Knots for Molecular Strings of Beads

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Three α,α,ω,ω-tetraaryl α,ω-diols **10** were synthesized via Grignard reactions of *p-tert*-butylbromobenzene with 1,10-bis(*p*-carbethoxyphenoxy)decane, dimethyl terephthalate, and dimethyl adipate (**8**). The diols **10** were converted to 1,10-bis{*p*-[bis(*p'-tert*-butylphenyl)(*p''*-hydroxyphenyl)-methyl]phenoxy}decane (**11a**), 1,4-bis[bis(*p-tert*-butylphenyl)(4′-amino-3′,5′-dimethylphenyl)methyl]-benzene (**11b**), and 1,1,6,6-tetrakis(*p-tert*-butylphenyl)hexane (**12**) via carbocation chemistry. Alkylation of **11a** with 2-(2-chloroethoxy)ethanol yielded 1,10-bis{*p*-{bis[*p'-tert*-butylphenyl) [*p''*-[2-(2′-hydroxyethoxy)ethoxy]phenyl]methyl}phenoxy}decane (**13**), containing two tetraarylmethyl groups. 1,4-Bis[bis(*p-tert*-butylphenyl)hydroxymethyl]benzene (**10b**) was reduced to 1,4-bis[bis(*p-tert*-butylphenylmethyl]benzene (**14**) by formic acid. The reaction of tetraarylhexanediol **10c** with formic acid produced 1,1,6,6-tetrakis(*p-tert*-butylphenyl)-1,5-hexadiene (**15**). Via two S_N2 reactions in a one-step route, diethyl bis(*p-tert*-butylbenzyl)malonate (**18**) was produced from diethyl malonate and *p-tert*-butylbenzyl bromide. A Grignard reaction of *p-tert*-butylbromobenzene with ethyl acetate generated 1,1-bis(*p-tert*-butylphenyl)ethanol (**20**) which was converted to 1,1-bis(*p-tert*-butylphenyl)-ethene (**21**) by water elimination. All the intermediates and final products are new compounds. While the bisphenol **11a**, bisaniline **11b**, diol **13**, diester **17**, and the alkanes **12** and **14** with two reactive protons are suitable difunctional knots for syntheses of rotaxanes and of polyrotaxanes via step growth polymerizations, the ethene **21** can be used for polyrotaxanes prepared by chain growth polymerizations.

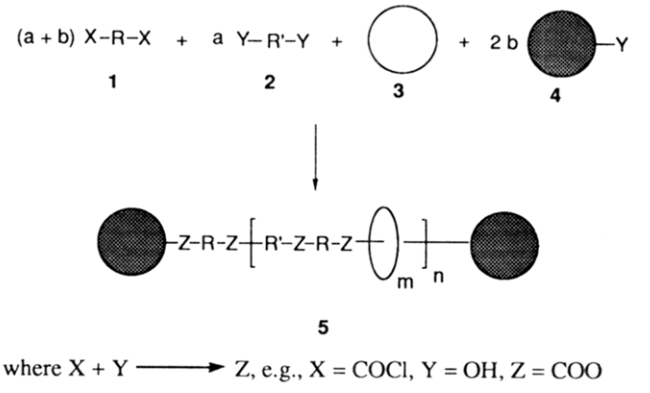
Introduction

Polyrotaxanes are molecular strings of beads consisting of macrocycles whose cavities are pierced by linear polymer chains.[1] Many traditional polyrotaxanes are made from the step growth (condensation) polymerization of monomers of types **1** and **2**, in the presence of macrocycles **3**, as dipicted by Scheme 1. In order to prevent threaded macrocycles from dethreading, monofunctional bulky species **4** are introduced at the polymer chain ends (**5**).

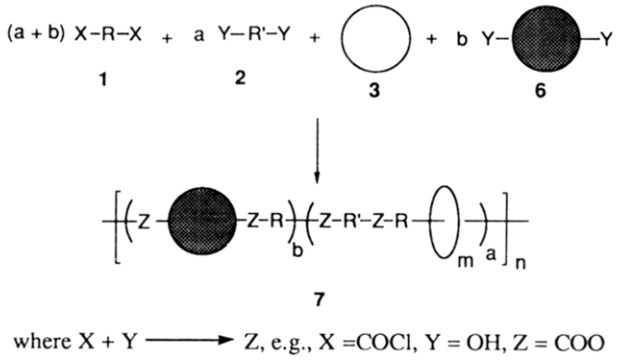
Triarylmethyl derivatives are a family of the monofunctional knots[2] used in the polyrotaxane syntheses.[1,3] However, the end capping of polymer chains by monofunctional knots is often not complete if a small amount of the bulky compound is used in the polymerization.[3] On the other hand, using a large amount of the monofunctional knot leads to low molecular weight polymers, i.e., a decrease in n, because of the stoichiometric imbalance.[3]

However, if the knots can be polymerized into molecular strings of beads, as depicted by Scheme 2, that is, involving difunctional knots **6** in the condensation polymerization of monomers **1** and **2**, we can permanently and completely constrain the macrocycles **3** onto polymer chains and still obtain polyrotaxanes **7** with high molecular weights because there is no stoichiometric imbalance of difunctional monomers. Furthermore, it has been found that polyrotaxanes show interesting behavior due to the movement, aggregation, and crystallization of threaded macrocycles along the polymer backbones.[1,3] This movement can be limited by the incorporation of knots along the polymer chains, and thus crystallization of the macrocyclic component can be supressed. Such systems are microcomposites in which two immiscible components are held together by physical barriers. The difunctional knots **6** can also form low molecular mass rotaxanes by their reactions with monofunctional knots in the presence of macrocycles.

Scheme 1



Scheme 2



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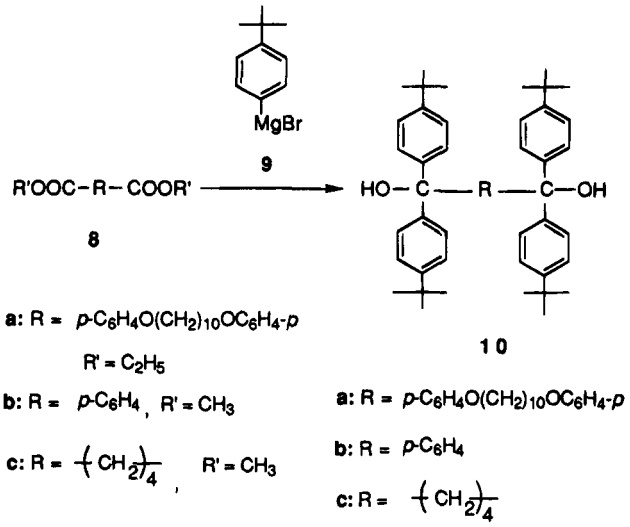
0022-3263/95/1960-3155$09.00/0

In this paper, the syntheses and characterization of several difunctional knots are reported.[4] All the compounds synthesized possess two or four *p-tert*-butylphenyl moieties, which confer solubility while exerting a large steric influence, capable of constraining rings comprised of up to 42 C, N, O, or S atoms.

Results and Discussion

I. Difunctional Knots for Step Growth Polymerization. A. α,α,ω,ω-Tetraaryl α,ω-Difunctional Knots. Similarly to the syntheses of monofunctional triarylmethyl derivatives,[2] syntheses of difunctional knots started from the reaction of α,ω-diesters **8** with the Grignard reagent **9** derived from *p*-bromo-*tert*-butylbenzene in tetrahydrofuran (THF), using the procedure reported by Marvel et al.,[5] Stoddart et al.,[6] and by ourselves.[2]

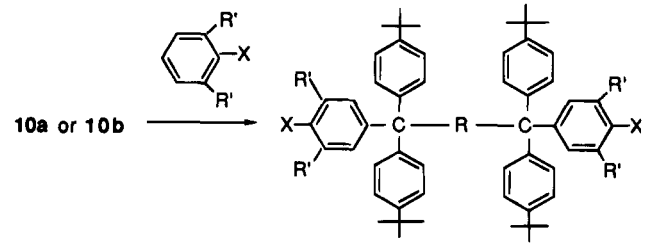
The starting material **8a** was prepared in 86% yield by the reaction of ethyl *p*-hydroxybenzoate with 1,10-dibromodecane in absolute ethanol under reflux, using sodium to deprotonate the phenol.[7] Usually a cold bath is required to absorb the heat generated during the formation of Grignard reagents. In this case, however, refluxing is needed due to the low reactivity of *p*-bromo-*tert*-butylbenzene. Using iodine as an initiator for the formation of the Grignard reagent was avoided because it also catalyzes a Gomberg-Bachmann reaction.[2,8] Compounds **10a**–**10c** were obtained in 40 –72% yields and were purified by recrystallization.



The Harrisons investigated the steric influence of various monofunctional knots. They reacted dicyclohexylacetyl chloride, triphenylmethyl chloride, and tris(*p-tert*-butylphenyl)methanol with 1,10-decanediol in the presence of a cyclic species[9] and found that these three knots could constrain macrocycles comprised of up to 28, 29, and 42 methylene groups, respectively.[10] Therefore, the α,α,ω,ω-tetraaryl α,ω-diols **10a** and **10b** can constrain 42-membered rings because of their larger size compared to tris(*p-tert*-butylphenyl)methanol. **10c** is also probably capable of blocking the loss of 42-membered rings.

However, diols **10** can not be used directly in the polyrotaxane syntheses because the steric hindrance around the functional group reduces the reactivities and also the resultant ether linkages are hydrolytically unstable. Therefore, it is necessary to have the functional groups remote from the region of steric hindrance. This was achieved by adding a spacer between the triarylmethyl moiety and the functional group. On the basis of our previous success with these methods for monofunctional knots,[2] we studied carbocationic processes to incorporate the spacer and functional group.

There are two approaches for this purpose. One approach involves the conversion of the alcohol to the corresponding chloride by reaction with acetyl chloride[5] followed by the Friedel–Crafts reaction with phenol, as reported by Mikroyannidis in his preparation of bis(*p*-hydroxphenyl)diphenylmethane.[11] Alternatively, we reported the direct reaction of tris(*p-tert*-butylphenyl)-methanol with an excess of phenol to produce the *p*-substituted trityl phenolic knot.[2] This approach is simpler compared to the first one and, therefore, was adopted in the present work. The bisphenol **11a** was generated (96%) via a carbocationic process by refluxing **10a** in phenol, using HCl as a catalyst. This is an aromatic electrophilic substitution reaction involving attack on the para position of phenol by the carbocation formed by the acid-catalyzed ionization of the tetraaryl diol. Two additional phenyl rings in bisphenol **11a** increase its crystallinity in comparison to its precursor, diol **10a**. Hence **11a** was easily purified by recrystallizations.



In the ^{1}H NMR spectrum of **11a** (Figure 1), the central 12 protons of the decamethylene unit (labeled a) and the *tert*-butyl protons (labeled d) appear at δ 1.29–1.47. The four protons β to ether oxygens (labeled b) appear at δ 1.76 as a pentet. The OCH_2 protons (labeled c) occur as a four-proton triplet at δ 3.93. The hydroxyl protons (k) appear at δ 4.66. The eight aromatic protons (labeled e and j) occur at δ 6.67 and 6.73 as two doublets. The remaining 24 aromatic protons appear at δ 7.02–7.24. The mass spectrum by fast atom bombardment (FAB) shows the signal of the molecular ion (M^+) at m/z = 1066 as well as signals of fragment ions at m/z = 974 ($M^+ - C_6H_4OH$), 934 ($M^+ - C_4H_9C_6H_4$), 371 [$(C_4H_9C_6H_4)_2C^+(C_6H_4OH)$], and 57 ($C_4H_9^+$).

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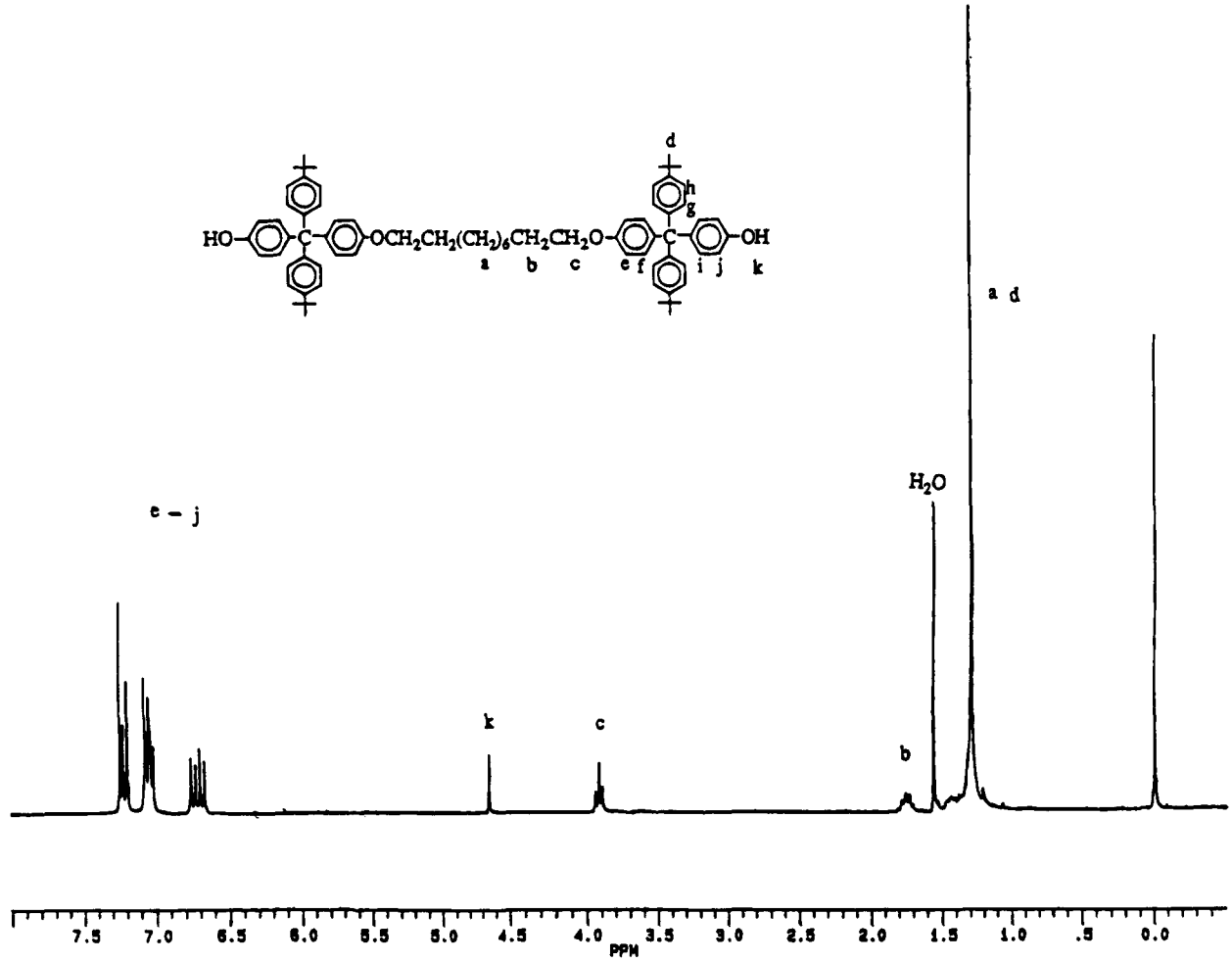
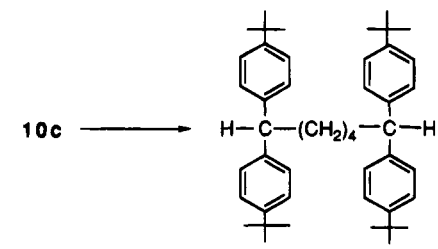


Figure 1. Proton NMR spectrum (270 MHz) of **11a** in $CDCl_3$. The peak at 7.26 ppm is due to $CHCl_3$.

The attempt to synthesize a bisphenol by the reaction of **10b** with phenol, however, led to a product which showed virtually no solubility in any common solvents. Consequently, purification and characterization efforts were severely hampered. The elemental analysis suggested the presence of impurities.

The reaction of **10b** with 2,6-dimethylaniline gave the bisaniline **11b** in 68% yield. **11b** was quite soluble in chloroform and methylene chloride. It did not melt up to 370 °C. The ^1H NMR spectrum contains signals as follows: δ 1.29, a singlet for 36 *tert*-butyl protons; δ 2.07, a singlet for 12 methyl protons; δ 3.49, a broad peak for four amino protons; δ 6.69–7.21, signals for aromatic protons. The mass spectrum by eletron-impact (EI) ionization shows the signal of the molecular ion (M^+) at m/z = 872.5 as well as signals of fragment ions at m/z =752.5 ($M^+ - C_6H_2(CH_3)_2NH_2$) and 619.4 ($M^+ - C_6H_4C_4H_9 - C_6H_2(CH_3)_2NH_2$).

The reaction of **10c** with phenol, surprisingly, did not generate the expected bisphenol, but instead produced $\alpha,\alpha,\omega,\omega$-tetraarylhexane **12** in 80% yield. The mechanism of the reaction is not clear at this time but plausibly could involve electron transfer from phenol to the diarylmethyl carbocation derived from **10c**, forming a diarylmethyl radical, followed by hydrogen atom abstraction to give **12**. **12** could be converted via its dianion to other difunctional knots by the addition of linear chains via nucleophilic substitution reactions of the type shown in our synthesis of monofunctional knots[2] and can possibly form polyrotaxanes directly by S_N2 reactions with dielectrophiles such as dihalides.



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The bisphenolic knot **11a** is itself useful. It has been incorporated into aliphatic polyester rotaxane backbones.[12] In fact, due to the lower reactivity of phenolic compared to alcoholic monomers, the knots are expected to be separated by long segments of alcohol-derived esteric units. Therefore, there is still enough freedom for the macrocycles to move along the polymer backbones so that both polymer backbone and macrocycle can aggregate and crystallize independently, the same as in the polyrotaxanes without in-chain knots. Indeed this phenomenon has been observed.[12] The polyrotaxane with in-chain knots originating from the bisphenolic knot **11a** showed two melting temperatures and two crystallization temperatures due to crystallization of both components (cyclic and linear),[12] as did the polyrotaxane without knots,[3] while its linear model polymer showed only one.[3]

On the other hand, we also wished to have an aliphatic hydroxyl-terminated difunctional knot. This was made

(12) Liu, S.; Gibson, H. W. Unpublished results.

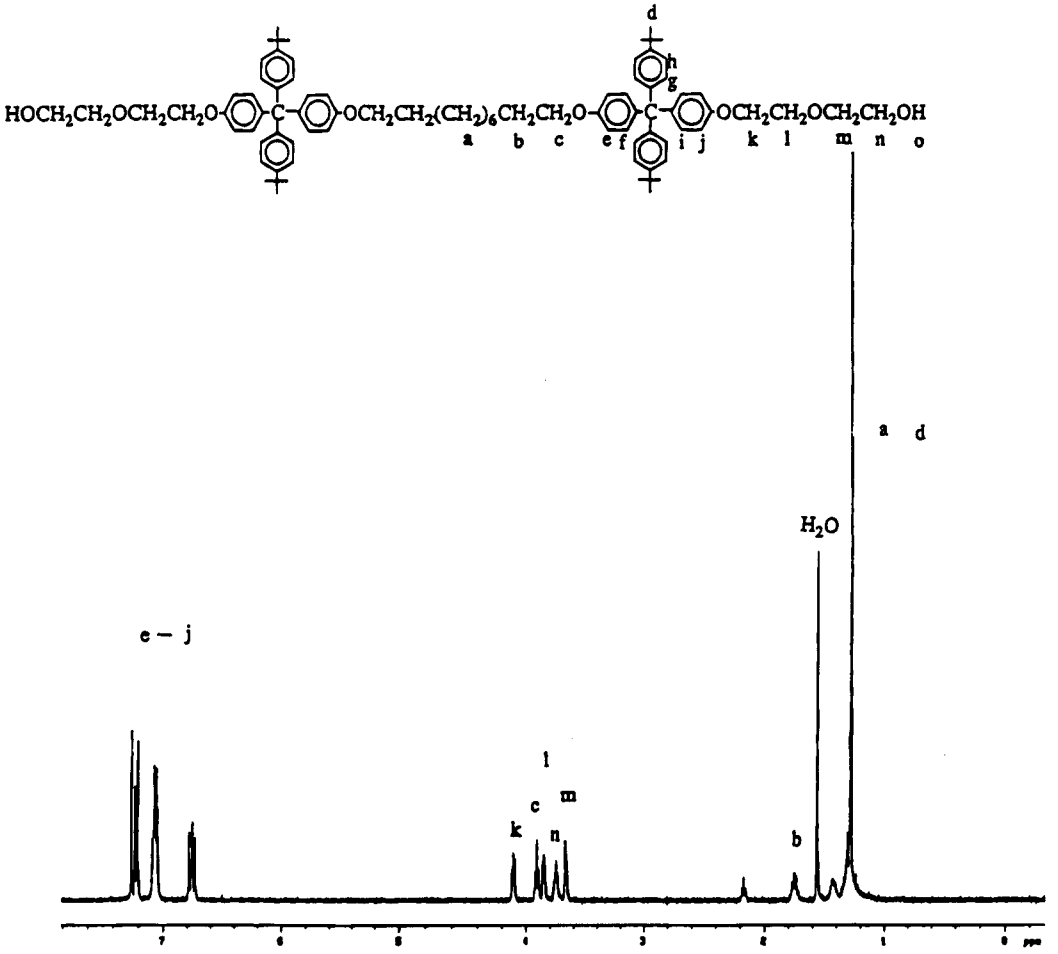
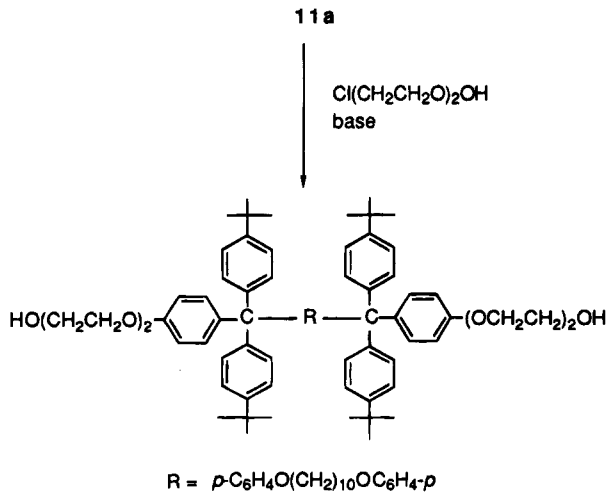


Figure 2. Proton NMR spectrum (400 MHz) of **13** in $CDCl_3$. The peak at 7.26 ppm is due to $CHCl_3$.

by elaboration of the bisphenol **11a**. **11a** was allowed to react with an excess of 2-(2-chloroethoxy)ethanol in butanol at reflux, using an excess of K_2CO_3 as a base. The product **13** was obtained in 83% yield and was purified by recrystallization in ethanol.

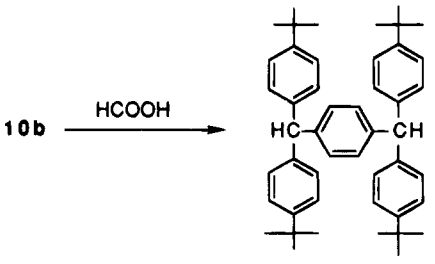


13

13 will be utilized in polyester syntheses as a comonomer, and the properties of the resultant polyrotaxanes will be compared with the polyrotaxanes synthesized using bisphenolic knot **11a**. Unlike **11a** which is incorporated at well-separated intervals due to its lower nucleophilicity, **13** is expected to be included randomly along polymer chains due to its equal reactivity with diol monomers. Therefore, the threaded macrocycles are expected to be randomly separated by the in-chain knots, and their movement along polymer backbones will be limited. Accordingly, crystallization of macrocycles may not occur, depending on the spacing of the knots and their effect on the ability of aggregates of critical nucleation size to form.

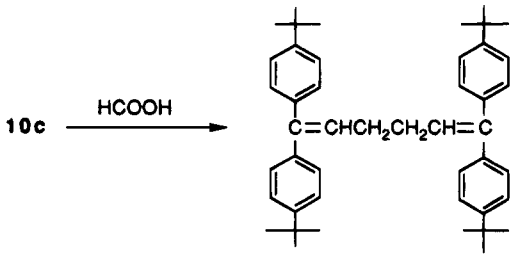
In the ^1H NMR spectrum of **13** (Figure 2), the signal of the phenolic OH protons of starting material **11a** is not present. The terminal hydroxyl protons (labeled o) appear at δ 2.17 as a triplet. The protons of the ethyleneoxy units (labeled k, l, m, and n) occur at δ 3.67, 3.75, 3.85, and 4.11. The signals of decamethylene protons and aromatic protons are similar to those of starting material **11a** in Figure 1.

In our syntheses of monofunctional knots, triarylmethanols were also modified by the carbanionic process.[2] The triarylmethanols were first reduced to triarymethanes by formic acid in toluene. The triarylmethanes were then allowed to react in THF with *n*-BuLi as base with tetrahydropyran-protected (THP-protected) ω-chloro alcohols to form chain-extended THP-protected alcohols which were subjected to deprotection with HCl to produce hydroxyl-terminated knots.[3] The same strategies were attempted in our difunctional knot syntheses. In order to generate a dicarbanionic precursor for nucleophilic substitution reactions, **10b** was reduced to 1,4-bis[bis(*p*-*tert*-butylphenylmethyl]benzene (**14**) by formic acid in toluene. This is essentially a quantitative reaction, and the product was easily separated and purified.



14

However, treatment of **10c** with formic acid in toluene leads to a double elimination reaction, and 1,1,6,6-tetrakis(*p-tert*-butylphenyl)-1,5-hexadiene (**15**) was formed. Thus, in both cationic and anionic processes, **10c** does not undergo substitution reactions but rather produces hydrocarbons (**12** and **15**).



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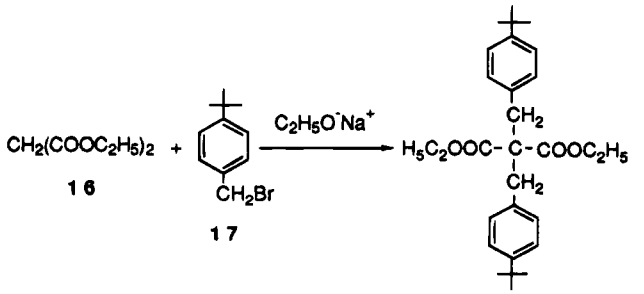
B. Diethyl Bis(*p-tert*-butylbenzyl)malonate. The Grignard approach for syntheses of difunctional knots involves several steps, and the final products are huge. A new smaller difunctional knot was synthesized via a one-step route. Diethyl malonate (**16**) is an ideal starting material for difunctional knot syntheses because it has two pairs of reactive sites: two methylene protons and two ester groups. The two pairs have different types of reactivities: one is nucleophilic while the other is electrophilic. Therefore, one can be used for the incorporation of bulky *tert*-butylphenyl groups while the the other can participate in polymerization. *p-tert*-Butylbenzyl bromide (**17**) was chosen because of its size and its high reactivity toward nucleophiles without the side reaction of elimination. However, the blocking ability of the product **18** is reduced by the free rotation of the methylene group. It is only able to constrain rings comprised of up to 30 atoms, according to a CPK model study.

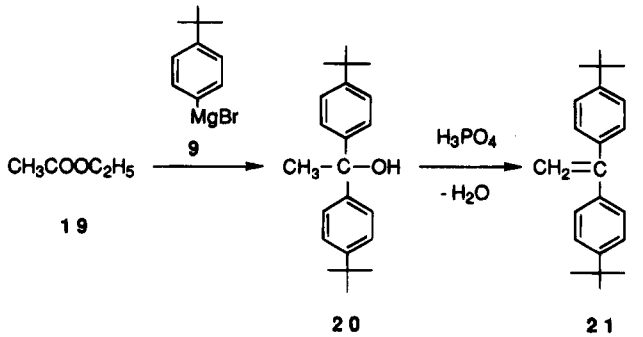


16 17 18

Antonioletti et al. found that reaction of dimethyl manolate with benzyl bromide in THF using lithium hydroxide gave mainly monoalkylation product.[13] Oediger and Möller demonstrated that use of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in DMF gave 84% dialkylation products.[14] However, application of the latter reaction conditions in our system did not generate the desired product. Therefore, we choose sodium as a base and ethanol as a solvent. This condition prevents the hydrolysis or transesterification of the ester groups of the malonate. Pure product was obtained by recrystallization in ethanol. The relatively low yield (55%) was attributed to the fact that ethanol can solvate the enolate anion and thus reduce its reactivity as a nucleophile, leading to the monoalkylation.[15] However, the byproducts generated by the monoalkylation and O-alkylation were easily removed by the recrystallization due to their low symmetry.

Figure 3 is the ^{1}H NMR spectrum of **18**. The ethyl protons appear at δ 1.13 (a) and 4.08 (b). The 18 *tert*-butyl protons appear at δ 1.29 (labeled d). The benzylic methylene protons occur as a four-proton singlet at δ 3.18 (labeled c). The signals of the eight aromatic protons appear at δ 7.09–7.29 (e and f).

II. A Difunctional Knot for Chain Growth Polymerization. We now have phenolic (**11a**), anilinic (**11b**), alkanic (**12**, **14**), alcoholic (**13**), and esteric (**18**) difunctional knots which can be used in step growth (condensation) polymerizations. We also wished to have difunctional knots for chain growth (addition) polymerizations. These compounds should be soluble, possess enough steric influence to constrain large macrocycles, and be polymerizable. Compound **21** was designed to meet these requirements. Because it has two *p-tert*-butylphenyl moieties, in rigid polymer chains such as polystyrene it can block 42-membered rings. The reaction of ethyl acetate (**19**) with Grignard reagent **9** generated bis(*p-tert*-butylphenylethanol (**20**) in 67% yield. The product was purified by recrystallization in a mixture of toluene and hexane (1:2). Removal of water (Dean–Stark trap) from **20** under acidic conditions in refluxing toluene gave desired product **21** in 82% yield. **21** was purified by recrystallization in ethanol. The procedure was similar to the classical synthesis of 1,1-diphenylethene.[16]



19 20 21

In the ^{1}H NMR spectrum of compound **21** (Figure 4), the signal for the 18 *tert*-butyl protons appears at δ 1.34 (labeled a). The two vinyl protons appear as a singlet at δ 5.40 (b). The eight aromatic protons occur at δ 7.27–7.37 (labeled c and d).

Conclusions

A series of three $\alpha,\alpha,\omega,\omega$-tetraaryl α,ω-dicarbinols **10** were synthesized via Grignard reactions. The tetraaryl

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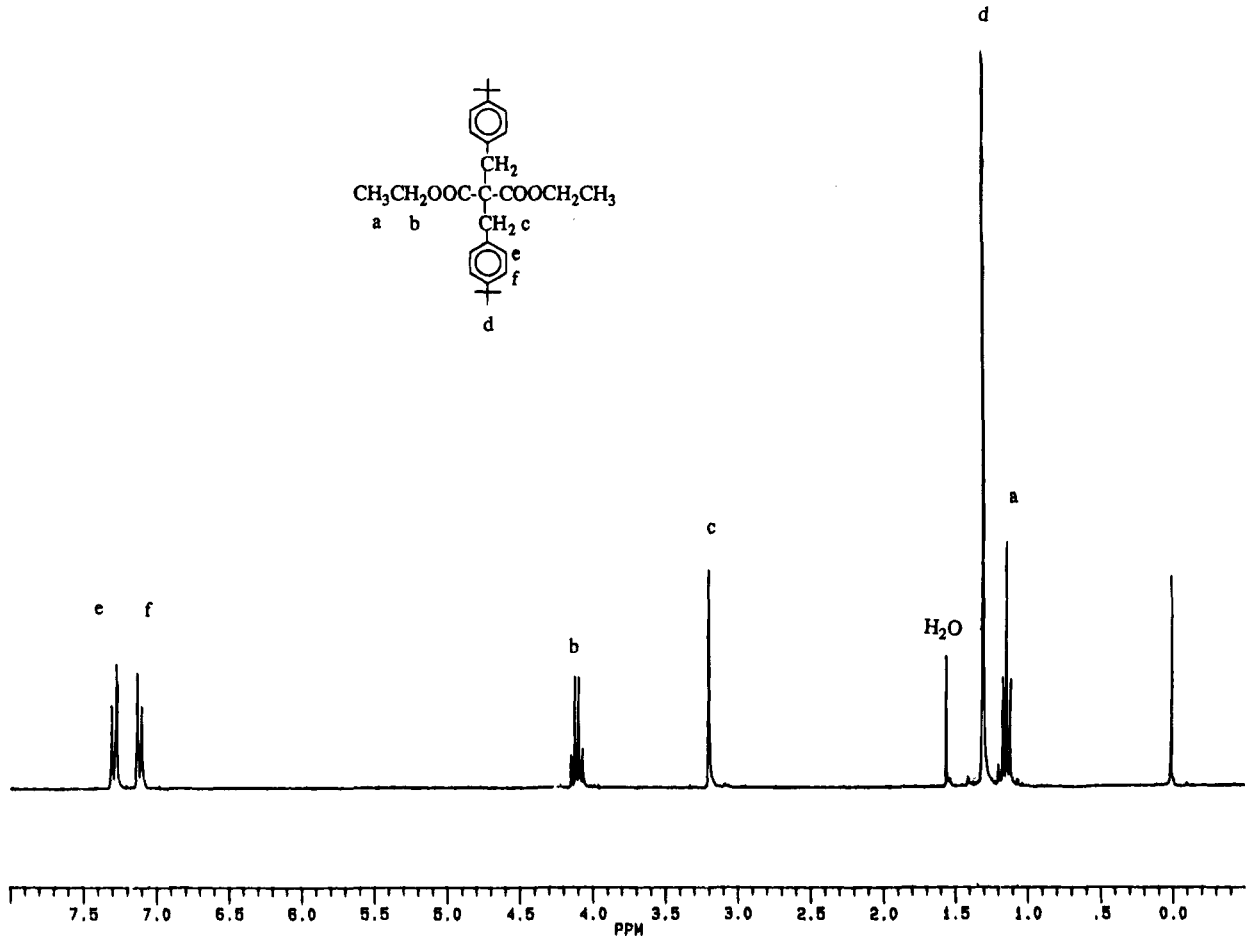

Figure 3. Proton NMR spectrum (270 MHz) of **18** in $CDCl_3$. The peak at 7.26 ppm is due to $CHCl_3$.

dicarbocations derived from the tetraaryl dicarbinols **10** were utilized in aromatic electrophilic substitution reactions on phenol and a substituted aniline, producing tetraaryl bisphenol **11a** and tetraaryl bisaniline **11b**. Tetraarylhexane **12** was produced via the reaction of tetraarylhexanediol **10c** and phenol. Williamson ether synthesis was applied to tetraaryl bisphenol **11a** to form aliphatic hydroxyl-terminated difunctional compound **13**. 1,4-Bis[bis(*p-tert*-butylphenylhydroxymethyl]benzene (**10b**) was reduced to 1,4-bis[bis(*p-tert*-butylphenylmethyl]benzene (**14**) by formic acid. The reaction of **10c** with formic acid produced 1,1,6,6-tetrakis(*p-tert*-butylphenyl)-1,5-hexadiene (**15**). Diethyl di(*p-tert*-butylbenzyl)malonate (**18**) was synthesized in one step via two nucleophilic substitution reactions, starting from diethyl malonate. 1,1-Bis(*p-tert*-butylphenylethene (**21**) was produced by the elimination of water from 1,1-bis(*p-tert*-butylphenylethanol (**20**), which was prepared via a Grignard reaction. In summary, several difunctional blocking groups were successfully synthesized. These compounds and their intermediates, **10a**, **10b**, **10c**, **11a**, **11b**, **12**, **13**, **14**, **15**, **18**, **20**, and **21**, are new compounds and all of them gave satisfactory ^1H NMR, ^{13}C NMR, and IR spectra and elemental analytical or mass spectrometry results. While compounds **11a**, **11b**, **12**, **13**, **14**, and **18** can be used in step growth polymerizations for polyrotaxanes, e.g., polyesters and polyurethanes, and for preparation of rotaxanes by reactions with monofunctional knots, compound **21** is suitable for chain growth polymerizations, e.g., free radical, anionic, and cationic polymerizations.

Experimental Section

Measurements. Melting points were taken in capillary tubes and have been corrected. Proton and carbon NMR spectra, reported in ppm, were obtained on 270 or 400 MHz spectrometers using chloroform-*d* solutions with tetramethylsilane as an internal standard. The following abbreviations have been used in describing the NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants are in hertz. FTIR or IR spectra, reported in cm^{-1}, were obtained using KBr pellets unless otherwise noted. Mass spectra (MS) are reported in units of *m/z* (fragmentation). Elemental analyses were performed by Atlantic Microlab of Norcross, GA.

Starting Materials. THF and xylene were dried over Na/benzophenone and distilled just before use. Diethyl malonate and *p-tert*-butylbenzyl bromide were dried over $CaCl_2$ before use. The other compounds were used without purification as obtained from commercial sources.

Clean Granulated Sodium. Lumps of sodium metal were immersed in dry xylene in an Erlenmeyer flask and heated carefully on an electric hot plate with gentle swirling until the sodium just melted and flowed away from the contaminating surface oxide. The flask was then removed from the hot plate, and upon cooling the sodium melt solidified in globules which were then removed with a spatula to be immediately reimmersed under dry xylene in a preweighed reaction flask equipped with a condenser and a magnetic stirrer. The flask was heated by an electric hot plate until the sodium melted. The stirrer was started, and after the sodium was suitably granulated, the electric hot plate was removed. When the contents of the flask had cooled to room temperature, the stirrer was stopped. The flask was weighed. Excess sodium was taken out with a spatula, and xylene was decanted.

1,10-Bis(*p*-carbethyoxyphenoxy)decane (8a). To a 1 L 3-necked flask equipped with a condenser, a dropping funnel,

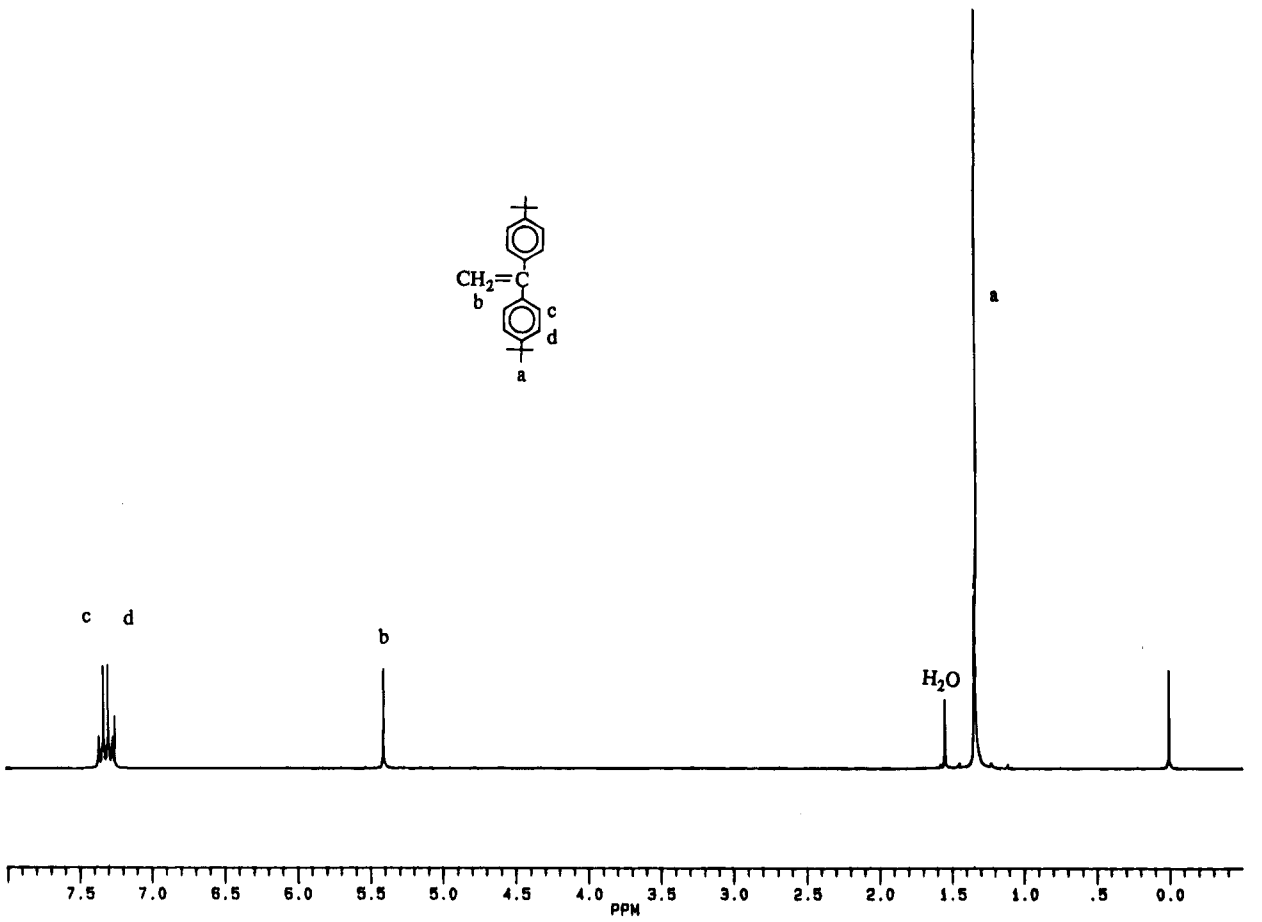

Figure 4. Proton NMR spectrum (270 MHz) of **21** in $CDCl_3$. The peak at 7.26 ppm is due to $CHCl_3$.

a mechanical stirrer, and nitrogen inlet was added clean granulated sodium (11.5 g, 500 mmol). Absolute ethanol (250 mL) was added dropwise. The mixture was heated to reflux, and all of the sodium was reacted. The mixture was cooled until ethoxide commenced to separate out. Ethyl p-hydroxybenzoate (83.1 g, 500 mmol) was added slowly. The mixture was refluxed for 1 h and then cooled until phenoxide commenced to separate out. 1,10-Dibromodecane (75.0 g, 250 mmol) was added slowly, and the mixture was refluxed for 4 h. After the mixture had been cooled to room temperature, it was poured into ice water (3 L). The product was filtered and washed with water and ethanol. The product was then recrystallized in ethanol to afford a white solid (101.2 g, 86%), mp 109.8–110.7 °C (lit.[7] 108.5–110 °C). ^{1}H NMR: 1.34–1.40 (m, 14 H), 1.46 (p, J = 7, 4 H), 1.80 (p, J = 7, 4 H), 4.00 (t, J = 7, 4 H), 4.33 (q, J = 7, 4 H), 6.89–7.99 (m, 8 H).

General Procedure for Grignard Reactions: 1,10-bis-{*p*-[bis(*p'*-*tert*-butylphenyl)hydroxymethyl]phenoxy}-decane (10a). In an oven-dried 500 mL 3-necked flask equipped with a condenser, a dropping funnel, a mechanical stirrer, and nitrogen system were placed magnesium turnings (8.75 g, 360 mmol) with dry THF (Na/benzophenone) (90 mL). *p*-*tert*-Butylbromobenzene (63.9 g, 300 mmol) in dry THF (60 mL) was added dropwise over 1 h. The flask was heated to initiate the reaction. The charge rate of *p*-*tert*-butylbromobenzene was adjusted so that the mixture kept refluxing. The reaction was allowed to go for 2 h at room temperature. A brown color was observed. **8a** (31.4 g, 66.7 mmol) in dry THF (60 mL) was added dropwise. The mixture was stirred at reflux under nitrogen for 12 h. After the solution had been cooled to room temperature, it was neutralized by 5% HCl (1.5 L) at 0 °C. The organic layer was separated from the aqueous layer in a separation funnel. After solvents had been removed by rotary evaporation, a sticky green solid was obtained. The solid (60.9 g) was recrystallized in a mixture of hexane and ethyl acetate (8:1) three times to afford a white powder (33.6 g, 56%), mp 130.5–132.0 °C. IR: 3560, 2950, 2850, 1610, 1500, 1470, 1250, 1180, 1020, 830, 580. ^{1}H NMR: 1.30–1.48 (m, 48 H), 1.76 (p, J = 7, 4 H), 2.69 (s, 2 H), 3.93 (t, J = 7, 4 H), 6.80–7.32 (m, 24 H). ^{13}C NMR: 26.0, 29.2, 29.3, 29.4, 31.3, 34.3, 67.8, 81.3, 113.5, 124.6, 127.4, 129.0, 139.2, 144.2, 149.7, 158.0 (16 signals as required). Anal. Calcd for $C_{64}H_{82}O_4$: C, 83.98; H, 9.03. Found: C, 83.71; H, 9.04.

1,4-Bis[bis(*p*-*tert*-butylphenylhydroxymethyl]benzene (10b) was prepared from 4-bromo-*tert*-butylbenzene and dimethyl terephthalate (**8b**). The product was crystallized from toluene, 16.7 g (40% yield), mp 291.5–295.5 °C. IR: 3566, 3027, 2959, 2903, 2869, 1508, 1502, 834, 818. ^{1}H NMR: 1.30 (s, 36 H), 2.75 (s, 2 H), 7.18 (d, J = 9, 8 H), 7.21 (s, 4 H), 7.31 (d, J = 9, 8 H,). ^{13}C NMR: 31.3, 34.4, 81.5, 124.7, 127.3, 127.5, 143.9, 145.8, 149.9 (9 signals as required). MS (EI): 666 (M^+), 649 (M^+ – OH), 533 (M^+ – $C_6H_4C_4H_9$), 307, 154.

1,1,6,6-Tetrakis(*p*-*tert*-butylphenyl)-1,6-hexanediol (10c) was prepared from 4-bromo-*tert*-butylbenzene and dimethyl adipate (**8c**). The product was crystallized from toluene, 10.5 g (72%), mp 259.7–260.6 °C. IR: 3592, 3036, 2959, 1911, 1510, 1468, 1405, 1363, 1271, 1201, 1110, 1018, 976, 864, 835, 828, 709, 653, 582, 547. ^{1}H NMR: 1.29 (m, 40 H), 2.01 (s, 2 H), 2.20 (t, J = 7, 4 H), 7.29 (s, 16 H). ^{13}C NMR: 22.1, 31.3, 34.4, 42.1, 78.0, 124.9, 125.6, 144.1, 149.4 (9 signals as required). Anal. Calcd for $C_{46}H_{62}O_2$: C, 85.53; H, 9.52. Found: C, 85.33; H, 9.62.

1,1-Bis(*p*-*tert*-butylphenylethanol (20) was prepared from 4-bromo-*tert*-butylbenzene (**9**) and ethyl acetate (**19**). The product was crystallized three times in a mixture of hexane and toluene, 20.6 g (67%), mp 138.7–139.9 °C. IR: 3560, 2960, 2860, 1400, 1270, 1170, 1090, 1020, 910, 840, 810, 690, 580. ^{1}H NMR: 1.30 (s, 18 H), 1.94 (s, 3 H), 2.13 (s, 1 H), 7.33 (m, 8 H). ^{13}C NMR: 30.9, 31.3, 34.4, 75.9, 124.9, 125.4, 145.1, 149.6 (8 signals as required). Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74. Found: C, 85.12; H, 9.78.

1,10-Bis{*p*-[bis(*p'*-*tert*-butylphenyl)-(*p''*-hydroxyphenyl)-methyl]phenoxy}decane (11a). 10a (13.4 g, 14.6 mmol) was dissolved in phenol (48.4 g, 514 mmol) by warming in a 500 mL 1-necked flask equipped with a condenser and nitrogen system. HCl (36%, 1.0 mL) was added as a catalyst. A deep

reddish color was observed immediately. The mixture was heated at reflux for 24 h. After the system had been cooled to room temperature, the product was boiled in water and then dissolved in toluene (200 mL). The solution was extracted with aqueous NaOH (20 g/L, 5 × 250 mL) and water (3 × 250 mL). A brown solid (14.9 g, 96%) was obtained after toluene had been removed. The solid was recrystallized in a mixture of hexane and ethyl acetate (4:1) three times to afford a white solid, mp 162.5–165.7 °C. IR: 3400, 2940, 2840, 1600, 1490, 1240, 1170, 1010, 830, 590. ^{1}H NMR: 1.29–1.47 (m, 48 H), 1.76 (p, J = 7, 4 H), 3.92 (t, J = 7, 4 H), 4.66 (s, 2 H), 6.68–7.27 (m, 32 H). ^{13}C NMR: 26.0, 29.2, 29.3, 29.4, 31.3, 34.2, 62.7, 67.8, 112.9, 113.9, 124.0, 130.5, 132.0, 132.3, 139.3, 139.8, 144.1, 148.2, 153.2, 156.8 (20 signals as required). Anal. Calcd for $C_{76}H_{90}O_4$: C, 85.51; H, 8.50. Found: C, 85.26; H, 8.43. MS (FAB): 1066 (M^+), 974 ($M^+ - C_6H_4OH$), 934 ($M^+ - C_4H_9C_6H_4$), 371 [$(C_4H_9C_6H_4)_2C^+(C_6H_4OH)$], 57 ($C_4H_9^+$).

1,4-Bis[bis(*p*-*tert*-butylphenyl-(4′-amino-3′,5′-dimethylphenyl)methyl]benzene (11b). In a 100-mL, 1-neck round-bottomed flask equipped with a condenser, a magnetic stirrer, and N_2 bubbler on the top of the condenser were placed **10b** (8.50 g, 12.7 mmol) and 2,6-dimethylaniline (30.0 g, 248 mmol). Toluene (13 mL) and 6 drops of concd H_2SO_4 were added to the mixture. The mixture was allowed to reflux with stirring for 5 days. The reaction mixture was poured into CH_2Cl_2 (400 mL), and aqueous NaOH (0.1 M, 250 mL) was added to make the solution slightly basic. The organic phase was separated and washed with water (250 mL). After CH_2Cl_2 had been removed, the product was recrystallized in toluene to afford a white solid (7.5 g, 68%). No melting point was observed up to 370 °C. IR: 3460, 3380, 3027, 2855, 2903, 2861, 1615, 1477, 815. ^{1}H NMR: 1.29 (s, 36 H), 2.07 (s, 12 H), 3.49 (br s, 4 H), 6.69 (s, 4 H), 7.01 (s, 4 H), 7.08 (d, J = 8, 8 H), 7.21 (d, J = 8, 8 H). ^{13}C NMR: 17.9, 31.4, 34.2, 63.0, 120.2, 123.8, 129.9, 130.8, 131.2, 136.7, 140.2, 144.3, 144.7, 148.0 (14 signals as required). MS (EI): 872.5 (M^+), 752.5 ($M^+ - C_6H_2(CH_3)_2NH_2$), 619. 4 ($M^+ - C_6H_4C_4H_9 - C_6H_2(CH_3)_2NH_2$), 460.1, 398.3, 307.1, 154.1.

1,1,6,6-Tetrakis(*p*-*tert*-butylphenyl)hexane (12). 10c (2.03 g, 3.14 mmol) was dissolved in phenol (10.2 g, 108 mmol) by warming in a 500 mL 1-necked flask equipped with a condenser and nitrogen system. HCl (36%, 3 mL) was added as a catalyst. A deep reddish color was observed immediately. The mixture was heated at reflux for 24 h. After the system had been cooled to room temperature, the product was dissolved in toluene (100 mL). The solution was extracted with aqueous NaOH (20 g/L, 5 × 100 mL) and water (3 × 100 mL). A brown solid was obtained after toluene had been removed. The solid was recrystallized in a mixture of hexane and ethanol three times to afford a white solid (1.54 g, 80%), mp 231.7–232.3 °C. IR: 2965, 2865, 1515, 1465, 1370, 1275, 1110, 1020, 820, 810, 590. ^{1}H NMR: 1.27 (m, 40 H), 1.95 (q, J = 8, 4 H), 3.75 (t, J = 8, 2 H), 7.15–7.27 (m, 16 H). ^{13}C NMR: 27.8, 31.3, 34.2, 35.6, 50.3, 125.0, 127.3, 142.3, 148.4 (9 signals as required). Anal. Calcd for $C_{46}H_{62}$: C, 89.84; H, 10.16. Found: C, 89.61; H, 10.22.

1,10-Bis{*p*-{bis[*p*′-*tert*-butylphenyl][*p*″-[2-(2′-hydroxyethoxy)ethoxy]phenyl]methyl}phenoxy}decane (13). 11a (2.00 g, 1.87 mmol) was dissolved in butanol (50 mL) by heating in a 250 mL one-necked flask equipped with a condenser and a magnetic stirring bar. K_2CO_3 (5.67 g, 41.0 mmol) in water (15 mL) was added, and the mixture was refluxed for 2 h. 2-(2′-Chloroethoxy)ethanol (7.30 g, 58.6 mmol) in butanol (10 mL) was added. The mixture was refluxed for 6 days. After it had been cooled to room temperature, the mixture was dissolved in methylene chloride (50 mL) and washed with water (2 × 50 mL). A transparent oil was obtained after methylene chloride had been removed. The oil was recrystallized in ethanol three times to afford a white solid (1.93 g, 83%), mp 146.7–151.2 °C. IR: 3500, 3080, 3000, 2900, 1630, 1520, 1420, 1385, 1270, 1205, 1150, 1080, 840. ^{1}H NMR: 1.29–1.47 (m, 48 H), 1.76 (p, J = 7, 4 H), 2.17 (t, J = 6, 2 H), 3.67 (t, J = 5, 4 H), 3.75 (m, 4 H), 3.85 (t, J = 5, 4 H), 3.92 (t, J = 7, 4 H), 4.11 (t, J = 5, 4 H), 6.73–7.23 (m, 32 H). ^{13}C NMR: 26.0, 29.3, 29.4, 29.5, 31.3, 34.2, 61.7, 62.7, 67.1, 67.8, 69.7, 72.5, 112.9, 113.0, 124.0, 130.6, 132.0, 132.1, 139.2, 140.0, 144.1, 148.2, 156.3, 156.9 (24 signals as required). Anal. Calcd for $C_{84}H_{106}O_8$: C, 81.12; H, 8.59. Found: C, 81.01; H, 8.67.

1,4-Bis[bis(*p*-*tert*-butylphenylmethyl]benzene (14). 10b (38.6 g, 0.578 mol) was dissolved in toluene (400 mL) in a 1 L, 1-necked flask equipped with a mechanical stirrer and a condenser. Formic acid (95–97%, 350 mL) was added, and the mixture was refluxed for 12 h. A white solid was obtained after the mixture had been cooled to room temperature and solvents had been removed. The solid was recrystallized in toluene three times to afford a white solid (22.0 g, 60%), mp 301.0–303.2 °C. ^{1}H NMR: 1.28 (s, 36 H), 5.39 (s, 2 H), 6.99 (s, 4 H), 7.00 (d, 8 H), 7.25 (d, 8 H). Anal. Calcd for $C_{48}H_{58}$: C, 90.79, H, 9.21. Found: C, 90.70, H, 9.19.

1,1,6,6-Tetrakis(*p*-*tert*-butylphenyl)-1,5-hexadiene (15). 10c (12.0 g, 18.5 mmol) was dissolved in toluene (300 mL) in a 1 L, 1-necked flask equipped with a magnetic stirrer and a condenser. Formic acid (95–97%, 100 mL) was added, and the mixture was refluxed for 12 h. A white solid (13.0 g) was obtained after the mixture had been cooled to room temperature and solvents had been removed. The solid was recrystallized in ethyl acetate three times to afford a white solid (11.0 g, 97%), mp 163.9–164.6 °C. ^{1}H NMR: 1.29 (s, 18 H), 1.35 (s, 18 H), 2.24 (m, 4 H), 6.03 (t, J = 6, 2 H), 7.03-7.35 (m, 16 H). Anal. Calcd for $C_{46}H_{58}$: C, 90.43, H, 9.57. Found: C, 90.39, H, 9.57.

Diethyl Bis(*p*-*tert*-butylbenzyl)malonate (18). To a 100 mL 3-necked flask equipped with a magnetic stirrer, a dropping funnel, and a condenser was added clean sodium (2.02 g, 88 mmol). Absolute ethanol (15 mL) was added dropwise. The mixture was heated to reflux, and all the sodium was reacted. The mixture was then cooled until ethoxide commenced to separate out. Diethyl malonate (**16**) (4.70 g, 29.4 mmol) was added dropwise. The mixture was then refluxed for 2 h. The solution was cooled. When the malonate salt commenced to separate out, *p*-*tert*-butylbenzyl bromide (**17**) was added dropwise. The mixture was refluxed for 19 h. After it had been cooled to room temperature, the mixture was poured into water (500 mL). The crystals formed were recrystallized in ethanol (7.2 g, 55%), mp 84.9–86.6 °C. IR: 2850, 2760, 1725, 1510, 1360, 1265, 1190, 1170, 1650, 860, 810, 570. ^{1}H NMR: 1.13 (t, J = 7, 6 H), 1.29, (s, 18 H), 3.18 (s, 4 H), 4.08 (q, J = 7, 4 H), 7.09–7.29 (m, 8 H). ^{13}C NMR: 13.8, 31.3, 34.3, 38.4, 60.2, 61.1, 125.0, 129.8, 133.2, 149.5, 171.1 (11 signals as required). Anal. Calcd for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found: C, 77.21, H, 8.90.

1,1-Bis(*p*-*tert*-butylphenylethene (21). 20 (3.00 g, 9.66 mmol) was dissolved in toluene (50 mL) in a 100 mL 3-necked flask equipped with a Dean–Stark trap, a condenser, and a magnetic stirrer. Phosphoric acid (10.1 g, 87.6 mmol) was added. The mixture was then refluxed overnight. After the mixture had been cooled to room temperature, it was filtered and a yellow solid was discarded. A white powder was obtained after toluene had been removed from the filtrate. The product was recrystallized in ethanol twice to afford a white solid (2.30 g, 82%), mp 100.8–101.6 °C. IR: 3080, 2960, 2870, 1840, 1685, 1605, 1470, 1370, 1275, 1120, 920, 845, 620, 580. ^{1}H NMR: 1.34 (s, 18 H), 5.40 (s, 2 H), 7.27–7.37(m, 8 H). ^{13}C NMR: 31.3, 34.5, 113.1, 124.9, 127.9, 138.6, 149.5, 150.6 (8 signals as required). Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.32; H, 9.62.

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