (0.236 mmol), and HI (0.73 mmol) were introduced under nitrogen in the polymerization reactor and cooled down to −60 °C. After 30 min of reaction the monomer (10 mmol) and the zinc salt (0.03 mmol) were successively introduced. The polymerizing solution remained colorless for about 5 h and finally slowly turned yellow. A fraction of the polymer solution was then collected and immediately deactivated at low temperature by adding a solution of methanol and ammonia.

(b) Cyclization. The remaining living star poly(CEVE) solution was maintained at −60 °C and added drop by drop, under nitrogen, within about 8–12 h into a 2-L solution of toluene containing 7 mmol of $SnCl_4$ thermostated at 0 °C. After the mixture was allowed to stand an additional 30 min, a solution of ammonia and methanol was introduced to neutralize the system. The polymer solution was finally washed and filtered, and the cyclized star polymer was recovered by solvent evaporation under vaccuum.

(3) Polymer Characterization. Proton and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brüker AC 250 FT apparatus. GPC measurements were performed in THF on a Varian apparatus equipped with refractive index/UV dual detection and fitted with five TSK columns calibrated with polystyrene standards. A trace of toluene, added to the sample, was used as internal reference. Glass transition temperatures of polymers were measured on a DSC Mettler apparatus at the second heating cycle and at a heating rate of 10 C/min.

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