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Early Stages of Styrene−Isoprene Copolymerization in Gas Phase Clusters Probed by Resonance Enhanced Multiphoton Ionization

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We present direct evidence for the formation of the covalent bonded styrene (isoprene)$_2$ oligomer and the isoprene dimer ions following resonance ionization of the gas phase styrene−isoprene binary clusters. The application of resonance ionization to study polymerization reactions in clusters provides new information on the structure and mechanism of formation of the early stages of polymerization and holds considerable promise for the discovery of new initiation mechanisms and for the development of novel materials with unique properties.

Most of the current knowledge of polymerization reactions and polymer properties comes from experiments dealing with bulk liquids or solutions.[1] A number of important phenomena, unique structures and novel properties may exist for gas phase and cluster polymerization.[2−8] In this regime, the structure of the growing polymer may change dramatically and the rate coefficient may vary significantly upon the addition of a single monomer molecule. These changes would be reflected in the properties of the oligomers. In addition, gas phase and cluster studies provide unique opportunities to quantitatively study the effects of solvents, chain transfer, and inhibitors on the mechanisms of polymerization. Several studies have demonstrated the value of gas phase and cluster studies both in fundamental information on polymerization[2−9] and in practical aspects such as novel methods for metal ion and atom-initiated polymerization.[10,11]

Styrene is known to undergo polymerization in bulk monomer or in solution by free radical, cationic and anionic mechanisms.[1] The radical cations of styrene react with isoprene by covalent addition, which may lead to sequential copolymerization. The addition reactions of a series of alkenes with a series of styrene and substituted styrene radical cations have been studied by laser flash photolysis in solutions.[12] These reactions, which are commonly termed radical cation dimerizations (or radical cation initiated cycloadditions), offer novel and useful methods for the synthesis of many cyclobutane derivatives.[13] However, it is well recognized that in solution studies, both the solvent and the method for generating the radical cation will play a role in determining the overall mechanism. Therefore, gas phase and cluster reactions are desirable to provide detailed information on the mechanisms of these reactions.

In this Letter, we present direct evidence for the formation of the covalent bonded styrene (isoprene)$_2$ oligomer and the isoprene dimer ions following resonance ionization of the gas phase styrene-isoprene binary clusters. The conversion of van der Waals (vdW) clusters into covalent-bonded, size specific oligomers holds considerable promise not only for a fundamental understanding of the polymerization reactions but also for the discovery of new initiation mechanisms and for the development of novel materials with unique properties. This includes, for example, synthesis of thin films of size-selected oligomers deposited from the gas phase on a variety of metal and semiconductor surfaces.

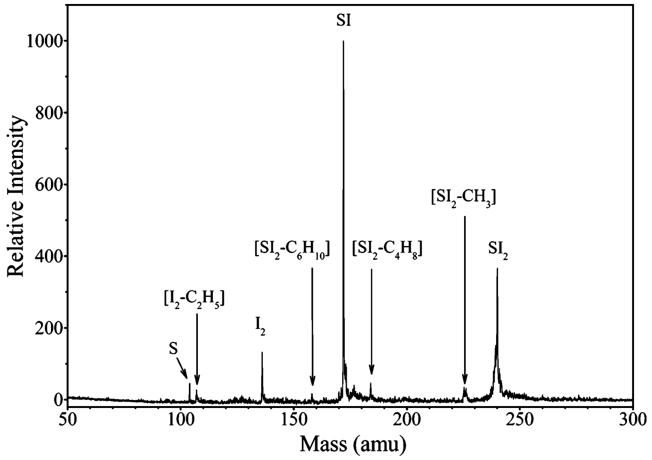

Figure 1. R2PI mass spectrum obtained at 288.64 nm.

The approach utilized in the present work is based on utilizing one color resonant two-photon ionization (R2PI) to selectively generate the styrene radical cation ($S^{\bullet+}$) within the gas-phase styrene−isoprene binary clusters (SI_n).[14] Covalent addition of I into $S^{\bullet+}$ deposits excess energy on the styrene−isoprene dimer ion as a result of the exothermicity of the covalent dimerization reaction. Because molecular ions dissipate excess internal energy into their vibrational modes, this could result in specific fragmentations by elimination of end groups from the dimer ion, and the observed product distributions should reflect this process. Furthermore, the addition of a second isoprene molecule on the $SI^{\bullet+}$ dimer results in covalent dimerization of isoprene, which imparts additional excess energy on the $SI_2^{\bullet+}$ oligomer that could break the $S-I_2^{\bullet+}$ bond. Because styrene has an ionization energy (IE = 8.46 eV) lower than that of isoprene

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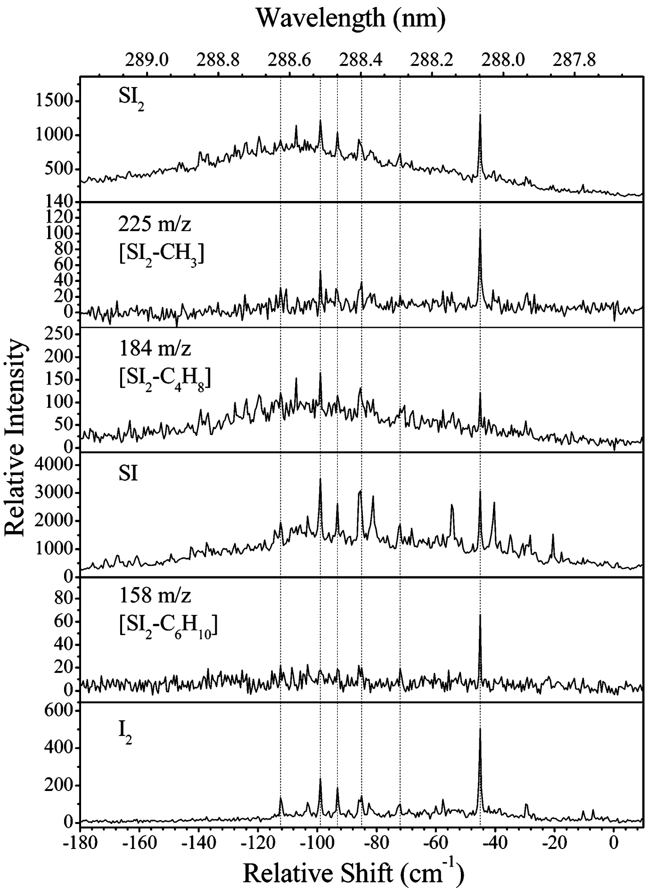


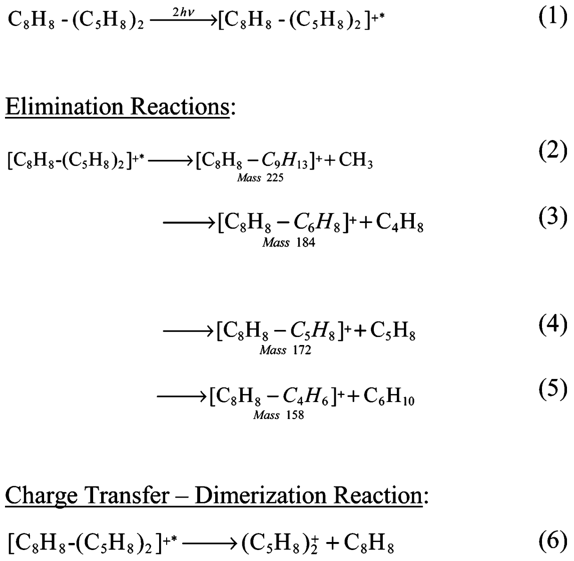
Figure 2. R2PI action spectra of the observed ions.

IE (8.86 eV),[15] direct charge transfer from $S^{\bullet+}$ to I is not possible, and isoprene ions $I^{\bullet+}$ should not be formed. In this case, the observation of isoprene dimer ion ($I_2^{\bullet+}$) provides a clear signature of the covalent formation of the SI_2 oligomer ion.

The styrene-isoprene clusters are formed in a He-seeded jet expansion and probed as a skimmed cluster beam in a collision-free high vacuum chamber with a delay between synthesis and probe (i.e., the neutral beam flight time) on the order of 1 ms.[14] During operation, a vapor mixture of styrene−isoprene (0.1%) in He (ultrahigh purity, Spectra Gases 99.999%) at a pressure of 8 atm is expanded through a conical nozzle (100 μm diameter) in pulses of 200−300 μs duration at repetition rates of 10−15 Hz. The collimated cluster beam passes into the ionization region of the TOF mass spectrometer where it intersects a laser pulse from a frequency-doubled dye laser. The tunable radiation is provided by a dye laser (Lambda Physik FL3002) pumped by an excimer laser (Lambda Physik LPX-101). Coumarin 540A (Exciton) dye laser output passes through a β-BaB_2O_4 crystal to generate a continuously tunable frequency-doubled output of 10^{-8} s pulses. The cluster ions formed by the R2PI are electrostatically accelerated in a two-stage acceleration region (300−400 V/cm) perpendicular to the direction of the neutral beam, and then travel a field-free region (170 cm in length) to a two-stage microchannel-plate detector. The TOF spectrum is recorded by digitizing the amplified current output of the detector with a 500 MHz digitizer (LeCroy 9350A) and averaged over 200 pulses.[14]

Figure 1 displays the R2PI mass spectrum obtained at 288.64 nm (corresponding to the electronic origin of the SI_2 cluster). In addition to the expected SI_2 ions (m/z 240), other ions such as SI_2-CH_3, $SI_2-C_4H_8$, $SI_2-C_6H_{10}$, I_2, and $I_2-C_2H_5$ corresponding to m/z 225, 184, 158, 136, and 107, respectively, are also observed.

SCHEME 1



$$C_8H_8\text{-}(C_5H_8)_2 \xrightarrow{2h\nu} [C_8H_8\text{-}(C_5H_8)_2]^{+*} \quad (1)$$

Elimination Reactions:

$$[C_8H_8\text{-}(C_5H_8)_2]^{+*} \longrightarrow \underset{Mass\ 225}{[C_8H_8 - C_9H_{13}]^{+}} + CH_3 \quad (2)$$

$$\longrightarrow \underset{Mass\ 184}{[C_8H_8 - C_6H_8]^{+}} + C_4H_8 \quad (3)$$

$$\longrightarrow \underset{Mass\ 172}{[C_8H_8 - C_5H_8]^{+}} + C_5H_8 \quad (4)$$

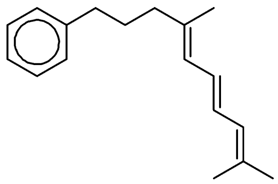
$$\longrightarrow \underset{Mass\ 158}{[C_8H_8 - C_4H_6]^{+}} + C_6H_{10} \quad (5)$$

Charge Transfer – Dimerization Reaction:

$$[C_8H_8\text{-}(C_5H_8)_2]^{+*} \longrightarrow (C_5H_8)_2^{+} + C_8H_8 \quad (6)$$

To identify the origins of the ions shown in Figure 1, the R2PI spectral features (action spectra) were measured for each of the observed ions. Figure 2 displays the R2PI spectra relative to the origin of the $S_1 \leftarrow S_0$ transition of styrene (34 758.79 cm^{-1}, 287.697 nm) obtained by monitoring the mass channels corresponding to the specified ions. The spectral features observed in the SI_2-CH_3, $SI_2-C_4H_8$, $SI_2-C_6H_{10}$ and I_2 mass channels, and several of the features observed in the SI mass channel (m/z 172) are identical to the features that appear in the SI_2 channel (m/z 240). These features are assigned to the R2PI spectrum of the SI_2 cluster, which consists of a weak electronic origin red shifted relative to the origin of styrene by 112 cm^{-1}, and several peaks representing vdW intermolecular vibrations of the SI_2 cluster. The remaining features in the SI mass channel are assigned to the R2PI spectrum of the SI cluster, which has a relatively strong origin red shifted relative to the origin of styrene by 55 cm^{-1}. It should be noted that the SI ion can be produced from the fragmentation of the SI_2 ion as well as from larger SI_n cluster ions. This explains both the additional features observed in the SI mass channel and the production of a dominant m/z 172 ion in the mass spectrum. The identical spectral features observed in the SI_2, SI_2-CH_3, $SI_2-C_4H_8$, SI, $SI_2-C_6H_{10}$, and I_2 mass channels provide clear evidence for the covalent addition and elimination reactions occurring in the SI_2 cluster following the R2PI of cluster. These reactions are summarized in Scheme 1.

On the basis of the R2PI results and the proposed reaction mechanism, the covalent SI_2 oligomer ion can be identified as an ion of a $C_{18}H_{24}$ molecule with a structure similar to A.



A

Ionization of A can readily result in the elimination of one of the two terminal CH_3 groups, thus producing the observed m/z 225 ion. Similarly, the eliminations of C_4H_8 and C_6H_{10} from

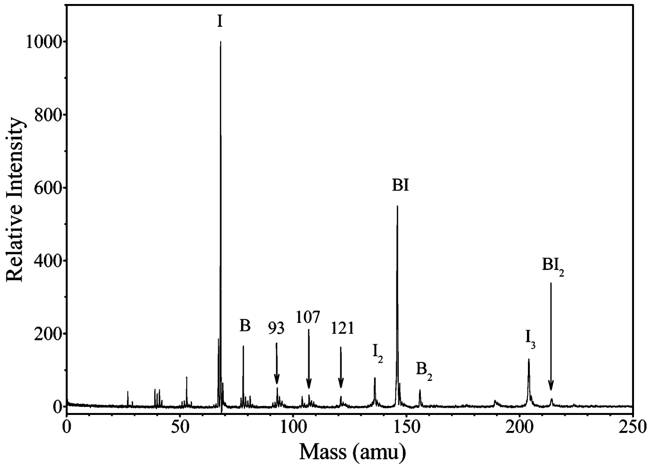


Figure 3. R2PI mass spectrum the benzene−isoprene (BI_n) clusters obtained at 259.74 nm (corresponds to the strongest peak observed in the BI mass channel at a frequency shift of −125.48 cm^{-1} relative to the 6_0^1 resonance of benzene as shown in Figure 4).

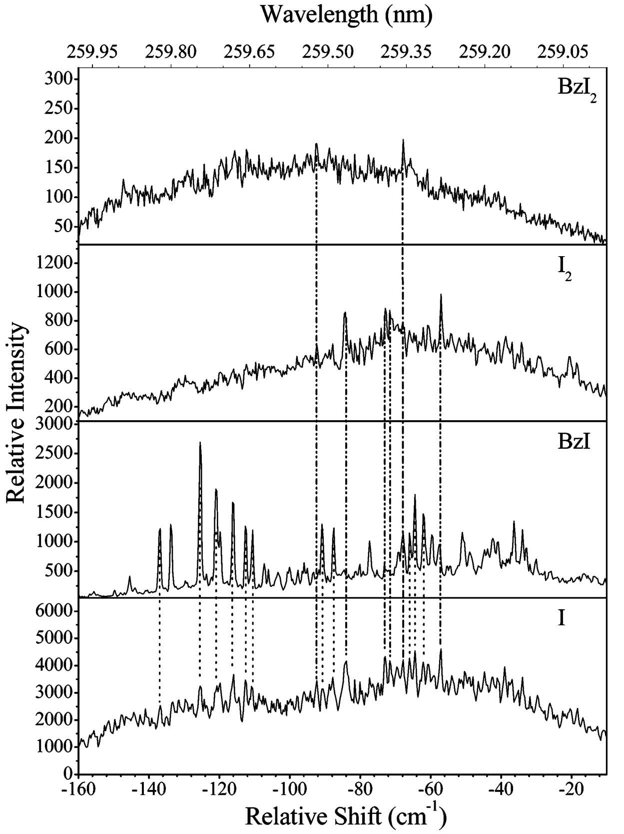
ionized A to generate the observed m/z 184 and 158, respectively can be directly explained.

To further support the covalent formation of the SI_2 oligomer ion, we examined the analogous benzene−isoprene (B−I) cluster system where the absence of the olefin group in the benzene cation is expected to make the covalent addition of isoprene less likely as compared to the addition on the styrene cation. Indeed, the R2PI mass spectrum of the B−I clusters, shown in Figure 3, did not show evidence for elimination reactions analogous to reactions 2−5 observed in the styrene−isoprene clusters. However, because the IE of benzene (9.24 eV)[15] is higher than that of isoprene, direct charge-transfer took place and the isoprene radical cation ($C_5H_8^{\bullet+}$) was observed (Figure 3). The peaks at m/z 121, 107, and 93 correspond to the known fragments from the limonene ion consistent with rearrangement of the isoprene dimer cation into the limonene ion.[2] Unlike the styrene−isoprene system, no evidence is present for elimination of end groups from the BI or the BI_2 ions.

Figure 4 displays the R2PI action spectra of the benzene−isoprene (BI_n) cluster beam recorded in the mass channels corresponding to BI_2, I_2, BI, and I. The frequency shift is relative to the 6_0^1 resonance of benzene. The spectra confirm that the BI ion dissociates to the isoprene ion (I) by a loss of a benzene molecule (IP of benzene > IP of isoprene). Unlike the styrene−isoprene system, no evidence is found for the loss of specific end groups (rather than isoprene or benzene units) from the BI or the BI_2 ions.

The observation of end group fragmentation products from the styrene(isoprene)$_2^{\bullet+}$, unlike the benzene(isoprene)$_2^{\bullet+}$, confirms the covalent addition of isoprene on the olefin group of the styrene radical cation.

In summary, we present here direct evidence for the formation of covalent bonded styrene(isoprene)$_2$ oligomer and isoprene dimer ions following the ionization of the gas phase styrene−isoprene binary clusters. This is a significant result because it provides information on the structure and mechanism of formation of the early stages of polymerization and copolymerization reactions. Furthermore, the conversion of vdW clusters into covalent bonded oligomer ions opens the possibility for depositing size-selected oligomers on a variety of surfaces for a wide range of potential applications.



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References and Notes

(1) Odian, G. *Principles of Polymerization,* 4th ed.; Wiley-Interscience: New York, 2004.
(2) El-Shall, M. S.; Marks, C. *J. Phys. Chem*. **1991**, *95*, 4932.
(3) Tsukuda, T.; Kondow, T. *J. Am. Chem. Soc.* **1994**, *116*, 9555.
(4) El-Shall, M. S.; Yu, Z. *J. Am. Chem. Soc.* **1996**, *118*, 13058.
(5) Reiss, H. *Acc. Chem. Res.* **1997**, *30*, 297.
(6) Pithawalla, Y. B.; Gao, J.; Yu, Z.; El-Shall, M. S. *Macromolecules* **1996**, *29*, 8558.
(7) Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 7125.
(8) Pithawalla, Y. B.; Meot-Ner, M.; Gao, J.; El Shall, M. S. *J. Phys. Chem. A* **2001**, *105*, 3908.
(9) Alsharaeh, E. H.; Ibrahim, Y. M.; El-Shall, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 6164.
(10) Vann, W.; El-Shall, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 4385.
(11) Deakin, L.; Den Auwer, C.; Revol, J. F.; Andrews, M. P. *J. Am. Chem. Soc*. **1995**, *117*, 9916.
(12) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc*. **1994**, *116*, 6895; **1996**, *118*, 2872.
(13) *(*13) *See for example*; Lewis, F. D. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Chapter 4. Bauld, N. L. *Adv. Electron-Transfer Chem.* **1992**, *2*, 1−66.
(14) Mahmoud, H.; Germanenko, I. N.; Ibrahim, Y.; El-Shall, M. S. *J. Phys. Chem. A* **2003**, *107*, 5920.
(15) Linstrom, P. J., Mallard, W. G., Eds. *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).