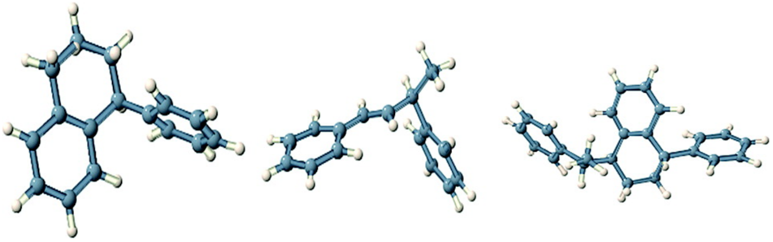
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Direct Evidence for the Gas Phase Thermal Polymerization of Styrene. Determination of the Initiation Mechanism and Structures of the Early Oligomers by Ion Mobility

Edreese H. Alsharaeh, Yehia M. Ibrahim, and M. Samy El-Shall

J. Am. Chem. Soc., **2005**, 127 (17), 6164-6165• DOI: 10.1021/ja042283r • Publication Date (Web): 07 April 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Direct Evidence for the Gas Phase Thermal Polymerization of Styrene. Determination of the Initiation Mechanism and Structures of the Early Oligomers by Ion Mobility

Edreese H. Alsharaeh, Yehia M. Ibrahim, and M. Samy El-Shall*

Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-2006

Received December 22, 2004; E-mail: selshall@hsc.vcu.edu

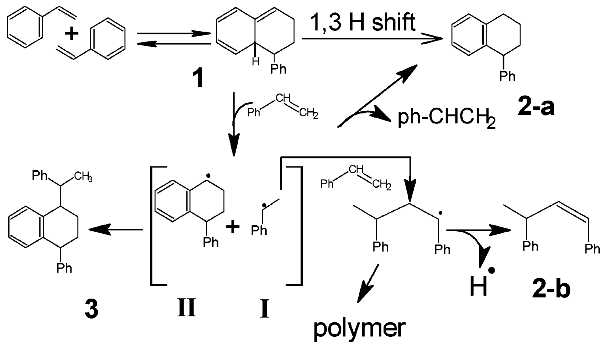
The mechanism of the self-initiated polymerization (or thermal polymerization) of styrene in bulk liquid or solution has been a challenging subject of research since the early days of polymer chemistry.[1,2] This is a phenomenon of not only fundamental inquiry but also of great economical interest related to the industrial production of polystyrene and many of its secondary products.[2] The gas phase thermal polymerization of styrene has been demonstrated more than 15 years ago using an elegant approach based on nucleation from the vapor phase.[3,4] Unfortunately, the nucleation approach provides no *direct* information on the initiation mechanism or on the structures of the growing oligomers. This information is still unavailable since it cannot be accurately obtained from the analysis of the condensed (deposited) polymer products from the gas phase.

In this communication, we present direct evidence for the thermally self-initiated polymerization of styrene in the gas phase and confirm that the dimers and trimers formed in the gas phase have indeed structures similar to those proposed by the Mayo mechanism.[5−8]

The Mayo mechanism (Scheme 1) is the most generally accepted mechanism for the spontaneous polymerization of styrene.[5−8] It proceeds via Diels−Alder dimerization to produce the transient dimer **1**, which reacts with styrene to generate radicals **I** and **II**. These radicals start the styrene propagation, couple to form trimer **3**, and disproportionate to form dimer **2-a** and styrene. The addition of styrene to radical **I** produces a dimer that can be terminated by chain transfer to form **2-b** or that can add additional styrene molecules to form polymers. A recent theoretical study supports polymerization via **1**, but shows that **1** is formed by a stepwise, not a concerted, reaction. [9]

The approach utilized in the present work is based on online analysis of the gas phase oligomers by mass-selected ion mobility.[10] In the experiments, a styrene−helium vapor mixture is heated to well-defined temperatures (350−370 K), thus allowing the establishment of a distribution of oligomers grown in the vapor phase by thermal self-initiation. The vapor mixture is then expanded into vacuum through a supersonic pulsed nozzle, thus resulting in an adiabatic cooling of the vapor and quenching of the polymerization process. The clusters (oligomers + monomers) are then ionized by EI, mass-selected through a quadrupole mass filter, and injected into a drift cell containing helium buffer gas at a pressure (P) of 1.5−3 Torr for the measurement of ion mobility. Both the ionization and ion injection processes lead to extensive evaporation of the nonreacted styrene monomers, thus leaving only the thermalized bare oligomer ions to travel through the drift cell under a uniform electric field of 1.5−3 V/cm. Ions exiting the cell are mass-analyzed and collected as a function of time, yielding the arrival time distributions (ATDs) as a function of P/V from which the mobilities and the collision cross sections (Ω) in helium are determined.[10]

Scheme 1



The mobility measurements can provide structural information on the ionized oligomers on the basis of their Ω, which depends on the geometric shapes of the ions.[10,11] Theoretical calculations of possible structural candidates of the mass-selected oligomer ions are then used to compute angle-averaged Ω at different temperatures (using the trajectory method)[11] for comparison with the measured ones. The agreement between the measured and calculated Ω of the candidate structures provides reliable assignments of the structures of the oligomers. Furthermore, collisional-induced dissociation (CID) of the mass-selected oligomer ions provides further support for the structures obtained from the mobility measurements.

That the oligomer ions represent ionized neutral oligomers formed by vapor phase thermal polymerization is supported by the following considerations: (i) the same ions are observed (although with much weaker intensity) by directly ionizing the heated styrene vapor (with no beam expansion), thus eliminating the possibility of forming styrene clusters. (ii) The appearance of larger oligomer ions depends on the temperature and the duration of heating of the styrene vapor. (iii) CID experiments of the mass-selected oligomer ions show elimination of specific molecular fragments (end groups) similar to typical polymer fragmentation,[12] thus confirming the covalent nature of the oligomer ions. (iv) Thermal dissociation experiments at temperatures as high as 470 K do not show the typical fragmentation by monomer evaporation expected from molecular cluster ions.[10]

DFT calculations [B3LYP/6-31G**][13] were used to obtain the lowest energy structures of several styrene dimer radical cation isomers (12 most likely isomers were considered) including the styrene ion-molecule head-to-tail and head-to-head parallel structures, *cis*- and *trans*-1,2-diphenylcyclobutanes, 1-methyl, 3-phenylindane, and structures **2-a** and **2-b** (see Supporting Information).

Figure 1 displays the ATDs of the styrene dimer cation obtained following the injection of the mass-selected dimer ions into the drift cell containing 1.5 Torr helium. No multiple peaks in the ATDs appear, but significant broadening at higher temperatures indicates that different styrene dimers with structures that have close cross sections are present. The mobility measurements yield average Ω

10.1021/ja042283r CCC: $30.25 © 2005 American Chemical Society

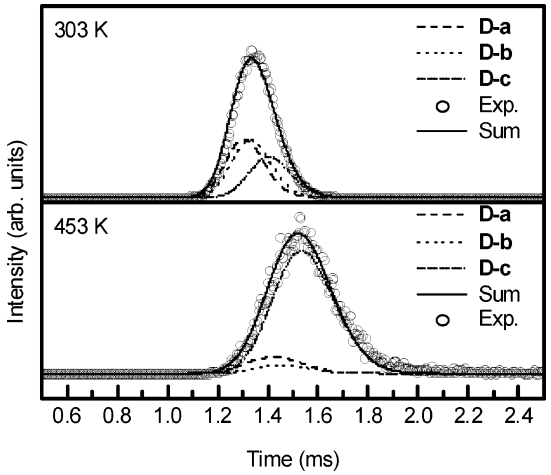
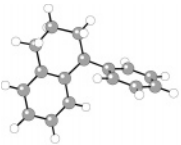
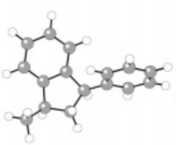


Figure 1. ATDs of the styrene dimer cation at (a) 303 K and (b) 453 K.

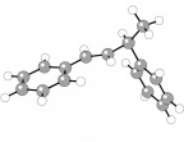
of 108 ± 3, 92 ± 3, and 90 ± 4 Å^2 at 125, 303, and 453 K, respectively. The DFT lowest energy structure calculated for the dimer cation (structure **D-a** corresponding to the neutral **2-a**) results in an average Ω of 107 Å^2 at 125 K. The DFT second and third lowest energy structures (**D-b** and **D-c**, respectively) result in an average Ω of 90.3 Å^2 at 303 K and 90 Å^2 at 453 K, respectively. It is clear that the dimer structures **D-a**, **D-b**, and **D-c** provide Ω in excellent agreement with the experimental values at the temperatures of 125, 303, and 453 K, respectively. However, none of these structures alone is capable of reproducing the measured ATDs at these temperatures. By varying the relative abundances of structures **D-a**, **D-b**, and **D-c**, we can obtain excellent fits to the measured ATDs at different temperatures, as shown in Figure 1.



D-a



D-b



D-c

While the neutral dimers **2-a** and **2-b** (corresponding to the cations **D-a** and **D-c**, respectively) can be formed by the radical reactions as shown in the Mayo's mechanism, the dimer cation **D-b** is formed by a cationic mechanism. In fact, previous work identified the dimer cation **D-b** as the covalent dimer formed in the gas phase and intracluster reactions of styrene radical cation with its neutral molecule.[14] Therefore, the dimer **D-b** could be formed in our experiment following the EI ionization of the neutral styrene clusters generated by the beam expansion. However, the dimer cations **D-a** and **D-c** are clearly formed by EI ionization of the neutral dimers **2-a** and **2-b**, respectively produced by the thermal polymerization of styrene vapor. Further evidence supporting structures **D-a** and **D-c** comes from the CID results. The mass-selected dimer ion shows fragmentation by the loss of a C_6H_6 unit consistent with structure **D-a**. In addition, the observed loss of CH_3 is consistent with isomer **D-c**. Thus, the correlations between calculated and experimental ATD values and the CID results allow us to determine that gas phase thermal polymerization of styrene results in dimers **2-a** and **2-b**, consistent with an initiation process that proceeds according to the Mayo mechanism (Scheme 1).

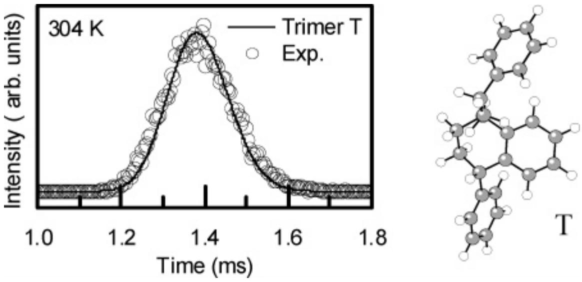


Figure 2. ATD of the styrene trimer cation at 304 K and the calculated lowest energy structure **T**.

Figure 2 displays the measured ATD of the mass-selected styrene trimer cation at 304 K and the calculated trimer structure **T** (corresponding to the neutral **3** in Scheme 1). The experimental Ω for the trimer (118 ± 4 Å^2) is in excellent agreement with the calculated Ω of structure **T** (119 Å^2). It is interesting that the structure of the gas phase trimer **T**, identified here for the first time, is identical to the structure of the trimer isolated by HPLC from the thermal polymerization of styrene in solution and characterized by NMR.[7,8] The observation of the abundant trimer **T** is consistent with the recent theoretical predictions that indicate that the barrier to the formation of **3** is lower than the barrier to generate the two benzylic monoradicals **I** and **II**.[9] Our results provide direct evidence for the trimer formation by recombination of the initially formed initiating radicals **I** and **II**. However, the present results do not provide information on whether the formation of **1** proceeds via the stepwise diradical or the concerted [4 + 2] cyclization.[9]

Finally, the similarity between the initiation mechanism of the thermal polymerization of styrene in the gas phase and in bulk liquid or solution is remarkable and *implies* that the structures of the early oligomers in the gas phase are relevant to the understanding of the polymerization mechanisms in condensed phases. This is a very significant result because it allows oligomer structures generated by different initiation mechanisms to be quickly and reliably determined using ion mobility methods. This approach provides a new and general way to study thermally and possibly photochemically initiated gas phase reactions and to identify the structures of the early products.

In summary, we present here direct evidence for the thermal self-initiated polymerization of styrene in the gas phase and establish that the initiation process proceeds via essentially the same mechanism (the Mayo mechanism) as in condensed phase polymerization. Furthermore, we provide structural identifications of the dimers and trimers formed in the gas phase.

Acknowledgment. We thank the National Science Foundation (CHE-0414613) for financial support of this research.

Supporting Information Available: Calculated low energy structures of styrene dimer and trimer cations and their total energies and complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Flory, P. J. *J. Am. Chem. Soc.* **1937**, *59*, 241.
(2) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: New York, 2004.
(3) El-Shall, M. S.; Bahta, A,; Rabeony, H. M.; Reiss, H. *J. Chem. Phys.* **1987**, *87*, 1329.
(4) Reiss, H. *Acc. Chem. Res.* **1997**, *30*, 297.
(5) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289.
(6) Pryor, W. A.; Lasswell, L. D. *Adv. Free Radical Chem.* **1975**, *5*, 27.
(7) Chong, Y. K.; Rizzardo, E.; Solomon, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 7761.
(8) Kothe, T.; Fischer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 4009.
(9) Khuong, K. S.; Jones, W. H.; Pryor, W. A.; Houk, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 1265.
(10) Rusyniak, M. J.; Ibrahim, Y. M.; Wright, D. L.; Khanna, S. N.; El-Shall, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 12001.
(11) Mesleh, M. F.; Hunter, J. M.; Shvatsburg, A. A.; Schatz, G. C.; Jarrold, M. F. *J. Phys. Chem.* **1996**, *100*, 16082.
(12) Gidden, J.; Bowers, M. T.; Jackson, A. T.; Scrivens, J. H. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 499.
(13) Frisch, M. J. et al., *Gaussian 98*, Revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.
(14) Pithawalla, Y. B.; Gao, J.; Yu, Z.; El-Shall, M. S. *Macromolecules* **1996**, *29*, 8558.

JA042283R