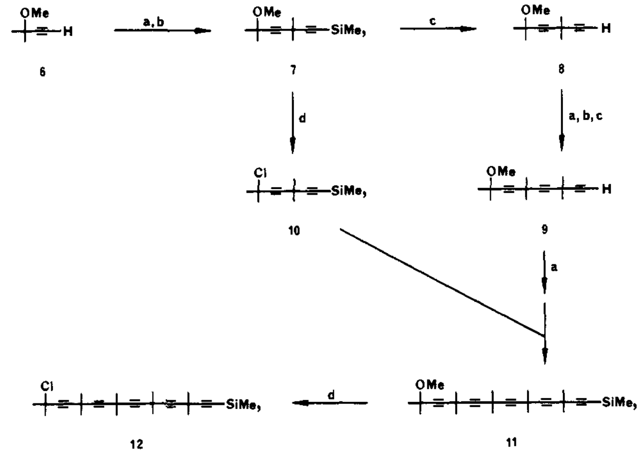
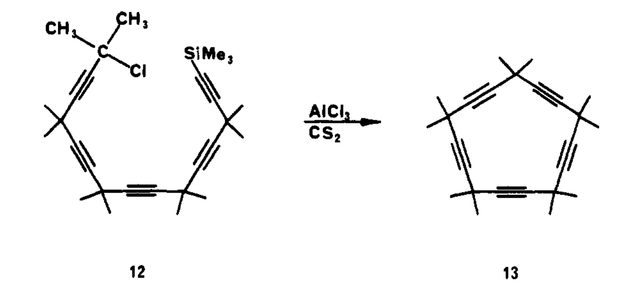
Scheme I



(a) EtMgBr then CuCl (b) 5 (c) KOH, MeOH (d) CH_3COCl, $SnCl_4$

Scheme II



blocks, **5** and **6**, can be easily prepared from **4** on a large scale.[4] Deprotonation of **6** with EtMgBr followed by CuCl-catalyzed coupling[5] with **5** gives the diacetylene **7**. Desilylation of **7** with KOH/MeOH then yields **8**, a simple homologue of **6**. Now **8** can likewise be deprotonated and coupled with **5** to give, after desilylation, the triacetylene **9**. Repetition of this homologation sequence through two more cycles builds up compounds containing all five acetylenic units. Alternatively, the convergent synthesis depicted in Scheme I represents a more efficient route. Thus, the last two acetylenic units can be attached to **9** in a single reaction by coupling with **10**, a homologue of **5**.

Preparation of **10** was conveniently accomplished by treatment of **7** with acetyl chloride at room temperature. This reaction presumably entails acylation of the ether oxygen followed by an S_N1 reaction; Lewis acids have an accelerating effect but are not essential. The same procedure converts the pentaacetylene ether **11** to the corresponding chloride **12**. Since the reactions in Scheme I all proceed in reasonable yield (couplings 65–70%, chlorinations 75–85%, desilylations >90%), pentaacetylene **12** can be easily prepared in multigram quantities.

Cyclization of **12** to the title compound (**13**) was achieved in 35% yield by the slow addition of **12** to $AlCl_3$ in refluxing carbon disulfide (Scheme II). This reaction undoubtedly involves electrophilic attack on the alkynyl silane by a tertiary propargylic cation to form the last C–C bond.[6] Decamethyl[5]pericyclyne[3] is a colorless, air-stable compound: mp 201–202 °C. Anal. C, H. Mass spectrum M^+ calcd for $C_{25}H_{30}$ 330.2348, found 330.2346, m/z (rel intensity) 330 (24), 315 (100), 300 (7), 285 (30), 270 (12), 257 (17), 255 (11); ^1H NMR ($CDCl_3$) δ 1.42; ^{13}C NMR ($CDCl_3$) δ 82.2, 31.1, 25.6; IR (KBr) no C≡C str; Raman (crystal) 2276 (s), 2256 (w), 2244 (m), 2230 (s) cm^{-1}; UV (pentane) end absorption, no max >200 nm, 230 sh (ϵ 30).

Photoelectron spectroscopy (PES) provides the most compelling evidence for cyclic homoconjugation in **13**: the spectrum[7] shows one sharp π ionization potential (π-IP) at 9.07 eV, three additional (incompletely resolved) strong π-IPs at 9.31, 9.64, and 9.90 eV, and a final sharp π-IP at 10.20 eV. In the absence of any electronic interaction among the acetylenic units, the molecule would have five degenerate in-plane π bonds and five degenerate out-of-plane π bonds.[8] Such an arrangement would give rise to just one π-IP for the in-plane π electrons and to one π-IP for the out-of-plane electrons, i.e., to only two π-IPs, which might or might not be distinguishable by PES. Any cyclic homoconjugative interaction among the 10 p orbitals within each set, on the other hand, would split the bonding orbitals into an extensive array of delocalized molecular orbitals (LCAO-MOs) spanning a range of energies. Clearly, the PES of **13** cannot be accommodated by the "localized orbital" picture. The large number of π-IPs observed is difficult to explain without invoking cyclic homoconjugation, and the range of π-IPs (1.13 eV) indicates that the orbital interactions in **13** must be quite substantial. A more detailed analysis of the PES of **13**, aided by theoretical calculations, has been initiated.

We are currently preparing other members of this family and exploring the potentially novel chemistry of pericyclynes, e.g., transition-metal complexation.

Acknowledgment. We are indebted to Prof. K. N. Houk for the first PES of the title compound. Financial support from the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

Registry No. **5**, 18387-63-8; **6**, 13994-57-5; **7**, 88057-35-6; **8**, 88057-36-7; **9**, 88057-37-8; **10**, 18306-51-9; **11**, 88057-38-9; **12**, 88057-39-0; **13**, 88057-40-3.

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(8) Assuming D_{5h} symmetry in the gas phase. A planar ring with perfectly linear acetylenes would have internal angles at the vertices of 108°.

Confirmation of the Mayo Mechanism for the Initiation of the Thermal Polymerization of Styrene

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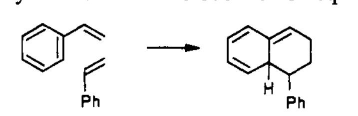
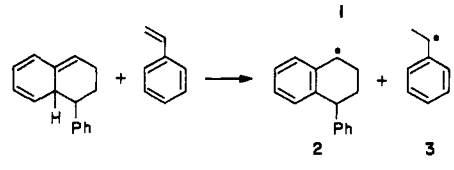
The mechanism of initiation in the thermal polymerization of styrene has challenged chemists for many years. The most widely accepted pathway for the spontaneous generation of radicals was proposed by Mayo in 1961 and is outlined in eq 1 and 2.[1] In



(1)



(2)

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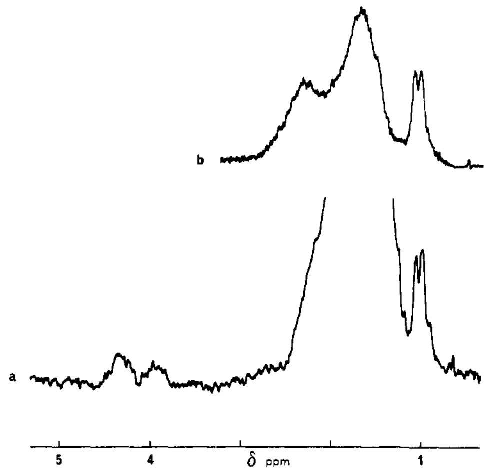


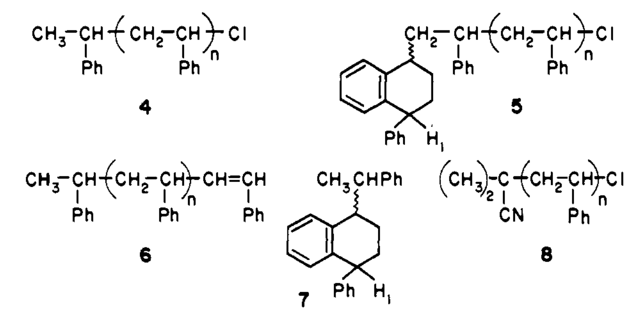
Figure 1. 90-MHz ^1H NMR spectra of oligostyrenes prepared by (a) thermal polymerization of styrene retarded with $FeCl_3$ in DMF and (b) oligomerization of styrene with $HClO_4$ in CH_2ClCH_2Cl.

spite of this acceptance, however, critical reviews of the area clearly establish that the mechanism is, at best, only consistent with the large body of available data.[2,3] Ample evidence exists for the transient formation of the Diels–Alder dimer **1** but its reaction with styrene (eq 2) and the identity of the radicals that initiate polymerization have remained speculative and controversial.[2–5] An alternative mechanism[2] involving 1,4-diradicals has recently recieved some support.[5] Attempts to trap the initiating species with radical scavengers, for example, diphenylpicrylhydrazyl[6] or nitroxides,[7] have failed due to their fast reaction with dimer **1**.

We now wish to report that the propagation step in the thermal polymerization of styrene can be retarded with suitable concentrations of $FeCl_3$ in DMF without, otherwise, any apparent interference with the normal course of the reaction. This gives rise to oligostyrenes, the structural analysis of which has confirmed that radicals **2** and **3** are indeed responsible for the initiation of polymerization.

In a typical experiment, a degassed solution of $FeCl_3$ (8×10^{-3} M) and styrene (5.5 M) in DMF was heated om vacuo at 100 °C in the absence of light for 160 h.[8] The oligostyrenes were then isolated by preparative HPLC from the methanol insoluble fraction.[9]

The ^1H NMR spectrum[10] of oligomers composed of 6–14 monomer units (distinct peaks on HPLC) and of $\bar{M}_n$ 930 (GPC) is shown in Figure 1a and can be readily attributed, from peak intensities and chemical shift data, to an approximately equal mixture of oligostyrenes **4** (average $n = 8$) and **5** (average $n = 6$). The signal at δ 1.03, assigned to the terminal CH_3 group in **4**, has been compared with that of oligomers **6** ($n = 3$–10, Figure 1b) (prepared from styrene by H^+ initiation with either $HClO_4$[11] or $BF_3 \cdot Et_2O$[12] in dichloroethane and isolated by HPLC). The chemical shift (δ 3.9) of the doubly benzylic proton (H_1) in oligomer **5** is the same as in trimers **7**[13] while the signal (δ 4.3) due



to the terminal proton adjacent to chloro and phenyl in **4** and **5** has been compared with its counterpart in oligomers **8** ($n = 4$ and 5).[14] The ^1H NMR spectrum of the highest molecular weight oligomers ($\bar{M}_n$ 2500) obtained in the above experiment, showed identical features to those in Figure 1a, demonstrating that all the oligostyrenes are initiated in the same way.

The UV spectrum of **4** and **5** showed only benzenoid absorption, and elemental analysis confirmed the presence of Cl. Dehydrogenation of the oligomer mixture (**4** and **5**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[16] established the presence of the 1-phenyl-1,2,3,4,-tetrahydronaphthalenyl end group. Thus, following this treatment, the NMR signal due to H_1 in **5** disappeared while the UV and flourescence spectra exhibited absorptions (λ_{max} 232 and 292 nm) and emission (λ_{max} 357 nm) bands characteristic of the 1-phenylnaphthalenyl moiety.[17]

That the $FeCl_3$ complexes act only by trapping the initiating and propagating radicals during the retarded polymerization of styrene is supported by the following considerations: (i) $FeCl_3$ in DMF solution is known to behave as an ideal inhibitor/retarder in the polymerization of styrene initiated by azobis(isobutyronitrile),[15,18] and prelimnary kinetic studies suggest that this is also the case for thermal initiation. (ii) The estimated rate of consumption of $FeCl_3$ (3.3×10^{-9} mol L^{-1} s^{-1}, 5.2 M styrene in DMF at 100 °C)[19] is consistent with the calculated rate of formation of initiating radicals (2.3×10^{-9} mol L^{-1} s^{-1})[20] (5.5×10^{-9} mol L^{-1} s^{-1})[21] on the basis of the rate of polymerization at 100 °C. (iii) The distribution and rate of formation of dimers (*cis*- and *trans*-1,2-diphenylcyclobutane, 1-phenyl-1,2-dihydronaphthalene, 1-phenyl-1,2,3,4-tetrahydronaphthalene) and trimers **7**, which on a molar basis are by far the major products formed during the thermal polymerization of styrene,[2,3] are essentially unaffected by the presence of $FeCl_3$ and DMF.

The results described herein establish the identity of the initiating radicals in the thermal polymerization of styrene as 1-phenylethyl and 1-phenyl-1,2,3,4-tetrahydronaphthalenyl, and this, taken with previous work,[2,3] confirms the operation of the Mayo mechanism (eq 1 and 2) for the initiation process.

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Registry No. Styrene, 100-42-5; 1,2,3,4-tetrahydro-1-phenylnaphthalene, 3018-20-0.

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