Figure 1. Fourier transform ^{13}C nmr spectra in PAA. (a) and (b) are in the isotropic phase. The undecoupled spectrum (a) aids in line assignment. (c) was taken in the nematic phase. Without proton decoupling in this phase a broad structureless resonance is obtained. The aromatic lines shift discontinuously downfield in the isotropic–nematic transitions and the lines from ^{13}C bound to nitrogen disappear due to severe broadening. (d) was obtained by proton-enhanced nmr in the solid phase.

least shielded element of δ is normally in the aromatic plane pointing radially out from the ring, and the most shielded element is perpendicular to the plane. Thus $\sigma_{||} - \sigma_{\perp} < 0$, and we expect a downfield shift in the isotropic–nematic transition exactly as observed. The lines remain sharp and no additional splittings occur indicating rapid motion of the benzene rings about the para axes in agreement with the conclusion of Rowell, et al.,[3] and our results on MBBA.[5]

The methoxy ^{13}C line remains sharp and does not shift appreciably in the isotropic–nematic transition. This indicates that the angle between the axis corresponding to $\sigma_{||}$ and the para axis of the ring is close to 55°, the magic angle. This is similar to the behavior we have observed in higher homologs of the azoxybenzenes.[8]

In the nematic–solid transition, the lines broaden due to chemical shielding anisotropy and the only tractable feature is assigned to the methoxy group, with a theoretical line inserted in Figure 1d corresponding to a tensor δ with elements: $\sigma_{11} = 49 \pm 3$, $\sigma_{22} = 55 \pm 3$, $\sigma_{33} = 114 \pm 3$, in parts per million relative to liquid benzene. The anisotropy is $\Delta\sigma = 62 \pm 6$ ppm which is similar to the value reported for methanol.[9]

Relative values of the order parameter are plotted

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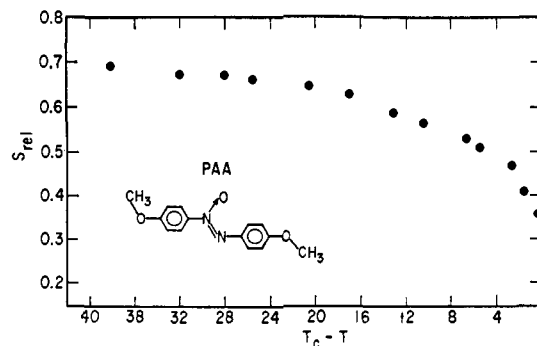
Figure 2. Temperature dependence of the relative order parameter in the nematic phase of PAA. These values were obtained by measuring the temperature dependence of σ for the intense aromatic lines and using average shielding tensors from model solids. The clearing point for this sample is $T_c = 133°$.

vs. temperature in Figure 2. These were obtained from the shifts of the aromatic lines and eq 2. Values of $\bar{\sigma}_{||}$ and $\bar{\sigma}_{\perp}$ were calculated by taking average δ tensors for aromatic ^{13}C nuclei from solid state work[9] and averaging about the long molecular axis which was taken as 10° from the para axes. These values of S are good to within a normalization factor, since neither the exact tensors δ nor the exact molecular conformation are known for this system. The overall behavior is similar to that reported previously. A determination of the full ^{13}C δ tensors from single-crystal work should permit a detailed determination of molecular ordering, conformation, and motion in the liquid crystal phase, and such work is currently under way in our laboratory. Measurements of ^{13}C spin relaxation, recently initiated by Wang, Grant, and coworkers,[10] should prove extremely useful in this regard.

The experiments were performed on a homebuilt double resonance spectrometer described briefly elsewhere.[11] We are grateful to Dr. S. Meiboom and Dr. M. P. Klein for helpful discussions and to T. W. Shattuck and D. N. Shirley for assistance with the experiments.

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A. Pines,* J. J. Chang
Department of Chemistry, University of California
and Inorganic Materials Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Radical Generation from Polymolecular Reactions of Closed Shell Molecules. Molecule-Assisted Homolysis (MAH). Hydrogen Atom Transfer from a Diels–Alder Adduct to an Alkene
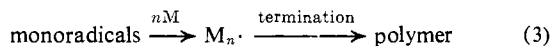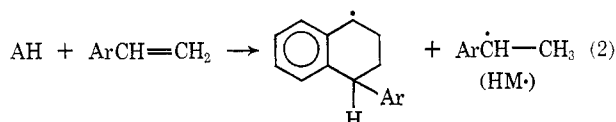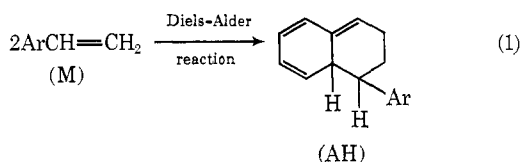
Sir:

There are three types of polymolecular processes by which radicals can be produced from the interaction of closed shell molecules. They are: molecule-assisted homolysis (MAH), in which acceleration of a

single-bond homolysis is caused by the interaction of one molecule with another;[1,2] interactions of two π systems leading to diradicals;[3-5] and one-electron-transfer reactions in which a donor and an acceptor exchange an electron to produce two radicals or radical ions.[6] "Thermal" polymerizations, because they allow the detection of very slow initiation processes, are excellent systems for the study of all three of these processes.[7]

A number of vinyl monomers undergo spontaneous, "thermal" self-initiated polymerizations; these reactions have accurately reproducible rates and are known to be free radical processes.[7] Monomers which exhibit this phenomenon include styrene, 2,6-dichlorostyrene (DCS), pentafluorostyrene (PFS), and methyl methacrylate (MMA); monomers which do not, include vinylmesitylene and methyl acrylate, among others.[7]

The mechanism of the polymerization of styrene has been studied in the most detail. Evidence from kinetics,[7-9] isotope effects,[10] and the isolation of several dimers and trimers[7,11] suggests that the chief mode by which styrene reacts with itself to produce radicals involves eq 1 and 2 as the key steps.[7-9,12] It does not,

$$2ArCH{=}CH_2 \xrightarrow[\text{reaction}]{\text{Diels-Alder}} \quad (1)$$

(M)

(AH)

$$AH + ArCH{=}CH_2 \longrightarrow \quad + Ar\dot{C}H{-}CH_3 \quad (2)$$

(HM·)

$$\text{monoradicals} \xrightarrow{nM} M_n\cdot \xrightarrow{\text{termination}} \text{polymer} \quad (3)$$

however, seem reasonable to apply the same mechanism to PFS, DCS, and MMA; we believe the most probable mechanism for these monomers involves 1,4 diradicals

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(2) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. 1, translated by J. E. S. Bradley, Pergamon Press, New York, N. Y., 1958, pp 260–271.

(3) All of these reactions can be considered to be the first step in a nonconcerted cycloaddition: R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971.

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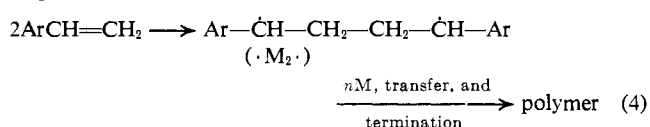
(8) F. R. Mayo, J. Amer. Chem. Soc., 75, 6133 (1953).

(9) R. R. Hiatt and P. D. Bartlett, J. Amer. Chem. Soc., 81, 1149 (1959).

(10) Research of Kirchner (1966), Kopecky and Eveni (1969), and W. A. Pryor et al. (1966, 1970, 1972), summarized in ref 7.

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(eq 4).[7,12c] In addition, we believe that from 0.01 to

$$2ArCH{=}CH_2 \longrightarrow Ar{-}\dot{C}H{-}CH_2{-}CH_2{-}\dot{C}H{-}Ar$$
$$(\cdot M_2\cdot)$$

$$\xrightarrow[\text{termination}]{nM, \text{ transfer, and}} \text{polymer} \quad (4)$$

1% of the polymerization of styrene is initiated by 1,4 diradicals.[7,12c]

The novelty of eq 2 has long excited our interest. Although numerous MAH reactions have been identified,[1,2] no other MAH reaction in solution is known in which a hydrocarbon transfers a hydrogen atom to an olefin. Equation 2 may be viewed as a displacement by the π electrons of styrene on a C–H bond; as such, it is analogous to nucleophilic displacements by olefins,[13a] especially those where a one-electron-transfer component can be identified.[13b-d]

A critical review of the evidence shows that the occurrence of eq 2 has not been proven; the data supporting the involvement of AH in the polymerization could also be rationalized by proposing that $\cdot M_2\cdot$ abstracts hydrogen from AH in a transfer step that produces monoradicals.[7] Clearly the most convincing evidence for eq 2 would be to relate the concentration of AH to the rate of the initiation step. Unfortunately, no worker has been able either to isolate AH or to measure its concentration. However, we have now synthesized a model of AH, BH, which appears to have the remarkable properties attributed to AH.

The compound BH was synthesized from the Diels–Alder reaction of 4-phenyl-1,2,4-triazoline-3,5-dione (PTD)[14] with vinylthiophene (VT) in methylene chloride at $-20°$ (eq 5). The 100-MHz nmr spectrum of BH

$$VT + PTD \longrightarrow \quad (5)$$

(BH)

$$BH + M \longrightarrow HM\cdot + \quad (6)$$

(B·)
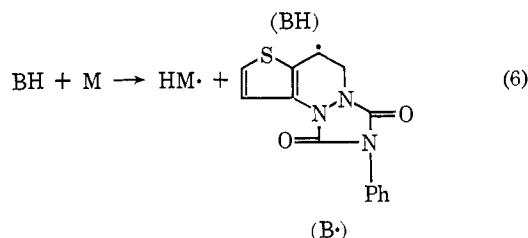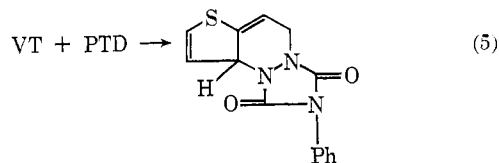
conclusively establishes its structure, particularly in comparison with the spectra of other models of AH which we synthesized and of aromatized BH. Detailed nmr, mass, and infrared spectra are presented elsewhere.[15]

A system which includes eq 1–3 and 6 should show rates of polymerization which are half-order in BH and

(13) (a) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill, New York, N. Y., 1970, p 398; J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 322 and 323; (b) M. L. Poutsma, J. Amer. Chem. Soc., 87, 2161, 2172 (1965); (c) F. D. Greene, W. Adam, J. E. Cantrill, ibid., 83, 3461 (1961); F. D. Greene and W. Adam, J. Org. Chem., 29, 136 (1964); (d) T. W. Koenig and J. C. Martin, ibid., 29, 1520 (1964); (e) D. Y. Myers, G. G. Stroebel, B. R. O. de Montellano, and P. D. Gardner, J. Amer. Chem. Soc., 95, 5832 (1973).

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1.5th order in monomer.[7,12d] Our preliminary data do not establish the order in BH with confidence, partly because of the very large transfer constant of BH which leads to high conversions of BH even at conversions of styrene as low as 2%. In styrene, at 60° the order in BH is about 0.5;[16a] at 98° it is about 0.3.[16b] The order in monomer also is somewhat complex. At 98° and at styrene concentrations above 5 M, the order in monomer is the expected 1.5. Below this concentration, the rearrangement of BH apparently competes with eq 6, the concentration of BH is lower than expected, thermal initiation (which is 2.5th order in styrene[8]) makes an appreciable contribution to the total rate of polymerization, and the observed order in styrene is about 2. The apparent activation energy for the BH-initiated polymerization of styrene is 13 kcal/mol. Plots of $1/\bar{P}_n$ versus $[BH]_{av}$ gave 6.8 and 4.6 for C, the transfer constant of BH, at 60 and 98°, respectively, and 10 kcal/mol for the activation energy for transfer, eq 7.[17]

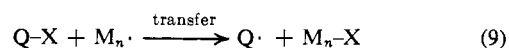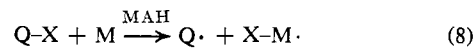$$BH + M_n \cdot \longrightarrow B \cdot + polymer \qquad (7)$$
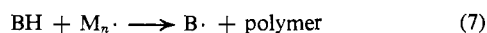
It is of special interest to determine whether BH will initiate the polymerization of a monomer which does not undergo self-initiated polymerization. Experiments with methyl acrylate at 60° show that BH does initiate this monomer, and the order in BH is approximately 0.6.[16d]

Clearly it is important to demonstrate that it is BH itself, rather than an adventitious impurity in it, which is responsible for the initiation we have observed. Although we were not able to perform prepolymerizations and vacuum transfers with BH, several arguments make it very unlikely that anything other than BH itself could explain our observations. First, brief aeration of BH did not change its mass spectrum. Second, even if the hydroperoxide of BH, BOOH, were formed *in situ*, it probably could not give the observed rates. All the hydroperoxides which have been studied decompose in styrene with similar rates.[18a,b] At 70°, 0.02 M tert-butyl hydroperoxide is needed to obtain a rate of polymerization, R_P, of 1 × 10⁻⁵ M sec⁻¹;[18a] we observe the same R_P at 60° using only 0.01 M BH. Third, and perhaps most convincing, the transfer constant of BH, about 5, is much larger than the transfer constant for any known peroxidic compound.[19] If a minor impurity in BH were the actual transfer agent, it would have to have a transfer constant of 100 or more; such compounds are virtually unknown,[19] and it is very doubtful that one is produced in our system. Thus, we conclude that BH shares with the styrene Diels–Alder adduct AH the remarkable property of being reactive enough to donate a hydrogen atom to an olefin.

We wish to suggest that MAH reactions such as eq 8 may be more common than has been recognized. (In eq 8, QX is any material with a labile atom or group and M is generally, although not necessarily, an olefin.) Systems in which there is evidence for an MAH reaction include *H-atom transfers from* AH,[7] BH,[15] hydroperoxides,[1,18] thiols,[20] dihydropyridine,[21] and even ethane[2] and *halogen-atom transfers from* fluorine,[22] chlorine,[13b] probably bromine,[1,2,13b] iodine,[23] and hypohalites.[24] In fact, we suggest that most compounds which have X atoms or groups which are sufficiently labile so as to transfer in styrene, eq 9, with a transfer constant near unity (*i.e.*, a rate constant near 10² M^{-1} sec⁻¹ at 60–100°) also undergo eq 8.

$$Q\text{-}X + M \xrightarrow{\text{MAH}} Q\cdot + X\text{-}M\cdot \qquad (8)$$

$$Q\text{-}X + M_n\cdot \xrightarrow{\text{transfer}} Q\cdot + M_n\text{-}X \qquad (9)$$

(20) At high RSH/M ratios, Hiatt and Bartlett⁹ observe an anomolous acceleration in radical production. They postulate that this is due to homolysis of adventitious disulfide impurities. However, an MAH reaction between thiol and styrene is much more likely.⁷

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William A. Pryor,* J. H. Coco, W. H. Daly, K. N. Houk
Department of Chemistry, Louisana State University
Baton Rouge, Louisana 70803
Received March 30, 1974

Spectroscopic Properties of Protoheme Complexes Undergoing Reversible Oxygenation

Sir:

Recently a number of reports[1-3] have appeared describing the reversible oxygenation of heme complexes as model systems for oxygen-carrying hemeproteins, *i.e.*, myoglobin. In each of these systems, a synthetic heme containing covalently attached axial ligand or sterically hindering groups was used to achieve a minimal structure which would enable reversible oxyheme formation. In addition these models contained an imidazole axial ligand, which has been considered an essential component of the system,[1,2] much as the proximal histidine residue functions in myoglobin. However, the spectroscopic properties of the deoxy- and oxyheme complexes in these reports only partially resemble those properties of the protein. In this com-

(16) (a) 10⁻² M BH for 4 hr produces: 2.2% conversion to polymer; 47% conversion of BH; $\bar{P}_n = 122$; $R_P = 1.3 \times 10^{-5} M^{-1}$ sec⁻¹; (b) 3 × 10⁻² M BH for 20 min produces: $\bar{P}_n = 55.9$; $R_P = 1.5 \times 10^{-5}$; (c) styrene varied from 8.0 to 2.7 M in benzene; (d) 10⁻¹ M BH for 18 hr produces $R_P = 1.2 \times 10^{-5}$.

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