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Efficient Free-Radical Cyclopolymerization of Oriented Styrenic Difunctional Monomers

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ABSTRACT: The synthesis of several difunctional monomers, derived from the introduction of two 4-styrene-substituted moieties into a covalent skeleton, is described. The more rigid ones, built around malonate moieties and more preorganized to give 3,3′-cyclophane repeating units, failed completely to give soluble, ordered cyclopolymers. The introduction of a certain degree of flexibility in the tethering moiety afforded, by using free-radical initiation, structurally stable cyclopolymers with a high degree of cyclization and good degrees of polymerization. Theoretical calculations detail and strongly support the experimental results. Further chemical elaboration of the obtained cyclopolymeric backbones, by means of the removal of a ketal group, is possible in mild conditions to give systems which can be easily cross-linked thermally, with the loss of H_2O, at temperatures higher than 100 °C.

Introduction

The design of new polymeric materials requires to gain information on their structure and dynamics and therefore to control with precision the connections among their units.[1] The most profound recent developments in polymer chemistry are based on a growing synergy between advanced organic chemistry and polymer synthesis.[2] A driving force is the realization that many of the promising applications of nanoscience rely on extending synthetic organic chemistry into the nanometer length scale, where polymer chains naturally belong, especially as nanodevices are designed with increasing sophistication. The level of control in polymer synthesis has been exploited in recent years in various directions.[3] Several intriguing investigations reporting novel approaches to the well-defined synthesis of cyclic polymers have recently emerged.[4]

Cyclopolymerization processes provide the unique ability to perform two things in the same polymerization process: make polymers efficiently and generate cyclic structures in the polymer backbone. As such, they offer the control of polymer rigidity, packing and solubility, and a certain spatial control of substituents one can insert onto the polymer backbone in order to modulate/improve/tailor the macromolecular properties. Seminal contributions by Mathias and co-workers demonstrated that difunctional diacrylates, derived for example by double alkylation of malonate esters, easily undergo cyclopolymerization, even in bulk conditions, to generate six-membered ring structures with a very high degree of regioregularity.[5] The efficient incorporation of styrene-like difunctional monomers into polymeric backbones by means of free-radical polymerization have been the subject of several reports in recent years. The main issue at stake is to properly design a covalent bond network joining the two polymerizable aromatic moieties, in such a way that the formation of large ring repeating units is somewhat allowed and possible. Wulff and co-workers have designed difunctional monomers obtained as styrene boronate esters of optically active diols. These monomers could be copolymerized, when used in a relatively low feed ratio, with a variety of other monomers (styrene, acrylates, etc.), and some chiral induction in the macromolecular backbone, after removal of the optically active diol template, has been reported.[6] Kakuchi and co-workers[7] have developed the synthesis of difunctional monomers derived from a large series of optically active diol tethers elaborated as 4-vinyl benzoate esters. Also in this case, chiral induction in the main chain after tether removal has been studied. Both in the former and latter case, however, no direct cyclopolymerization has been reported, but rather a copolymerization of these difunctional monomers with other monomers. The possibility of introducing large ring structures in the macromolecular chains was nevertheless demonstrated.[8] More recently, both the groups of Holmes, in two back-to-back communications,[9] and that of Prata[10] demonstrated how, in diluted conditions, difunctional styrenic-like monomers (A and B in Figure 1) can efficiently generate repeating large ring-containing *homopolymers*.

In both systems A and B, the two styrene moieties are covalently linked to functional "tethers" possessing a high degree of steric hindrance, which clearly helps keeping the two polymerizable moieties in close proximity,[11] thus orienting them, during propagation. However, some structural features are remarkably different: the two monomers are obtained by alkylation of either alkoxy (A) or phenoxy (B) functionalitites,

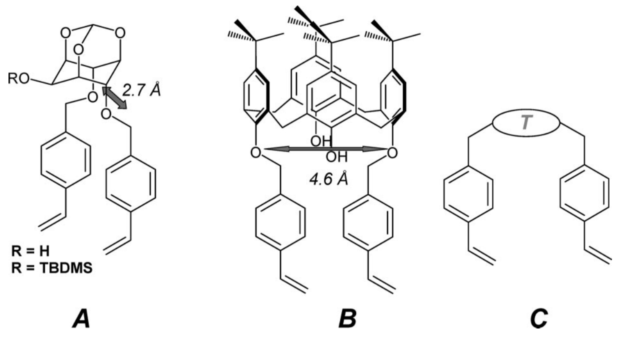

Figure 1. Difunctional monomers undergoing efficient cyclopolymerization as reported by Holmes (A) and Prata (B) and a general cartoon representation for the systems studied in this paper (C).

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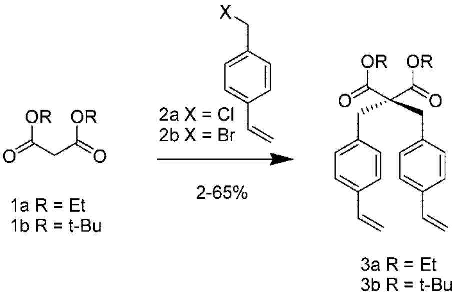
Scheme 1. Synthesis of Difunctional Monomers 3 Derived from Malonates



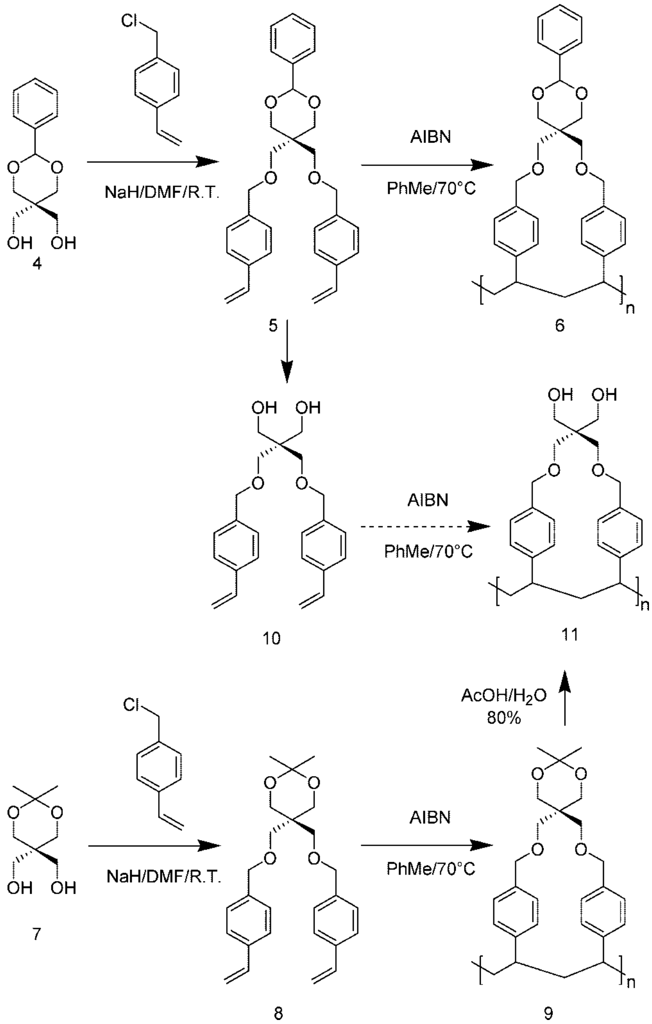
and the average distance between the oxygens of the two styrene derivatives goes from 2.7 Å (A) to 4.6 Å (B). This observation prompted us into an investigation on the flexibility and the structure of chemically more straightforward scaffolds (or "tethers", T in Figure 1C) one might introduce within the two polymerizable sytrenic moieties in order to achieve efficient cyclopolymerization. A reliable, efficient architecture would be the basis for the design of advanced ones in which different functionalities and/or chemically removable tethers could be introduced. In this paper, we report on the synthesis and cyclopolymerization of difunctional 4-vinylbenzyl systems built around two different tethering moieties (approach C in Figure 1); we also report on the further chemical elaboration of the resulting cyclopolymers, on their thermal characterization, and on a rationalization of the results obtained by using computational modeling techniques.

Results and Discussion

Monomer and Polymer Synthesis. The design of the first family of monomers relies on the use of a malonate moiety, which can be alkylated to afford difunctional compounds. We were encouraged to adopt such tethering moiety by the very limited degree of conformational freedom associated with the rigidly fixed and oriented CH_2 benzylic methylene groups. Although the resulting 14-membered macrocycles (3,3′-cyclophanes), as the repeating units, have been reported to possess a certain degree of strain,[12] a large family of compounds bearing this common skeleton have been previously synthesized, characterized, and reported to be stable at room temperature.[13] We chose to test two malonate esters **1a** and **1b**, possessing different degrees of steric hindrance (ethyl vs *tert*-butyl), in order to verify any possible assistance of bulky groups to the cyclopolymerization process. The double alkylation under basic conditions of both esters using the commercially available 4-vinylbenzyl chloride proved to be quite disappointing in terms of isolated yields (see Supporting Information); switching to the corresponding benzylic bromide **2b**, with the bromide being a better leaving group in nucleophylic substitutions, gave much better yields with reproducible results on both substrates.

The cyclopolymerization of both substrates **3a** and **3b** was attempted under free-radical conditions (with AIBN as the initiator) in deoxygenated toluene or THF under a variety of monomer concentrations (down to 0.005 M), giving invariably insoluble, cross-linked residues as the largely predominant product. In an attempt to redesign the tether moiety, a more flexible ether bridge was introduced between the polymerizable moieties. The synthesis was performed starting from deprotected pentaerythritols **4** or **7**, and the two polymerizable styrenic groups were appended by alkylation to the 1,3-alcoholic functionalities using classical conditions (NaH or NaO*t*Bu, dry THF or toluene, Scheme 2). The monomers were obtained after purification by column chromatography: by using the commercially available benzylic chloride **2b**, satisfactory yields were obtained in this case. The ^1H NMR spectra of the purified monomers are reported in Figure 2 (a and c, 300 MHz in $CDCl_3$). For monomer **5**, the resonances associated with the benzylic protons, and those belonging to the pentaerythritol moiety (protons H_a, H_b, and H_c) appear as split set of signals, probably as a consequence of conformational equilibria related to the six-membered ring 1,3-dioxane skeleton, which are slow on the NMR time scale. The same did not apply in the case of monomer **8**: it is likely that the less bulkier methyl substituents in **8** (when compared to the phenyl in **5**) attached to the six-membered ring are less effective in slowing down the above-mentioned conformational flipping of the dioxane ring on the NMR time scale. The free-radical cyclopolymerizations of both monomers were carried out at different monomer concentrations. As shown in Table 1, the optimal reaction conditions for both monomers were found to be at a concentration around 0.05 M; in these cases, both the yields of purified polymers and the degree of polymerizations were substantially higher than in the other cases.[14] In both cases, furthermore, the polydispersity index increased gradually with the increasing of the concentration of the monomer solution used for the polymerization, and in parallel, the yield, obtained after precipitation of the reaction mixture in the nonsolvent after filtration and removal of any cross-linked, insoluble material, decreased. These considerations demonstrate that efficient cyclization is induced by low monomer concentration, able to greatly suppress the tendency to cross-linking during propagation. Lower concentrations (entries 1 and 6 in Table 1) tended to yield lower yields and oligomeric

Scheme 2. Synthesis of Difunctional Monomers 5, 8, and 10 and of Cyclopolymers 6, 9, and 11



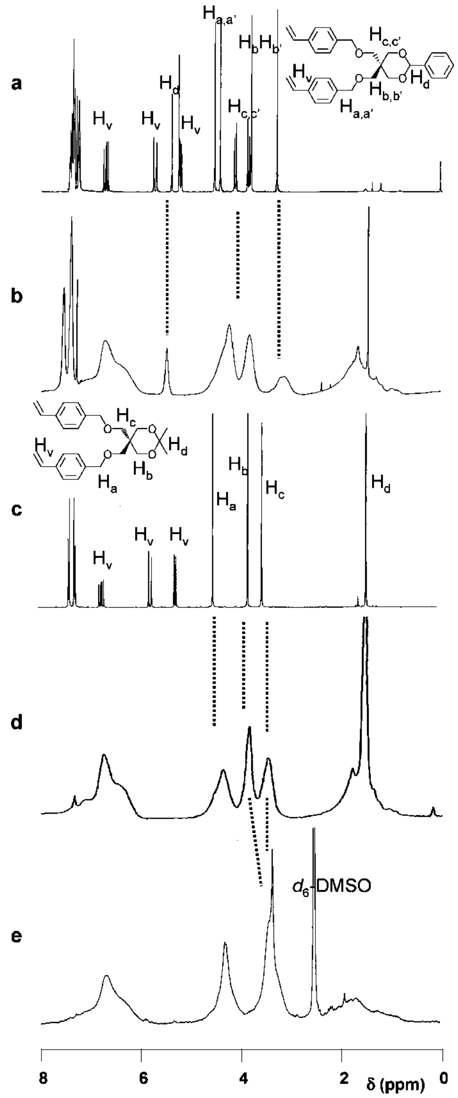


Figure 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of (a) monomer **7**, (b) monomer **6**, (c) polymer **9**, (d) polymer **10**, and (e) copolymer **11**.

Table 1. Cyclopolymerization of Monomers 5 and 8 under Free-Radical Conditions[a]

entry	monomer	[M]/ [%AIBN][b]	M_n[c]	PDI[c]	DP[d]	yield, % (nonsolvent)[e]	polymer
1	**5**	0.01/3	9200	2.0	20	12 (hexane)	**6**
2	**5**	0.05/3	14000	1.8	31	70 (hexane)	**6**
3	**5**	0.1/3	7300	3.0	16	49 (hexane)	**6**
4	**5**	0.5/3				cross-linked	
5	**8**	0.01/4				no polymer	
6	**8**	0.02/4	6400	1.3	16	2 (MeOH)	**9**
7	**8**	0.04/4	9640	1.6	24	79 (MeOH)	**9**
8	**8**	0.04/4	9750	1.9	24	72 (MeOH)	**9**
9	**8**	0.08/4	6990	1.7	17	49 (MeOH)	**9**
10	**8**	0.13/4	13130	1.9	32	30 (MeOH)	**9**
11	entry 8		6850	1.4			**11**

[a] Polymerizations were run at 70 °C in toluene for 48 h. [b] [M] refers to the monomer **5** or **8** concentration. [c] As determined by GPC relative to polystyrene standards. PDI = polydispersity. [d] Degree of polymerization; calculated on the basis of the average number molecular weight. [e] Yield determined on the basis of the molecular weight of monomer. The solvent used for polymer purification (nonsolvent) is indicated in parentheses.

products, as propagation becomes problematic. Results could be reproduced with a high degree of fidelity (entries 7 and 8). The purified cyclopolymers **6** and **9** obtained in these cases were fully soluble in a variety of organic solvents.

Characterization by ^{1}H NMR spectroscopy of cyclopolymers **6** and **9** (see Figure 2b,d) showed the complete disappearance of the vinyl proton resonances, testifying for an efficient cyclization during propagation and ruling out the presence of detectable vinyl pendant groups within the polymer backbone. ^{13}C NMR spectroscopies also confirmed the disappearances of resonances attributable to residual vinyl functional groups. The other significant proton resonances were, as expected, broadened and showed virtually no shift when compared to the corresponding proton resonances in monomers **5** and **8**. The relative integration of the proton resonances in the spectra gave a close correspondence to the calculated ones, indicating a nice match between the observed and the proposed structure.

As one of our aims was to verify the possibility of introducing an "oriented" 1,3-diol skeleton within the cyclopolymeric backbone, we also synthesized monomer **10** by deprotection in acidic conditions of the benzaldehyde acetal functionality present in the protected monomer **5**. By running polymerizations in both toluene, or THF (also a good solvent in the case of compound **10**), no linear soluble polymeric products could be obtained by the polymerization of **10** in any of the concentration conditions reported in Table 2. There are two possible explanations for that (a) the reduction of the steric hindrance on the other side with respect to the reactive functionalities (e.g., the removal of the bulky acetal in **10** vs **5** or **8**) plays an important role in controlling the cyclization step; (b) prolongued heating (usually 48 h at 60 or 70 °C, as reported in Table 1) might cause intermolecular etherification and cross-linking (vide infra and Figure 4). Direct deprotection of the acetal functionalities in polymer **6** under the conditions used for monomer **5** (HCl in a dioxane/H_2O mixture, reflux) resulted in intractable solid residues (Scheme 2). The deprotection was therefore attempted on cyclopolymer **8**, where the acetone ketal functionalities are present; even though several conditions were tested,[15] the successful ones were to dissolve cyclopolymer **8** in the minimum amount of glacial AcOH (and of a small percentage of H_2O, as stoichiometric reagent in the cleavage of ketals), stirring at room temperature for a few hours. The reaction did not work without the addition of H_2O directly in the reaction mixture. The complete disappearance of the signals associated with the ketal protecting groups was evident in both ^{1}H NMR (Figure 2e) and ^{13}C NMR spectra (Supporting Information). Furthermore, the resonances associated with protons H_b in the polymeric structures are clearly shifted downfield (being close to an OH and not to a cyclic ether group anymore), similarly to what is observed in the comparison between monomers **8** and **10** (see Experimental Section).

Modeling Experiments. In this study, the intramolecular cyclization of monomers **3** and **8** has been modeled by using DFT with Becke's three-parameter hybrid exchange functional and the Lee−Yang−Parr correlation functional (B3LYP)[16] with the 6-31G(d) basis set using the Gaussian 03 program.[17] Single point energies were calculated by using the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) methodology. The stationary points along the potential energy minima have been characterized by positive vibrational frequencies. Single point free energy calculations were also performed in toluene ($\varepsilon = 2.4$) with the IEF-PCM methodology at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory.[18]

The strategy followed in modeling the intramolecular cyclization of monomers **3** and **8** is described in what follows. A methyl radical ($CH_3^\bullet$) has been added to **3** and **8** in order to mimic the radicalic nature of the monomers during propagation. These species (**Rad-3**, **Rad-8**) have been subjected to conformational search around every single bond with the semiempirical AM1 method. The most stable conformers in each case (within range of 3 kcal/mol) have been further optimized with B3LYP3/6-31G(d). The cyclization of **Rad-3** and **Rad-8** has been accomplished by locating a cyclic transition structure (**TS-3** and

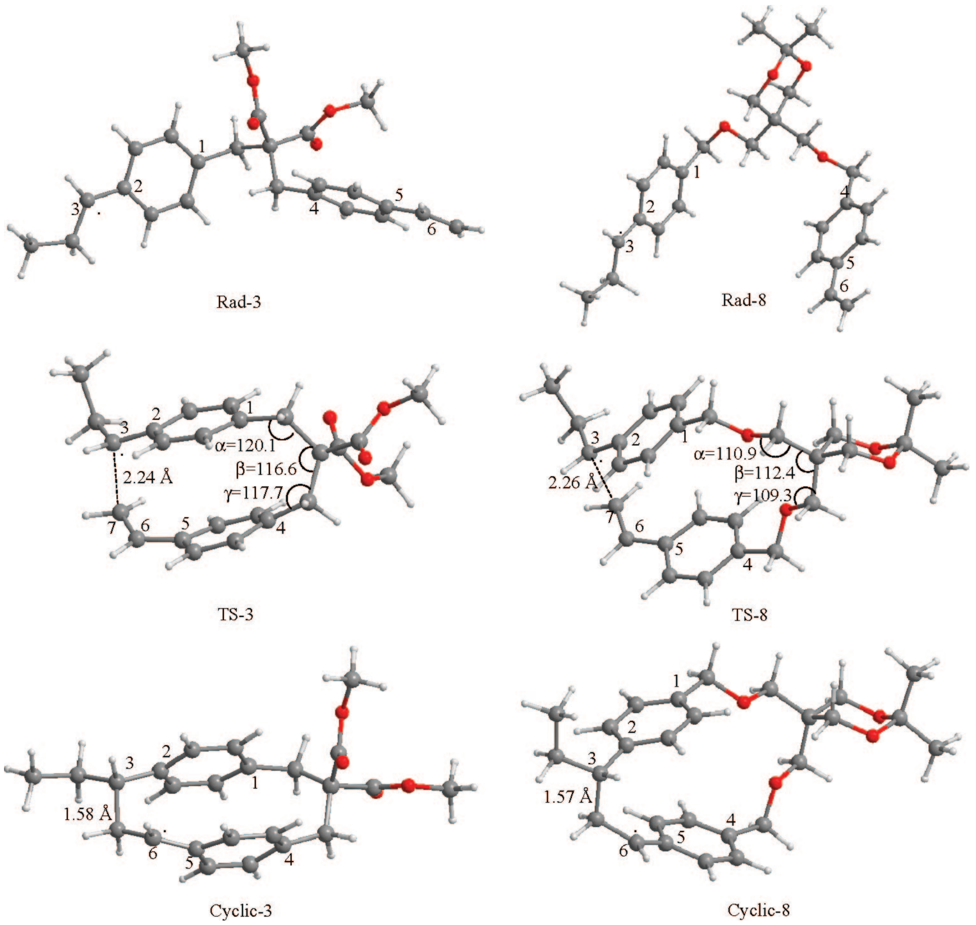


Figure 3. Most stable 3D structures for the derivatives of **3** and **8**.

Table 2. Calculated Activation Energies (E_a) Including Zero Point Vibrational Energy (ZPE) Corrections and Reaction Free Energies (ΔG_{rxn}) at the B3LYP/6-31G(d) Level (kcal mol^{-1})

	B3LYP/6-31G(d)//B3LYP/6-31G(d)		B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)	
	E_a	ΔG_{rxn}	E_a	ΔG_{rxn}
Rad-3	21.9	7.3	23.7 (20.5)[a]	11.0
Rad-8	16.3	0.8	16.7 (15.5)[a]	3.6

[a] Values in parentheses are free energies in solution.

TS-8) in each case. The transition structures have one imaginary frequency along the forming C3−C7 bond. This bond is 2.24 Å in **TS-3** and 2.26 Å in **TS-8**. Finally, the cyclized product in each case (**Cyclic-3**, **Cyclic-8**) have been located, and the lowest energy conformers have been chosen for further analysis.

In each case activation barriers and reaction energies have been evaluated. The energetics displayed in Table 2 show that **Rad-8** cyclizes easier than **Rad-3**. The energy difference between the activation energies and activation free energies for these two species is ~5 kcal/mol, suggesting that **Rad-8** cyclizes easier than **Rad-3**. The geometric parameters displayed in Table 3 show that the planarity of the phenyl rings is distorted in **TS-3** (C4−C5−C6 ~ 165.13°); furthermore, the α, β, and γ angles in **TS-3** are 120.1°, 116.6°, and 117.7°, showing quasi-sp^2 hybridization with a strained character. Notice also that the cyclization of **Rad-3** is highly endothermic. These findings corroborate the experimental results where **Rad-8** polymerizes via cyclopolymerization.

In summary, modeling the cyclization pathway of **Rad-3** and **Rad-8** shows that the latter cyclizes easier than the former, yielding a cyclic structure where sp^3 carbon atoms keep their identity (α = 110.9°, β = 112.4°, γ = 109.3°). On the other

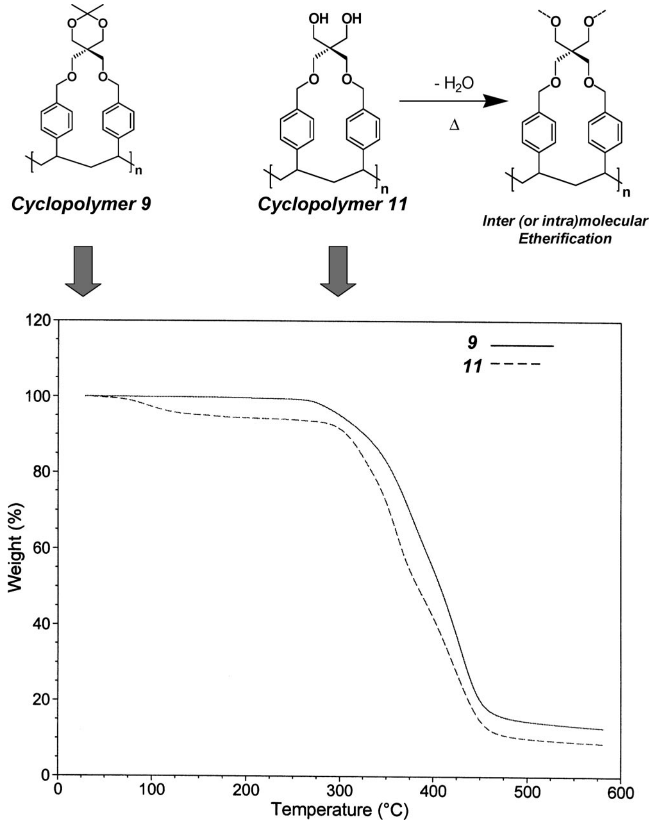


Figure 4. TGA profiles for polymers **9** and **11**.

Table 3. Geometrical Parameters for the Derivatives of 3 and 8 (B3LYP/6-31G(d))

compounds	C1−C2−C3 (deg)	C4−C5−C6 (deg)
Rad-3	178.75	177.62
Rad-8	178.68	177.69
TS-3	172.30	165.13
TS-8	177.96	174.95
Cyclic-3	167.63	162.64
Cyclic-8	174.10	173.30

hand, the cyclization of **Rad-3** would yield an unfavorable, highly strained cyclic structure.

Thermal Properties. The thermal properties of cyclopolymers **9** and **11** were examined both by DSC and by TGA, in order to characterize the interplay between their structure and their thermal characteristics. TGA analysis was very informative: a sample of cyclopolymer **9** did not show any weight loss until well above 250 °C, demonstrating that the ketal protecting groups on the polymer backbone is thermally stable in neutral conditions, as expected (Figure 4, left). The TGA scan on a sample of cyclic polymer **11** revealed mass loss corresponding to exactly 1 mol of H_2O (calculated 4.9% weight loss, observed 5.6% weight loss average), thus strongly suggesting the formation of ether units originating by intramolecular or intermolecular etherification of the 1,3 diols repeating units (Figure 4). By running a sample of polymer **9** in the presence of catalytic amounts of *p*-toluenesulfonic acid, a significantly more pronounced and continued loss was observed, with a weight loss average (up to 100 °C) of 13%, corresponding to both the acid-catalyzed cleavage of the ketal and the ether formation process (calculated 14.2% weight loss),[19] thus strongly reaffirming the mechanism postulated in Figure 4.

Samples of cylopolymers **9** and **11** were also analyzed by DSC: runs for polymer **9** showed no trace of thermal events, including glass transitions, for temperatures up to 150 °C, indicating the stiff, rigid structure of these styrenic cyclopolymers. In samples of cyclopolymer **11** the concurrent thermal reactivity (highlighted by the TGA runs) taking place around 100 °C, evidenced by a broad, nonreversible exothermic transition (see Figure S5) made the interpretation of any further event occurring above 100 °C very difficult to be properly discerned.

Conclusions

We have synthesized and characterized novel cyclopolymers derived from simple styrenic difunctional monomers. We have shown, both experimentally and computationally, that, whereas the use of malonate-derived covalent tether moieties brings about systems unable to cyclize efficiently in free-radical-initiated polymerizations, the use of a more flexible, and more versatile, tether allows the synthesis of cyclopolymers with good degrees of cyclopolymerization and structural fidelity. The C_2 symmetry of the chemical architecture might open intriguing possibilities for the main-chain stereochemical control, via the use of suitable stereodirecting, identical chiral auxiliaries deriving from the quaternary center. The possibility of postmodification of the cyclopolymers via deprotection of ketal functionalities, their thermal robustness when in their ketal protected version, and the unusual thermal reactivity warranted by the 1,3-diol moiety periodically disposed within the polymer backbone undoubtedly make these intriguing novel structures of interest for functional applications in complex, nanostructured materials.

Experimental Section

All commercially available compounds were purchased from Aldrich and used as received. THF (CaH_2) and CH_2Cl_2 (CaH_2) were dried and distilled before use. Compounds **2b**,[20] **4**,[21] and **7**[22] were prepared according to literature procedures. Flash chromatography was carried out using silica gel (Merck 60, 0.040−0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded from solutions in the appropriate deuterated solvent on Bruker 200 or AMX300 instruments with the solvent residual proton signal or tetramethylsilane (TMS) as a standard. Infrared spectra were recorded on a FT-IR PE Paragon 1000 spectrophotometer equipped with a diffuse reflectance accessory using KBr as the matrix. Size-exclusion chromatography was carried out on a Waters system equipped with a DRI detector. The UV/vis spectroscopic studies were recorded using a Hewlett-Packard 452A or a Perkin-Elmer LS50B spectrophotometer. Low polydispersity polystyrene standards (Fluka) were used for the calibration curve, and the mobile phase was tetrahydrofuran (1 mL/min, 40 °C). A bank of two columns (Styragel 4E and 5E) in series was used. Elemental analyses were done on a Carlo Erba 1106 elemental analyzer. TGA and DSC analyses were run on a Universal TA Instruments.

Monomer 3a. A suspension of diethyl malonate (380 mg, 2.37 mmol) and potassium *tert*-butoxide (532 mg, 4.75 mmol) in dry THF (40 mL) was stirred at room temperature for 1 h. 4-Vinylbenzyl bromide, **2b** (870 mg, 4.75 mmol), was added, stirring at room temperature was continued for 1 h, and the temperature then raised to 65 °C for an additional 4.5 h. The reaction was quenched with H_2O, the organic layer separated, and the aqueous layer washed with CH_2Cl_2. The combined organic layers were dried, and the product was purified by column chromatography (SiO_2; AcOEt/hexanes 0/10 to 1/9) to afford **3a** as colorless oil (492 mg, 53%). IR (cm^{-1}) = 2980, 1727, 1629, 1248, 1194. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (m, 8H; Ar*H*), 6.72 (2H, dd; ArC*H*=CH$_2$), 5.75 (2H, d; ArCH=C*H$_2$*), 5.27 (2H, d; ArCH=C*H$_2$*), 4.15 (4H, q; −C*H$_2$*CH$_3$), 3.25 (4H, s; ArC*H$_2$*), 1.20 (6H, t; −CH$_2$C*H$_3$*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (C=O), 136.1 (Ar), 135.7 (vin), 130.1 (Ar), 127.2 (Ar), 125.4 (Ar), 113.1 (vin), 60.2 (*C*quat), 58.0 (COO*C*H$_2$CH$_3$), 38.0 (Ar*C*H$_2$−), 13.4 (COOCH$_2$*C*H$_3$).

Monomer 3b. A suspension of di-*tert*-butyl malonate (562 mg, 2.6 mmol) and potassium *tert*-butoxide (611 mg, 5.46 mmol) in dry THF (60 mL) was stirred at room temperature for 1 h. 4-Vinylbenzyl bromide, **2b** (1 g, 5.4 mmol), was added, stirring at room temperature was continued for 1 h, and the temperature was then raised to 65 °C for an additional 4.5 h. The reaction was quenched with H_2O, the organic layer separated, and the aqueous layer washed with CH_2Cl_2. The combined organic layers were dried, and the product was purified by column chromatography (SiO_2; AcOEt/hexanes 0/10 to 1/20) to afford **3b** as colorless oil (743 mg, 65%). IR (cm^{-1}) = 2978, 1722, 1629, 1255, 1163, 847. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (m, 8H; Ar*H*), 6.76 (2H, dd; ArC*H*=CH$_2$), 5.78 (2H, d; ArCH=C*H$_2$*), 5.28 (2H, d; ArCH=C*H$_2$*), 3.25 (4H, s; ArC*H$_2$*−), 1.48 (18H, s; −C(C*H$_3$*)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ =170.0 (C=O), 136.4 (Ar), 135.9 (vin), 130.4 (Ar), 127.6 (Ar), 125.8 (Ar), 113.2 (vin), 81.7 (*C*CH$_3$)$_3$, 60.0 (Cquat), 38.3 (Ar*C*H$_2$), 27.7 (C*C*H$_3$)$_3$.

Monomer 5. A solution of compound **4** (3.01 g, 14.2 mmol) in dry THF (100 mL) was added to a suspension of NaH (60% in mineral oil, 1.25 g, 31 mmol) in dry THF (100 mL) cooled to 0 °C with an ice bath. The suspension was left stirring for 1 h. 4-Vinylbenzyl chloride (5.4 g, 35.5 mmol) was added at once to the mixture at 0 °C, and the reaction mixture was stirred for an additional 12 h at reflux. The reaction was quenched by addition of H_2O, acidified until neutral with 1 N HCl, extracted with CH_2Cl_2, and the organic phase dried ($MgSO_4$). Purification by column chromatography (SiO_2; AcOEt/hexanes 3/7) afforded **5** as a yellow solid (2.72 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4−7.1 (9H, m; Ar*H*), 6.75 (2H, dd; ArC*H*=CH$_2$), 5.78 (2H, d; ArCH=C*H$_2$*), 5.41 (1H, s; C$_6$H$_5$C*H*−), 5.31 (2H, d; ArCH=C*H$_2$*), 4.51 (2H, s; ArC*H$_2$*O−), 4.42 (2H, s; ArC*H$_2$*O−), 4.21 (2H, d; −OCH*H$_2$*CCH$_2$O−), 3.93 (2H, d; −OCH*H$_2$*CCH$_2$O−), 3.88 (2H, s; −OCHH$_2$CC*H$_2$*O−), 3.38 (2H, s; −OCHH$_2$CC*H$_2$*O−). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2 (Ar), 137.8 (Ar), 136.6 (Ar), 136.4 (vin), 128.9 (Ar), 128.2 (Ar), 127.7 (Ar), 126.2 (Ar), 113.8 (Ar), 113.6 (vin), 101.7 (*C*acetal), 73.1 (CH$_2$O), 70.1 (CH$_2$O), 68.6 (CH$_2$O), 38.9 (*C*quat). UV/vis (MeCN): λ_{max} (ε) = 255 (120.000).

Monomer 8.[23] A solution of compound **7** (650 mg, 3.7 mmol) in dry DMF (2 mL) was added to a suspension of NaH (0.53 g, 22.15 mmol) in DMF (8 mL) cooled to 0 °C with an ice bath. The suspension was left stirring for 2 h. A solution of 4-vinylbenzyl chloride (1.3 g, 8.8 mmol) in DMF (3 mL) was added dropwise to the mixture at 0 °C, and the reaction mixture was stirred for an additional 24 h at room temperature. The reaction was quenched by addition of H_2O, extracted with CH_2Cl_2, and the organic phase dried ($MgSO_4$). Purification by column chromatography (SiO_2; AcOEt/hexanes 1/9) afforded **8** as a yellow solid (0.74 g, 50%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.38$ (4H, d; Ar*H*), 7.26 (4H, d; Ar*H*), 6.73 (2H, dd; ArC*H*=CH_2), 5.75 (2H, d; ArCH=CH_2), 5.25 (2H, d; ArCH=CH_2), 4.50 (4H, s; ArCH_2O−), 3.89 (4H, s; −OCHH_2CCH$_2$O−), 3.52 (4H, s; −OCHH$_2$CCH_2O−), 1.43 (6H, s; (CH_3)$_2$C−). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): $\delta = 138.0$ (Ar Cquat), 136.7 (Ar Cquat), 136.5 (vin), 127.5 (Ar), 126.1 (Ar CH), 113.6 (vin), 98.1 (*C*quat ketal), 73.0 (CH_2O), 70.0 (CH_2O), 62.8 (CH_{2O}), 39.0 (Cquat), 23.7 (CH_3).

Monomer 10.[24] Concentrated HCl (1 mL) was added to a solution of monomer **5** (200 mg, 0.44 mmol) in dioxane/H_2O 5/1 (60 mL). The solution was stirred under reflux for 12 h, then solvent was removed in vacuo down to ca. 10 mL, and the resulting suspension was extracted with CH_2Cl_2. The organic layer was separated and dried ($MgSO_4$). Purification by column chromatography (SiO_2; AcOEt/hexanes 1/9) afforded **10** as a white solid (125 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.35$ (4H, d; Ar*H*), 7.21 (4H, d; Ar*H*), 6.73 (2H, dd; ArC*H*=CH_2), 5.72 (2H, d; ArC*H*=CH_2), 5.43 (1H, s; C_6H_5C*H*−), 4.51 (4H, s; ArCH_2O−), 3.72 (4H, s; HOCH_2CCH$_2$O−), 3.53 (4H, s; HOCH$_2$CCH_2O−). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.0$ (Ar), 136.4 (vin), 127.7 (Ar), 126.2 (Ar), 113.9 (Ar), 113.5 (vin), 73.1 (CH_2O), 69.6 (CH_2O), 62.8 (CH_2O), 38.9 (Cquat). UV/Vis (MeCN) λ_{max} (ε) = 257 (180.000).

General Procedure for the Free-Radical Polymerization. The monomer and the initiator (AIBN, mol % vs monomer as indicated in Table 2) were dissolved in toluene (at a monomer concentration as indicated in Table 2). The solution was deoxygenated by bubbling N_2 for 30 min and then heated under magnetic stirring at 70 °C in a temperature-controlled oil bath. The solvent was then removed in vacuo, the remaining solid was dissolved in a minimum amount of CH_2Cl_2, and the solution was added dropwise to the nonsolvent (20 times its cosolvent volume). The purified, precipitated polymer sample was filtered and dried. Polymer **6**: From monomer **5** (378 mg, 0.85 mmol) and AIBN (4 mg, 0.03 mmol) in toluene (17 mL). Yield (266 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.8-7.4$ (bs; Ar*H*), 7.1−6.1 (bs; Ar*H*), 5.4 (bs, C_6H_5C*H*−), 4.5−4.0 (bs, ArC*H*−O− and −OCHH_2CCH$_2$O−), 3.3 (bs, −OCHH$_2$CCH_2O−), 2.0-1.0 (bs, −C*H*− and −CH_2− polymer chain). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145-125$ (Ar), 101.8 (*C*acetal), 70−60 (CH_2O), 45−20 (Cquat and CH and CH_2). Polymer **9**: From monomer **8** (500 mg, 1.22 mmol) and AIBN (8 mg, 0.05 mmol) in toluene (31 mL). Yield (396 mg, 79%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.3-6.1$ (bs; ArH), 4.7−4.1 (bs; ArCH_2O−), 4.0−3.6 (bs; −OCHH_2−CH$_2$O−), 3.5−3.2 (bs; −OCHH$_2$CCH_2O−), 2.0−1.0 (bs; (CH_3)$_2$C−, −C*H*− and −CH_2− polymer chain). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145-125$ (Ar), 98.2 (*C*quat ketal), 70−60 (CH_2O), 45−20 (Cquat and CH and CH_2). Polymer **11**: polymer **10** (205 mg) was dissolved in AcOH (10 mL). H_2O (2 mL) was added, and the solution became immediately turbid but turned homogeneous after 4 h of stirring at room temperature. The solvent was removed in vacuo, the residue dissolved in a minumum amount of THF, and precipitated in hexanes (200 mL) to obtain **11** as a white powder (160 mg, 80%). ^1H NMR (300 MHz, CD_3SOCD_3): $\delta = 7.3-6.0$ (bs; ArH), 4.4-4.1 (bs; ArCH_2O−), 3.8-3.2 (bs; HOCH_2CCH_2O−), 2.2-1.0 (bs; −CH− and −CH_2− polymer chain). ^{13}C NMR (75 MHz, CD_3SOCD_3): $\delta = 145-125$ (Ar), 70−60 (CH_2O), 45−20 (Cquat and CH and CH_2).

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Supporting Information Available: Additional synthetic data, TGA graphs, and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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