

# Concerted Reactions of Charge Transfer and Covalent Bond Formation in Ionized Alkylbenzene–Isobutene Clusters. Copolymerization of Styrene–Isobutene and $\alpha$ -Methylstyrene–Isobutene Clusters

M. Samy El-Shall\* and Zhongde Yu

Contribution from the Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-2006

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**Abstract:** Mixed aromatic–isobutene clusters ( $A_mI_n$ , where A = toluene, *p*-xylene, mesitylene, 1,2,4-trimethylbenzene, styrene, and  $\alpha$ -methylstyrene) have been ionized by resonant two-photon ionization in the vicinity of the aromatic's  $0_0^0$  transition, and by two-photon ionization using 248 nm and 193 nm photons. Intracluster reactions leading to the formation of isobutene dimer cation  $C_8H_{16}^{+}$  are observed following the two photon ionization of the binary clusters only when the aromatic precursor has an ionization potential greater than or equal to that of the isobutene dimer. The observation of this process in the gas phase and within clusters suggests that a similar initiation mechanism may take place in solution following the photoionization of an appropriate aromatic initiator. Evidence has been presented that points to the successive covalent additions of isobutene molecules on styrene and  $\alpha$ -methylstyrene radical cations within the binary clusters. The intracluster reactions appear to yield two intermediate isomers. One isomer is consistent with an acyclic 1,4-radical cation which can initiate further polymerization via cationic or radical propagation depending on the nature of the available monomers in the cluster. The second isomer has probably a cyclic structure in which the ionic and the radical sites are interacting, and this gives rise to a stable product which manifests itself in the appearance of an enhanced ion intensity for the styrene–isobutene or the  $\alpha$ -methylstyrene–isobutene radical cation. The effect of water on the cluster copolymerization has been examined. Intracluster proton transfer reactions within the  $(\alpha\text{-methylstyrene})(\text{isobutene})(\text{water})_n$  species with  $n \geq 3$  producing protonated water clusters have been observed. The results are consistent with the distonic structure of the  $\alpha$ -methylstyrene–isobutene radical cation which can initiate either cationic or radical propagation. These cluster studies present good model systems to examine the early stages of copolymerization and the reactivity ratios of different monomers.

## 1. Introduction

Despite the fact that solutions and bulk liquids are the preferred medium for many industrial and laboratory polymerization processes, our fundamental understanding of the complex reactions in solution which include initiation, propagation, chain transfer, inhibition, termination, and solvent effects remains limited.<sup>1–3</sup> In an effort to elucidate the mechanisms of initiation and the early stages of cationic polymerization, we and others have studied the cationic reactions in the gas phase and within molecular clusters.<sup>4–17</sup> The goal of our research has been to establish a multidisciplinary approach by initiating

a close dialogue between gas phase, clusters, and condensed phase polymer chemistry with the implicit assumption that this

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 1, 1996.

(1) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; John Wiley: New York, 1982.

(2) Jenkins, A. D.; Ledwith, A. *Reactivity, Mechanism and Structure in Polymer Chemistry*; John Wiley: London, 1974.

(3) Odian, G. *Principles of Polymerization*; McGraw-Hill: New York, 1970.

(4) El-Shall, M. S.; Marks, C. *J. Phys. Chem.* **1991**, *95*, 4932. El-Shall, M. S.; Schriver, K. E. *J. Chem. Phys.* **1991**, *95*, 3001 (1991). El-Shall, M. S. In *The Physics and Chemistry of Finite Systems: From Clusters to Crystals*; Jena, P., Rao, B. K., Khanna, S., Eds.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. II, 1083.

(5) Coolbaugh, M. T.; Vaidyanathan, G.; Peifer, W. R.; Garvey, J. F. *J. Phys. Chem.* **1991**, *95*, 8337. Coolbaugh, M. T.; Whitney, S. G.; Vaidyanathan, G.; Garvey, J. F. *J. Phys. Chem.* **1992**, *96*, 9139.

(6) Tsukuda, T.; Kondow, T. *J. Chem. Phys.* **1991**, *95*, 6989. Tsukuda, T.; Kondow, T. *J. Phys. Chem.* **1992**, *96*, 5671. Tsukuda, T.; Terasuki, A.; Kondow, T.; Scarton, M. G.; Dessent, C. E.; Bishea, G. A.; Johnson, M. A. *Chem. Phys. Lett.* **1993**, *201*, 351. Tsukuda, T.; Kondow, T. *Chem. Phys. Lett.* **1992**, *197*, 438. Tsukuda, T.; Kondow, T. *J. Am. Chem. Soc.* **1994**, *116*, 9555.

(7) Meot-Ner (Mautner), M.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 5576.

(8) Guo, B. C.; Castleman, A. W., Jr. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 464. Guo, B. C.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6152.

(9) Daly, G. M.; El-Shall, M. S. *Z. Phys. D.* **1993**, *26S*, 186. Daly, G. M.; El-Shall, M. S. *J. Phys. Chem.* **1994**, *98*, 696. Daly, G. M.; El-Shall, M. S. *J. Phys. Chem.* **1995**, *99*, 5283. Daly, G. M.; Pithawalla, Y. B.; Yu, Z.; El-Shall, M. S. *Chem. Phys. Lett.* **1995**, *237*, 97. El-Shall, M. S. *Polym. Preprints* **1996**, *37*, 367.

(10) Brodbelt, J. S.; Liou, C. C.; Maleknia, S.; Lin, T. J.; Lagow, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 11069.

(11) Raksit, A. B.; Bohme, D. K. *Can. J. Chem.* **1984**, *62*, 2123. Forte, L.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 87. Forte, L.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1989**, *67*, 1576. Wang, J.; Javahery, G.; Petrie, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9665. Wang, J.; Javahery, G.; Petrie, S.; Hopkinson, A. C.; Bohme, D. K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 206. Wang, J.; Baranov, V.; Bohme, D. K. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 261.

(12) Desai, S. R.; Feigerle, C. S.; Miller, J. *J. Phys. Chem.* **1995**, *99*, 1786.

(13) Meot-Ner (Mautner), M.; Sieck, L. W.; El-Shall, M. S.; Daly, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 7737.

(14) El-Shall, M. S.; Daly, G. M.; Yu, Z.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1995**, *117*, 7744.

(15) Vann, W.; El-Shall, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 4385. Vann, W.; Daly, G. M.; El-Shall, M. S. In *Laser Ablation in Materials Processing: Fundamentals and Applications*; Braren, B., Dubowski, J., Norton, D., Eds.; Materials Research Society Symposium Proceedings Series, 1993; pp 285, 593.

(16) Deakin, L.; Den Auwer, C.; Revol, J. F.; Andrews, M. P. *J. Am. Chem. Soc.* **1995**, *117*, 9916.

(17) El-Shall, M. S.; Slack, W. *Macromolecules* **1995**, *28*, 8546. El-Shall, M. S. *Appl. Surface Sci.*, in press. El-Shall, M. S. In *Laser Processing: Surface Treatment and Film Deposition*; Mazumder, J., Ed.; NATO-ASI Series, Kluwer Academic Publishers: Dordrecht, 1996.

dialogue will provide a molecular level understanding of the competitive reaction channels in a typical polymerization system. Of particular interest is the process of cluster polymerization where sequential addition reactions can be studied in a medium intermediate between the gas and condensed phases. A significant challenge lies in the possibility of converting van der Waals (vdw) molecular clusters into covalent-bonded, size specific polymeric species which 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.<sup>15–17</sup>

In a recent paper,<sup>18</sup> we reported a new class of gas phase charge transfer reactions from ionized aromatics to neutral olefins, concerted with olefin dimerization. These reactions suggest that nucleophilic attack by olefin molecules in ionic condensation is possible on reactants bearing only a small fractional molecular charge. These reactions can also be studied within vdw clusters of the olefin monomers doped with an aromatic molecule of a lower ionization potential (IP). Selective ionization of the aromatic dopant will produce the desired radical cation to which the olefin monomers are already attached by ion–neutral forces within the cluster. This situation may result in an efficient charge transfer concerted with covalent dimerization of the olefins which may be followed by sequential additions on the resulting dimer cation to produce larger olefin oligomers.

In the present paper we address this issue by investigating the intracuster reactions following the multiphoton ionization of the binary aromatic–isobutene clusters ( $AI_n$ , I = isobutene) where the aromatic components (A) are toluene, *p*-xylene, mesitylene, and 1,2,4-trimethylbenzene. Since the ionization potential of A is lower than that of isobutene (IP = 9.239 eV),<sup>19</sup> the initially formed cluster ion ( $A^+I_n$ ) can undergo a charge transfer reaction concerted with dimerization to generate the  $I_2^{+}$  species if  $IP(I_2) < IP(A)$ . The efficiency of this process is determined by the relative IP of  $I_2$  and of the aromatic chromophore (A). The aim here is to establish whether a correlation exists between the IP of the aromatic dopant and the generation of the isobutene dimer cation within the binary cluster. This correlation is expected if an intracuster charge transfer mechanism is responsible for activating the dimerization reaction.

Of particular interest is the effect of the excess energy deposited within the cluster ion as a result of the ionization process. Since cluster ions may dissipate any internal energy into the heat bath of the cluster modes, the product distributions should reflect this process.<sup>20,21</sup> Therefore, the effect of excess energy can be examined by varying the energy of the two photons to ionize the binary clusters  $A \cdot I_n$  and measuring the product distributions corresponding to different reaction channels. To investigate this effect, we compare the  $0_0^0$  resonant two-photon ionization (R2PI) of the  $AI_n$  clusters where the energy of the two photons is similar to or less than the IP of isobutene with ionization using the 248 nm or the 193 nm photons where the two photons' energies are 10.00 eV and 12.85 eV, respectively.

Another objective of the present work is to investigate the intracuster reactions between the radical cations of styrene and

$\alpha$ -methylstyrene with neutral isobutene. These systems are interesting from several points of view. Unlike the alkylbenzene radical cations with which neutral isobutene may interact noncovalently similar to ionic charge transfer complexes,<sup>22</sup> the radical cations of styrene and  $\alpha$ -methylstyrene will most likely react with isobutene by covalent addition which may lead to sequential polymerization. The addition reactions of a series of alkenes with a series of styrene and substituted styrene radical cations have recently been studied by laser flash photolysis in solutions.<sup>23,24</sup> 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.<sup>25</sup> 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.<sup>23</sup> Therefore, gas phase and intracuster reactions are desirable in order to provide detailed information on the mechanisms of these reactions. Furthermore, these reactions offer excellent model systems to study the early stages of copolymerization initiated by radical cations where competitive sequential additions and concerted charge transfer may take place. The comparison between gas phase, cluster, and condensed phase reactions should also provide new information on the conditions required to optimize the yield of these reactions which may have some practical relevance for developing new synthesis approaches.

## 2. Experimental Section

Aromatic–isobutene binary clusters were generated by pulsed adiabatic expansion in a supersonic cluster beam apparatus.<sup>14</sup> The essential elements of the apparatus are jet and beam chambers coupled to a time-of-flight (TOF) mass spectrometer. During operation, a vapor mixture of 2–4% aromatic compound, 1–10% isobutene (Aldrich, 99.9% purity) in He (ultrahigh purity, Spectra Gases 99.99%) at a pressure of 2–4 bar, is expanded through a conical nozzle (500  $\mu$ m diameter) in pulses of 200–300  $\mu$ s duration at repetition rates of 6–10 Hz. The concentration of the aromatic compound is kept as small as possible in order to minimize the formation of aromatic clusters or higher aromatic–isobutene clusters ( $A_mI_n$ ). The jet is skimmed and passed into a high vacuum chamber which is maintained at  $8 \times 10^{-8} - 2 \times 10^{-7}$  mbar. 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 was provided by a dye laser (Lambda Physik FL3002) pumped by an excimer laser (Lambda Physik LPX-101). Coumarin 503 or 540 dye (Exciton) was used with a  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> crystal (CSK Co.) cut at 52° to generate a tunable frequency-doubled output of  $10^{-8}$  s pulses. The spatially filtered ultraviolet radiation (0.1–0.3 mJ per pulse) was shaped with a 60 cm lens to provide a 1–2 mm<sup>2</sup> beam in the ionization region. The laser system has  $\approx 0.10$  cm<sup>-1</sup> bandwidth at 40 000 cm<sup>-1</sup> (250 nm). The two photon ionization at a fixed frequency was achieved by either KrF (248 nm) or ArF (193 nm) radiation provided by an excimer laser (Lumonics Hyper Ex-400). Our TOF mass spectrometer is based on

(18) Meot-Ner (Mautner), M.; Pithawalla, Y. B.; Gao, J.; El-Shall, M. S. *J. Am. Chem. Soc.*, submitted for publication.

(19) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements, 1971–1981*, National Bureau of Standards: Washington, DC, 1982.

(20) Castleman, A. W., Jr.; Wei, S. *Annu. Rev. Phys. Chem.* **1994**, *45*, 685.

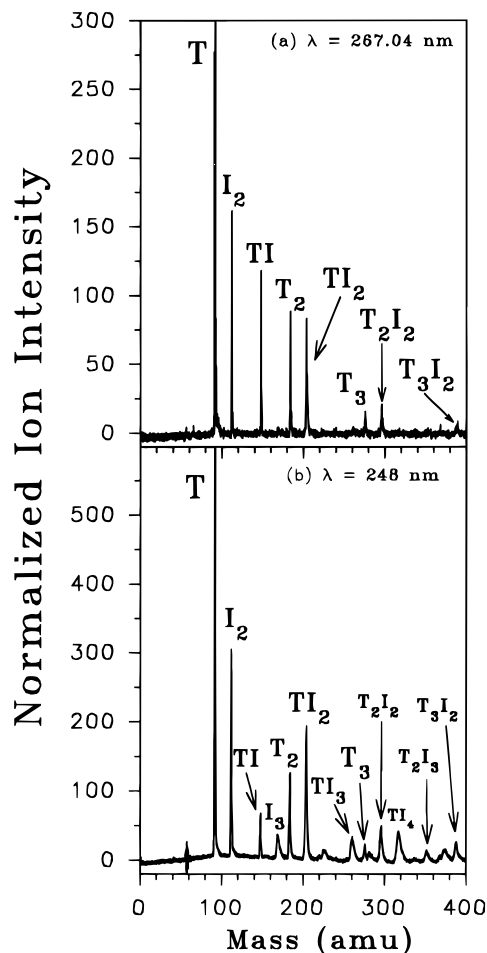
(21) Brutschy, B. *Chem. Rev.* **1992**, *92*, 1567.

(22) Meot-Ner (Mautner), M.; El-Shall, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 4386. El-Shall, M. S.; Kafafi, S. A.; Meot-Ner (Mautner), M.; Kertesz, M. *J. Am. Chem. Soc.* **1986**, *108*, 4391. El-Shall, M. S.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1987**, *91*, 1088.

(23) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872.

(24) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895. Johnston, L.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564. Workentin, M. S.; Schepp, N. P.; Johnston, L. J.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1994**, *116*, 1141. Johnston, L.; Schepp, N. P. *J. Pure Appl. Chem. Soc.* **1995**, *67*, 71.

(25) 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. Hoffmann, U.; Gao, Y.; Pandey, B.; Klinge, S.; Warzecha, K. D.; Kruger, C.; Roth, H. D.; Demuth, M. *J. Am. Chem. Soc.* **1993**, *115*, 10358. Connor, D. A.; Arnold, D. R.; Bakshi, P. K.; Cameron, T. S. *Can. J. Chem.* **1995**, *73*, 762.



**Figure 1.** Mass spectra of toluene-isobutene mixed clusters ( $T_nI_n$ ) taken at different wavelengths as indicated.

the Wiley-McLaren three-grid space focusing design.<sup>26</sup> The cluster ions are electrostatically accelerated in a two-stage acceleration region (300–400V/cm), travel a field-free region ( $\approx 110$  cm in length), and are then accelerated to a two-stage microchannel-plate detector. Deflection plates are used to compensate for the cluster beam velocity. The deflection voltage is adjusted to optimize the signal for a particular mass range of interest. The TOF spectrum is recorded by digitizing the amplified current output of the detector with a 350 MHz digitizer (LeCroy 9450) and averaged over 500–1000 pulses.

### 3. Results and Discussion

**A. Toluene-Isobutene Binary Clusters (T/I).** The origin of the S1 electronic state of toluene (i.e., the  $0_0^0$  transition) occurs at  $37\,482\text{ cm}^{-1}$  (266.79 nm).<sup>27</sup> This is more than half the ionization energy of toluene (8.82 eV), and thus R2PI could result in an excess energy of at least 0.44 eV in the binary cluster ions  $T^+I_n$ . Most of this energy is carried away by the ejected electron, and the remaining energy can be distributed among the vibrational modes of the cluster. Since the IP (toluene) < IP (isobutene), no direct charge transfer can take place under low laser power conditions where most of the ionization events are accomplished by two photon processes. Indeed, no  $C_4H_8^+$  ion signal is observed as shown in Figure 1a which displays the mass spectrum of isobutene/toluene mixed clusters obtained by R2PI at  $\lambda = 267.04$  nm, (i.e., to the red of the toluene  $0_0^0$  transition). A significant signal corresponding to the mass of the isobutene dimer ( $I_2$ ,  $m/z$  112) is, however, clearly visible.

Since the energy of the two photons is similar to the IP of isobutene (IP = 9.239 eV), one must consider the possibility of direct two photon ionization of isobutene or charge transfer from excited toluene<sup>+</sup> to isobutene as possible explanations for the origin of  $I_2^+$ . For neat isobutene clusters, i.e., in the absence of toluene, no ions could be detected by using the same laser power and frequency range used in the photoionization of the mixed toluene-isobutene clusters. Therefore, direct photoionization of isobutene clusters present in the toluene/isobutene-beam is very improbable. This means that all the observed ions must be derived either from the mixed clusters  $T_nI_n$  or from the neat toluene clusters,  $T_n$ .

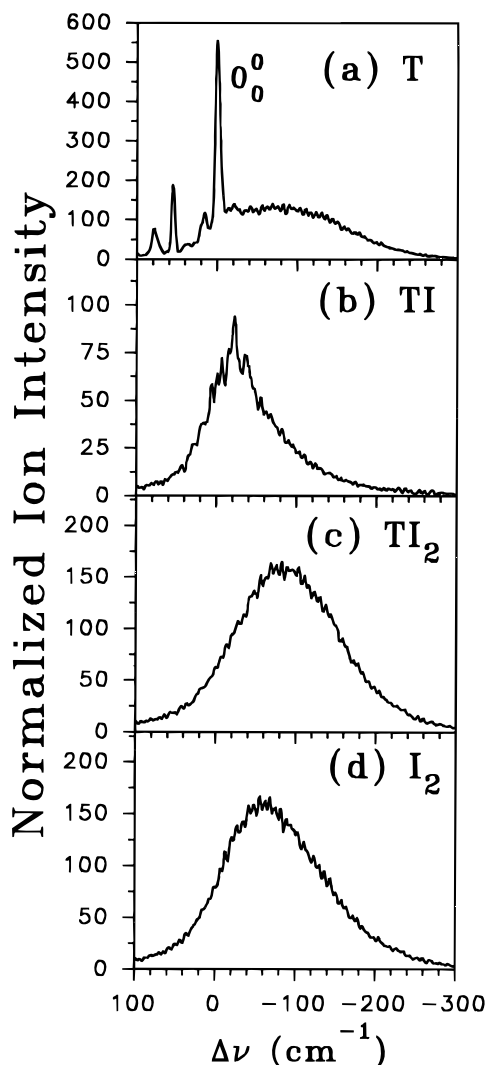
The absence of ion signal corresponding to  $C_4H_8^+$  argues against direct charge transfer from excited  $T^+$  to isobutene followed by a reaction with another isobutene molecule to form the dimer cation  $I_2^+$  within the cluster. This is consistent with the small amount of excess energy available for  $T^+$  which is most likely distributed within the vibrational modes of the ion. It is also important to note that the *tert*-butyl carbocation,  $C_4H_9^+$  (a product of the reaction of  $C_4H_8^+$  with neutral isobutene),<sup>13</sup> is not detected under the two photon ionization regime. It should be noted, however, that in the case of benzene/isobutene clusters<sup>14</sup> where direct charge transfer from benzene<sup>+</sup> to isobutene is exothermic (IP (benzene) > IP (isobutene)), the  $C_4H_8^+$  ion is observed along with its two reaction products with isobutene to form  $C_4H_9^+$  and  $C_8H_{16}^+$ . Therefore, the toluene/isobutene results suggest that the  $C_8H_{16}^+$  dimer is produced by an intracuster reaction involving the toluene ion and a neutral isobutene subcluster,  $I_n$ , with  $n \geq 2$  rather than a reaction of the  $C_4H_8^+$  ion with its neutral molecule.

To further investigate the mechanism leading to the  $I_2^+$  production, the dependence of the  $I_2^+$  signal on the two photon ionization energy was examined. The mixed toluene-isobutene clusters were ionized using the KrF excimer laser (248 nm); the resulting mass spectrum is shown in Figure 1b. Since the sum of the two photon energies (10.0 eV) is now significantly higher than the IP of isobutene (9.23 eV), one must consider the possibility of fragmentation of the  $(T \cdot I)^+$  dimer into  $I^+ + T$  channel (i.e., producing the  $C_4H_8^+$  ion). However, a careful laser power study revealed no evidence for dissociation yielding either  $C_4H_8^+$  or  $C_4H_9^+$  within the two photons' regime. This seems surprising considering that the 248 nm two photon ionization results in an excess energy of about 0.8 eV above the dissociation threshold into the  $I^+ + T$  channel. As shown in Figure 1b, the mass spectrum obtained at 248 nm is very similar to that obtained at the 267 nm (Figure 1a). This indicates that most of the excess energy is rapidly distributed among the vibrational modes of the ion and electronically excited ions are not formed. Only when we increase the laser fluence, thus enhancing the  $1 + 2$  ionization, can we induce fragmentation into the  $C_4H_8^+$  channel which is accompanied by the observation of the  $C_4H_9^+$  ion and also chemical fragmentation from toluene<sup>+</sup>. This suggests that these fragments are produced by subsequent absorption of photons by the isobutene dimer and the toluene radical cations. We note that a similar behavior was observed by Castleman's group in their study of the *p*-xylene/ $NH_3$  mixed clusters.<sup>28</sup> They observed no fragmentation into  $C_3H_{10}^+$  or  $NH_4^+$  channels even with ionizing energy about 0.5 eV above the dissociation thresholds into these channels.

In order to gain information regarding the origin of the isobutene dimer ion, the mixed toluene-isobutene clusters were ionized by scanning the tunable radiation across the  $0_0^0$  resonance region of the S1  $\leftarrow$  S0 transition of toluene and

(26) Wiley, W. C.; McLaren, I. H. *Rev. Sci. Instrum.* **1955**, *26*, 1150.  
 (27) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.

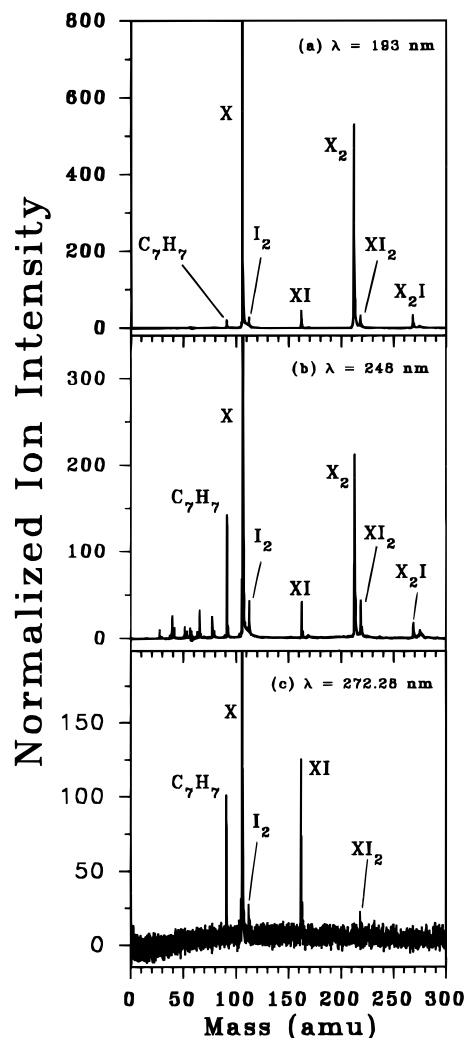
(28) Dao, P. D.; Castleman, A. W., Jr. *J. Chem. Phys.* **1986**, *84*, 1435.



**Figure 2.** Integrated ion intensities as a function of spectral shift (with respect to the  $0_0^0$  transition of the bare toluene molecule) recorded for the mass channels corresponding to (a) toluene (T), (b) toluene-isobutene (TI), (c) toluene-(isobutene)<sub>2</sub> (TI<sub>2</sub>), and (d) (isobutene)<sub>2</sub> (I<sub>2</sub>).

measuring the ions produced mass selectively by TOF mass spectrometry. The resulting spectral features in the mass channels corresponding to T, T·I, T·I<sub>2</sub> and I<sub>2</sub> are shown in Figure 2. It is clear that the mixed clusters (T·I<sub>n</sub>) exhibit spectral features red shifted with respect to the toluene  $0_0^0$  origin. This is expected based on the predominant dispersive nature of the intermolecular interactions between toluene and isobutene. For example, previous R2PI studies of toluene clustering with alkane and alkene have shown appreciable red shifts in the electronic origin of the S1 state in the toluene  $0_0^0$  transition.<sup>29</sup> It is clear that the magnitude of the red shift increases in going from T·I to T·I<sub>2</sub> which reflects the increase in the attractive dispersion interaction in larger neutral clusters. It is also readily apparent that the width and the peak positions of the spectral features recorded in the T·I<sub>2</sub> and I<sub>2</sub> channels are rather similar but quite different from the T·I channel. Therefore, the data suggest that the I<sub>2</sub><sup>•+</sup> ion is generated as a result of a dissociative charge transfer within the T·I<sub>2</sub> cluster following its resonance ionization. However, we can't exclude the possibility that larger T·I<sub>n</sub> clusters with  $n > 2$  could be the actual precursors of the I<sub>2</sub><sup>•+</sup> ions. Since the lower limit of the binding energy of the isobutene dimer cation has been measured<sup>13</sup> as 32 kcal/mol, it

(29) Bernstein, E. R. In *Atomic and Molecular Clusters*; Bernstein, E. R., Ed.; Elsevier: New York, 1990; pp 551–764.

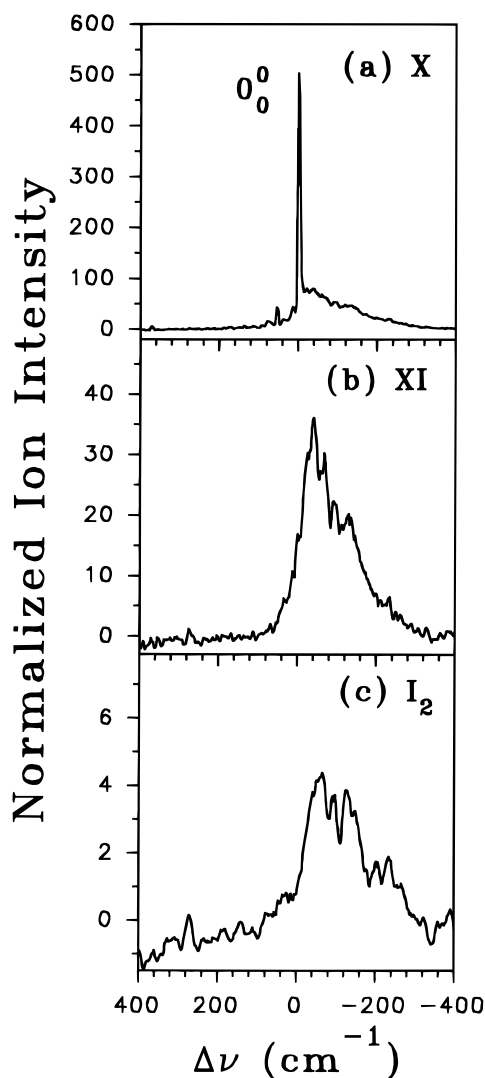


**Figure 3.** Mass spectra of *p*-xylene-isobutene mixed clusters (X<sub>m</sub>I<sub>n</sub>) taken at different wavelengths as indicated.

appears reasonable to assume that this energy would cause rapid evaporation of few isobutene molecules from the larger T·I<sub>n</sub> clusters. For smaller clusters such as T·I<sub>2</sub> or T·I<sub>3</sub>, hot I<sub>2</sub><sup>•+</sup> ions could be produced since efficient evaporative cooling may not be achieved.

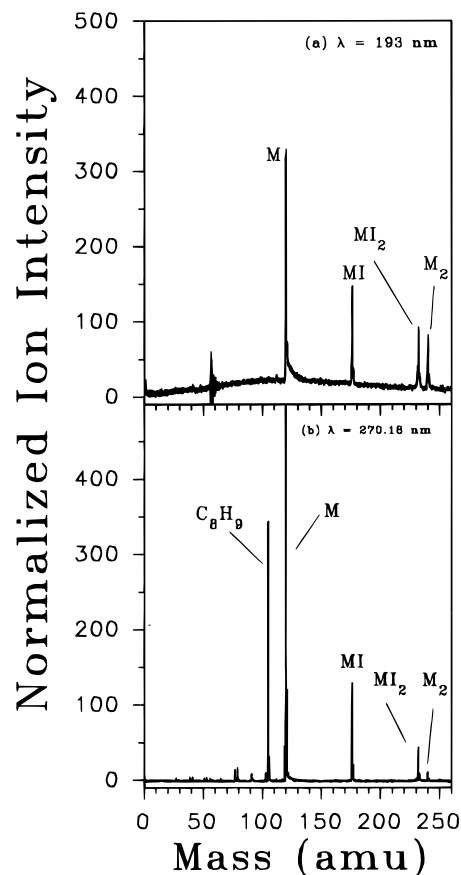
It is instructive to compare the intracluster reactions of the toluene-isobutene system with the benzene-isobutene clusters previously studied.<sup>14</sup> As mentioned above, in the latter case, intracluster charge transfer generates the C<sub>4</sub>H<sub>8</sub><sup>•+</sup> ion which then undergoes the proton transfer and the dimerization reactions to generate the C<sub>4</sub>H<sub>9</sub><sup>+</sup> and C<sub>8</sub>H<sub>16</sub><sup>•+</sup> ions, respectively, within the cluster. Because of the low IP of the isobutene dimer (8.5 eV), the most prominent species in the mass spectrum are those containing the isobutene dimer cation, i.e., I<sub>2</sub><sup>•+</sup>B<sub>m</sub> series (where B is benzene). The persistent dominance of the clusters containing I<sub>2</sub><sup>•+</sup> ions is also observed in the toluene system under a wide range of clustering conditions (vapor composition, carrier gas, seed ratio, etc.) as well as different ionization energies. This indicates that in both systems (benzene and toluene) the charge resides on the I<sub>2</sub> moiety and not on B or T. Interestingly, this particular distribution is not observed in other mixed clusters of isobutene with chromophores that have lower IP than I<sub>2</sub> such as *p*-xylene (IP = 8.44 eV) and 1,2,4-trimethylbenzene (IP = 8.27 eV) as will be discussed in the following sections.

**B. *p*-Xylene-Isobutene Binary Clusters (X/I).** Figure 3 displays the mass spectra of the *p*-xylene/isobutene binary



**Figure 4.** Integrated ion intensities as a function of spectral shift (with respect to the  $0_0^0$  transition of the bare *p*-xylene molecule) recorded for the mass channels corresponding to (a) *p*-xylene (X), (b) *p*-xylene-isobutene (XI), and (c) (isobutene) $_2$  ( $I_2$ ).

clusters obtained at different photoionization energies. In all cases, the generation of  $I_2^{*+}$  is observed at a diminished yield. For example, the intensity ratio of the  $I_2^{*+}$  ion signal to the *p*-xylene ( $X^{*+}$ ) ion signal (the strongest peak in the clusters mass spectrum) is 0.03 and 0.04 at laser ionization with 193 nm and 248 nm, respectively. The mixed clusters can be resonantly ionized by two photon absorption red shifted from the  $0_0^0$  transition of *p*-xylene ( $37\,000\text{ cm}^{-1}$ )<sup>27</sup> as shown in Figure 3c. The integrated ion intensities as a function of laser wavelength obtained by monitoring the mass channels corresponding to *p*-xylene (X), *p*-xylene-isobutene ( $X\cdot I$ ), and isobutene dimer ( $I_2$ ) are shown in Figure 4. Because of the lack of sufficient ion intensity corresponding to the  $X\cdot I_2$  channel, it is not possible to compare the integrated ion intensities of  $I_2$  and  $X\cdot I_2$ . However, from the amount of the red shift observed in Figure 4c, it can be concluded that  $I_2^{*+}$  is generated via resonance ionization of larger  $X\cdot I_n$  clusters followed by dissociation into the  $I_2^{*+}$  channel. As shown in Figure 3c, a small signal corresponding to  $I_2^{*+}$  appears in the mass spectrum obtained by resonant ionization at  $\lambda = 272.28\text{ nm}$ . This can be explained by comparing the ionization energy of X (8.44 eV) with that measured for  $I_2$  (8.5 eV). Because of the small difference in the  $\Delta\text{IP}$ , both cluster ions  $X^{*+}\cdot I_2$  and  $X\cdot I_2^{*+}$  are expected to be present. Since the energy of the two photons at  $\lambda = 272.28$

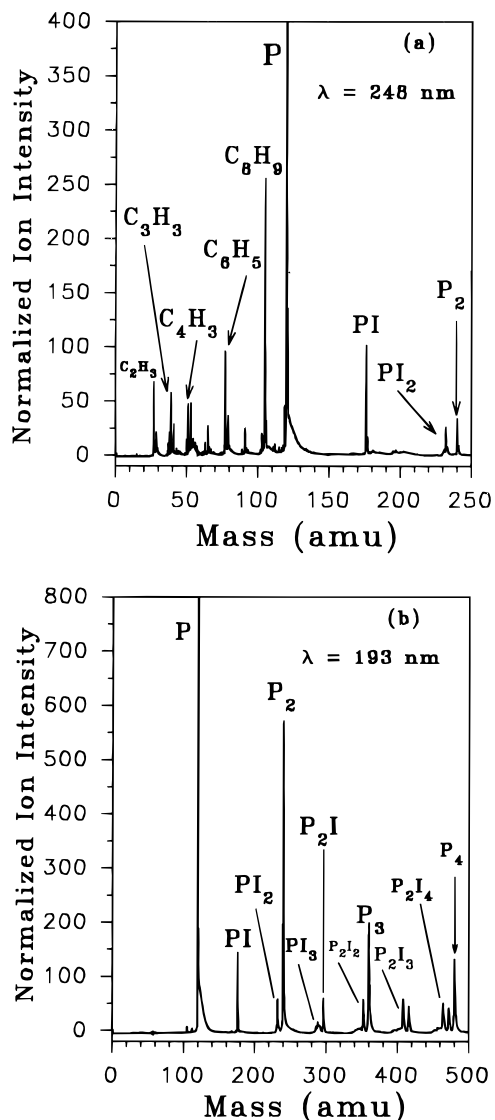


**Figure 5.** Mass spectra of mesitylene-isobutene mixed clusters ( $M_nI_n$ ) taken at different wavelengths as indicated.

nm is 9.11 eV (i.e., 0.7 eV higher than the ionization energy of X), the vibrationally excited  $X^{*+}\cdot I_2$  and  $X\cdot I_2^{*+}$  ions can dissociate into the  $X^{*+}$  and  $I_2^{*+}$  channels, respectively, with the major product appearing in the former channel (low energy channel).

**C. Mesitylene-Isobutene (M/I) and 1,2,4-Trimethylbenzene-Isobutene Binary Clusters.** Figure 5 displays the TOF mass spectra of mesitylene-isobutene ( $M_n\cdot I_n$ ) binary clusters obtained by excimer laser photoionization (193 nm, Figure 5a) and also by resonance ionization at 270.18 nm (Figure 5b). In both cases the mixed clusters  $M_n\cdot I_n$  are observed but no signal due to  $I_2^{*+}$  could be detected. This indicates that the main dissociation channel of the  $M\cdot I_2^{*+}$  cluster ion is to  $M^+$  and not  $I_2^{*+}$ . This is consistent with the ionization energy of mesitylene (IP (M) = 8.4 eV) which is lower than that of  $I_2$  (8.5 eV).<sup>13</sup> Thus, the charge mainly resides on M, i.e.,  $M^{*+}\cdot I_2$ . It is also significant to indicate that experiments carried out under increased laser fluences to enhance the 1 + 2 fragmentation did not yield a signal corresponding to  $I_2^{*+}$  or to any of its dissociation products ( $C_7H_{13}^+$ ,  $C_6H_{11}^+$ ,  $C_4H_9^+$ , or  $C_4H_8^{*+}$ ).<sup>14</sup>

The system 1,2,4-trimethylbenzene [here denoted P (pseudocumene)]-isobutene exhibits similar results to the mesitylene-isobutene clusters. As shown in Figure 6, the TOF mass spectra obtained by excimer laser ionization at 248 nm and 193 nm reveal no signal due to  $I_2^{*+}$  although the binary cluster ions  $P_m\cdot I_n^{*+}$  are clearly abundant. Of particular interest is the mass spectrum in Figure 6a obtained under high laser fluence as evident from the extensive fragmentation of the 1,2,4-trimethylbenzene parent ion. The absence of any fragment products from  $I_2^{*+}$  clearly precludes its generation. This again is in accord with the low ionization energy of 1,2,4-trimethylbenzene (8.27 eV) which makes the intracluster charge transfer process producing  $I_2^{*+}$  prohibitively endothermic.



**Figure 6.** Mass spectra of 1,2,4-trimethylbenzene (pseudocumene)–isobutene mixed clusters ( $P_mI_n$ ) taken at (a) 248 nm with high laser fluence and (b) 193 nm with low laser fluence.

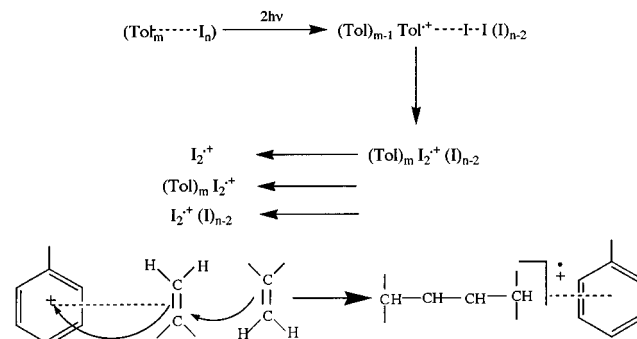
**Table 1.** Relative Yields of the Isobutene Radical Cation Dimer ( $C_8H_{16}^{+\bullet}$ ) Formed in Mixed Clusters with Different Chromophores

chromophore (A)	ionization potential, eV	$R^a = I_2/A$
benzene	9.25	1.64
toluene	8.82	0.36
<i>p</i> -xylene	8.44	0.04
mesitylene	8.41	0.01
1,2,4-trimethylbenzene	8.27	>0.01

<sup>a</sup>  $R$  is the ion intensity ratio of  $I_2$ , ( $C_8H_{16}^{+\bullet}$ ) to the parent chromophore ion signal ( $A^{+\bullet}$ ).

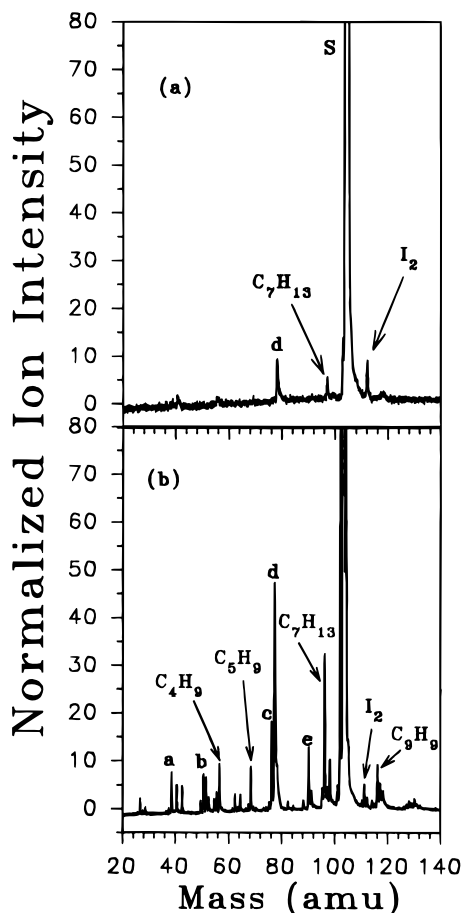
**D. Intracluster Charge Transfer Mechanism.** The above results indicate that the dimerization of isobutene is induced by an intracluster charge transfer reaction from the ionized aromatic chromophore (A). The important point is that the process occurs when  $IP(A) < IP(I)$ ; i.e., the reaction is energetically possible only when it is concerted with covalent condensation to produce  $I_2^{+\bullet}$ . Table 1 compares the relative yield of  $I_2^{+\bullet}$  formed in binary clusters with different aromatic chromophores. It is important to note that the ion intensity ratio  $AI_n/A$  is almost the same for all the chromophores studied. In all cases, the ion intensity of the chromophore A is the largest peak in the mass spectrum. The strong correlation observed between the production of  $I_2^{+\bullet}$  and the IP of the chromophore

### Scheme 1



supports the mechanism of intracluster charge transfer concerted with covalent condensation. This also argues against the mechanism of ion-assisted neutral reaction. According to this mechanism, two isobutene molecules can cluster on the aromatic ion and react to form a condensation product (isobutene neutral dimer,  $I_2$ ) which has a lower IP than the chromophore (A), and therefore an exothermic electron transfer from  $I_2$  to  $A^{+\bullet}$  takes place. This mechanism can explain the correlation between the extent of  $I_2^{+\bullet}$  formation and the IP of the chromophore since the efficiency of the charge transfer process is expected to depend on the IP of the chromophore. However, the results of the high laser fluence photoionization experiments can't be explained based on this mechanism. For example, if  $I_2$  neutral is formed but could not be ionized via charge transfer from the aromatic ion  $A^{+\bullet}$ , it is expected that the  $I_2^{+\bullet}$  ion should be produced under high laser fluence. This is because the 1 + 2 ionization of the aromatic molecule produces molecular fragments having ionization potentials higher than that of the isobutene dimer. Therefore, exothermic charge transfer from these fragments should generate  $I_2^{+\bullet}$  within the cluster. These fragment ions were observed (Figures 5b and 6a) but no  $I_2^{+\bullet}$  was detected. Therefore, we conclude that a neutral reaction producing a covalent bonded  $I_2$  within the cluster is very improbable and that the binary neutral cluster  $A \cdot I_n$  is best described as an aromatic chromophore (A) solvated within a cluster of isobutene molecules. The overall process starting with the ionization of the aromatic center and the charge transfer concerted with the formation of  $I_2^{+\bullet}$  is illustrated in Scheme 1. It is expected that the energy released by the covalent bond formation of the dimer serves to blow off the surrounding toluene and isobutene molecules, enabling the isobutene dimer ion to be detected as a bare molecule,  $I_2^{+\bullet}$ . For small clusters, the  $I_2^{+\bullet}$  could evaporate before all of its excess energy is transferred to the cluster. In this case, a vibrationally hot  $I_2^{+\bullet}$  is formed and species larger than the dimer are not expected to appear.

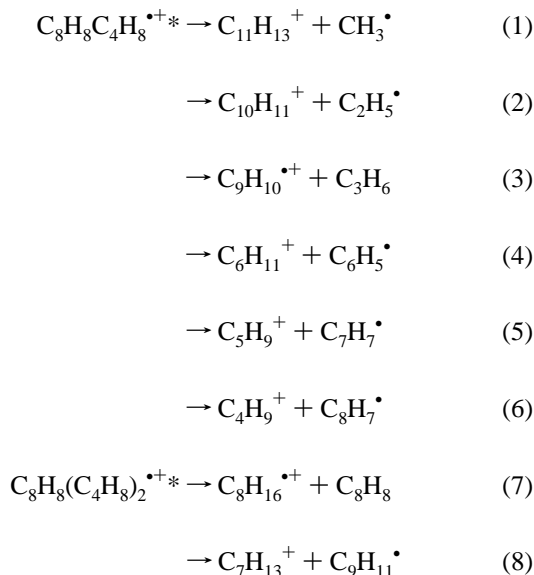
**E. Styrene–Isobutene (S/I) and  $\alpha$ -Methylstyrene–Isobutene (MS/I) Binary Clusters.** Figures 7 and 8 display the mass spectra obtained by the 248 nm ionization of the styrene–isobutene ( $S_m \cdot I_n$ ) and  $\alpha$ -methylstyrene–isobutene ( $MS_m \cdot I_n$ ) binary clusters, respectively. In both systems, isobutene dimer cation is observed with a diminished yield as expected from the IP values of styrene and  $\alpha$ -methylstyrene (8.42 and 8.5 eV, respectively). In addition, the mass spectra of the binary clusters reveal the generation of new ions which are not observed from the ionization of the single component aromatic clusters (i.e., styrene or  $\alpha$ -methylstyrene). For example, in the styrene–isobutene system under high laser fluences, peaks corresponding to  $m/z$  145, 131, 130, 118, 117, 112, 97, 83, 69, and 57 are observed. These peaks are assigned to the molecular formulas  $C_{11}H_{13}$ ,  $C_{10}H_{11}$ ,  $C_{10}H_{10}$ ,  $C_9H_{10}$ ,  $C_9H_9$ ,  $C_8H_{16}$ ,  $C_7H_{13}$ ,  $C_6H_{11}$ ,  $C_5H_9$ ,



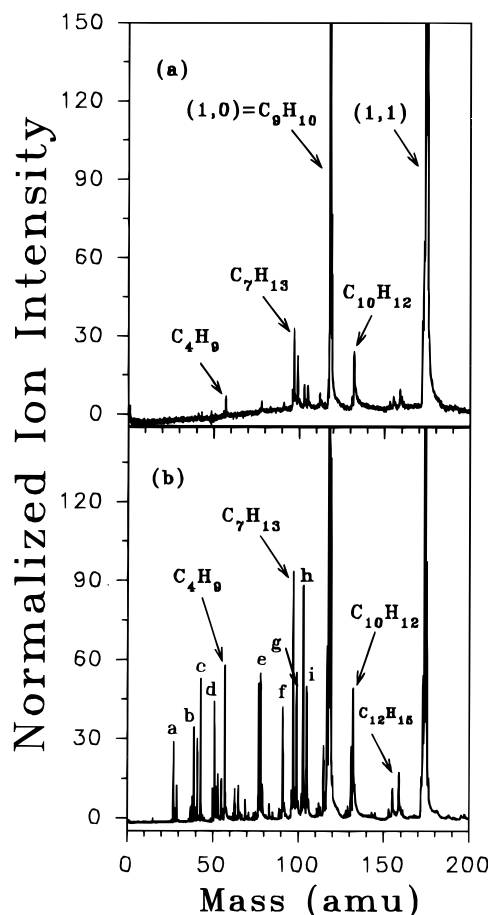
**Figure 7.** Mass spectra of styrene–isobutene mixed clusters ( $S_m I_n$ ) taken at 248 nm with (a) low laser fluence and (b) high laser fluence. Peaks a, b, c, d, and e with  $m/z$  39 ( $C_3H_3$ ), 51 ( $C_4H_3$ ), 77 ( $C_6H_5$ ), 78 ( $C_6H_6$ ), and 91 ( $C_7H_7$ ), respectively are due to known fragments from the photodissociation of the styrene parent ion.

and  $C_4H_9$ , respectively. These ions correspond to dissociation products from the excited styrene (isobutene) $_n^{*+}$ ,  $SI_n^{*+}$ , series as shown in Scheme 2 for the SI and  $SI_2$  ions.

#### Scheme 2



Similar results were obtained for the  $\alpha$ -methylstyrene–isobutene (MS/I) system, and product ions corresponding to the loss of

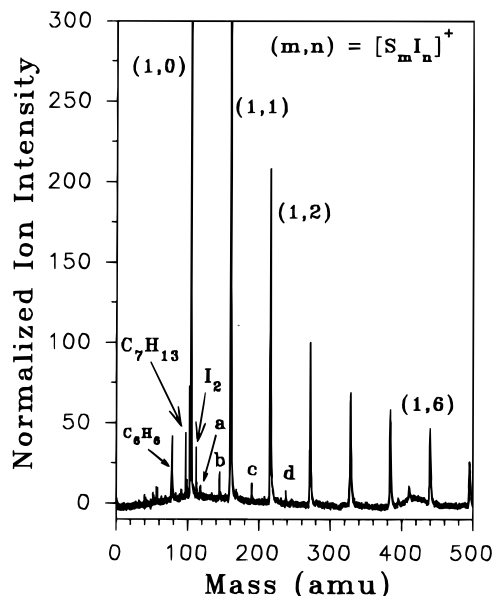


**Figure 8.** Mass spectra of  $\alpha$ -methylstyrene–isobutene mixed clusters ( $MS_m I_n$ ) taken at 248 nm with (a) low laser fluence and (b) high laser fluence. Peaks a, b, c, d, e, f, g, h, and i with  $m/z$  27 ( $C_2H_3$ ), 39 ( $C_3H_3$ ), 43 ( $C_3H_7$ ), 51 ( $C_4H_3$ ), 78 ( $C_6H_6$ ), 91 ( $C_7H_7$ ), 99 ( $C_7H_{15}$ ), 103 ( $C_8H_7$ ), and 105 ( $C_8H_9$ ), respectively, are due to known fragments from the photodissociation of the  $\alpha$ -methylstyrene parent ion.

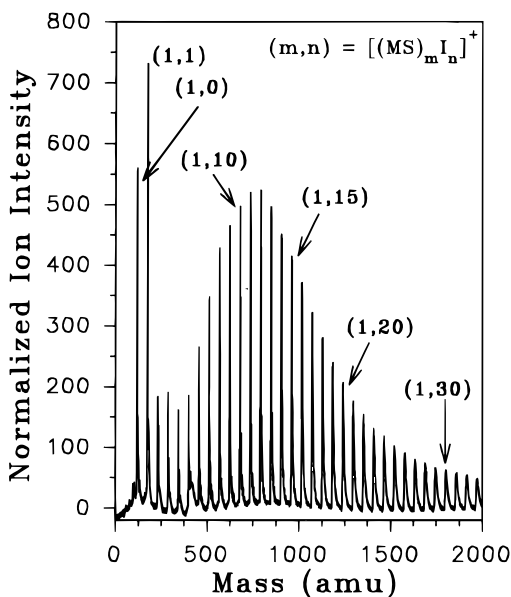
$CH_3^\bullet$ ,  $C_2H_5^\bullet$ ,  $C_3H_6$ ,  $C_3H_7^\bullet$ ,  $C_8H_{10}^\bullet$ ,  $C_9H_{10}^\bullet$ , and  $C_{10}H_{14}^\bullet$  were observed as shown in the mass spectrum displayed in Figure 8.

The observation of dissociation products corresponding to the loss of  $CH_3^\bullet$ ,  $C_2H_5^\bullet$ ,  $C_3H_7^\bullet$ , etc., provides strong evidence for the covalent additions of isobutene on the styrene or  $\alpha$ -methylstyrene radical cations. The projected extra energy resulting from the formation of covalent bonds would promote the dissociation of the newly formed oligomers, thus leading to the generation of the observed fragment ions. This behavior is quite common in intracuster polymerization and has been observed in the reactions of both radical cations and anions.<sup>4–6</sup>

Another characteristic feature of the SI/I and MS/I cluster mass spectra is the enhancement of the ion intensities corresponding to the  $SI_n$  and  $MSI_n$  series as shown in Figures 9 and 10 for styrene–isobutene and  $\alpha$ -methylstyrene–isobutene systems, respectively. This feature is observed over a wide range of experimental conditions including the relative concentrations of the styrene (or  $\alpha$ -methylstyrene) and isobutene vapors in the pre-expansion mixtures. It is interesting to note that the predominance of one particular ion series is not observed in the alkylbenzene–isobutene systems. The difference can clearly be seen by comparing the mass spectra of the *p*-xylene–isobutene (Figure 3) and styrene–isobutene (Figure 9) systems. Since *p*-xylene and styrene have similar ionization potentials, their clusters with isobutene are expected to show similar distributions if no intracuster polymerization were occurring in the styrene–isobutene system.



**Figure 9.** Mass spectrum of styrene–isobutene mixed clusters ( $S_m I_n$ ) taken at 248 nm. Peaks a, b, c, and d with  $m/z$  117 ( $C_9H_9$ ), 145 ( $C_{11}H_{13}$ ), 190 ( $C_{14}H_{22}$ ), and 238 ( $C_{18}H_{22}$ ), respectively, are due to loss of  $C_3H_7$ ,  $CH_3$ ,  $C_2H_2$ , and  $C_2H_2$  from the product ions  $SI$ ,  $SI$ ,  $SI_2$ , and  $S_2I$ , respectively.



**Figure 10.** Mass spectrum of  $\alpha$ -methylstyrene–isobutene mixed clusters ( $MS_m I_n$ ) taken at 248 nm.

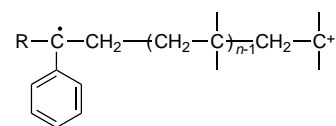
The mass spectra displayed in Figures 9 and 10 also show that the relative ion intensities within the  $SI_n^{+\bullet}$  and  $MSI_n^{+\bullet}$  sequences exhibit maxima at  $n = 1$  and clear drops or discontinuities past  $n = 1$ . These maxima in ion intensities could reflect the extra stability or the weak reactivity of the  $SI^{+\bullet}$  and  $MSI^{+\bullet}$  ions which could be attributed to cyclization of these radical cations.

The covalent additions of isobutene on styrene or  $\alpha$ -methylstyrene radical cations are not surprising but rather expected based on the recently studied radical cation dimerization of styrene and substituted styrene in solution. It is interesting, however, to discuss the observed intracluster reactions in relation to the corresponding reactions in the condensed phase. In solution, radical cations can be generated by pulse radiolysis, pulsed laser excitations, or photoinduced electron acceptor sensitizers.<sup>23,24,30,31</sup> The reactions of alkene radical cations with

neutral alkenes are now well established as a useful method for the synthesis of cyclobutane derivatives and Diels–Alder products.<sup>25</sup> In solution, these reactions are typically complete within minutes at low temperatures, and they typically involve two channels: either addition of the neutral alkene to give a cyclobutane derivative or electron transfer from the neutral alkene to the radical cation.<sup>23–25</sup> The addition of a radical cation to an alkene can in principle occur via either a stepwise<sup>30,31</sup> or concerted pathway.<sup>23,32</sup> Despite a large amount of mechanistic and theoretical work, neither the concerted nor the stepwise mechanism can satisfactorily explain all the available data in solution.<sup>23</sup>

In the gas phase, radical cation cycloaddition reactions have been investigated in several systems involving *o*-xylene, fulvene, 1,3-butadiene, and methyl vinyl ether.<sup>33</sup> Of particular interest to the present study is the gas phase reaction of the styrene radical cation and neutral styrene. This reaction has been studied by Gross and co-workers using collisionally activated decomposition (CAD) to characterize the structures of the various adducts.<sup>34</sup> Their study has suggested the formation of a stable 1,4-radical cation intermediate (distonic ion) in the [2+1] cycloaddition of alkene radical cations and alkene neutrals which supports the stepwise pathway. However, it has been concluded that it is not possible to distinguish between the 1,4-acyclic radical cation and a long-bond cyclobutane radical cation.<sup>34</sup> Under low pressure (collision free) conditions, the acyclic intermediates are likely to be short-lived and, therefore, difficult to observe before they cyclize. Thus, the acyclic 1,4-radical cation can only be observed in the gas phase by stabilizing it in a relatively high pressure of an inert bath gas. In clusters, the role of collisional stabilization is replaced by evaporative cooling through energy transfer to the low frequency modes of the cluster.<sup>20,21</sup> This process can lead to efficient stabilization of the reaction intermediates particularly within larger clusters.

On the basis of the gas phase and solution studies of the mechanism of cycloaddition reactions and our observation of fragment ions resulting from the covalent addition reactions, we propose the following structures for the styrene:(isobutene)<sub>n</sub><sup>+</sup> and  $\alpha$ -methylstyrene:(isobutene)<sub>n</sub><sup>+</sup> oligomer ions:



**I**, R = H (styrene),  $CH_3$  ( $\alpha$ -methylstyrene)

The proposed structure of the styrene:(isobutene)<sup>+</sup> dimer is similar to the structure of the styrene dimer cation radical

(30) Egusa, S.; Tabata, Y.; Kira, A.; Imamura, M. *J. Polym. Sci.* **1978**, *16*, 729. Tojo, S.; Toki, S.; Takamuku, S. *J. Org. Chem.* **1991**, *56*, 6240. Brede, O.; David, F.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 23.

(31) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356. Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

(32) Bauld, N. L.; Pabon, R. *J. Am. Chem. Soc.* **1983**, *105*, 633. Lewis, F. D.; Kojima, M. *J. Am. Chem. Soc.* **1988**, *110*, 8664. Bauld, N. L. *Adv. Electron Transfer Chem.* **1992**, *2*, 1–66. Jungwirth, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5783.

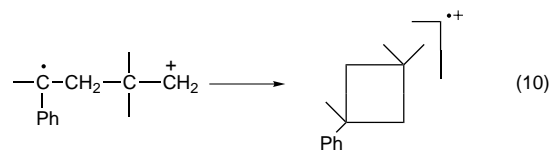
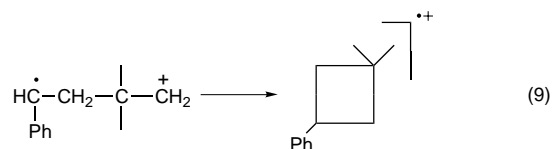
(33) Chess, E. K.; Lin, P. H.; Gross, M. L. *J. Org. Chem.* **1983**, *48*, 1522. Russell, D. H.; Gross, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 6279. van Doorn, R.; Nibbering, N. M. M.; Ferrer-Correia, A. J. V.; Jennings, K. R. *Org. Mass Spectrom.* **1978**, *13*, 729. Groenewold, G. S.; Gross, M. J. *Am. Chem. Soc.* **1984**, *106*, 6575, 6569. Holman, R. W.; Rozeboom, M. D.; Gross, M. L.; Warner, C. D. *Tetrahedron* **1986**, *42*, 6235.

(34) Groenewold, G. S.; Chess, E. K.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 539.



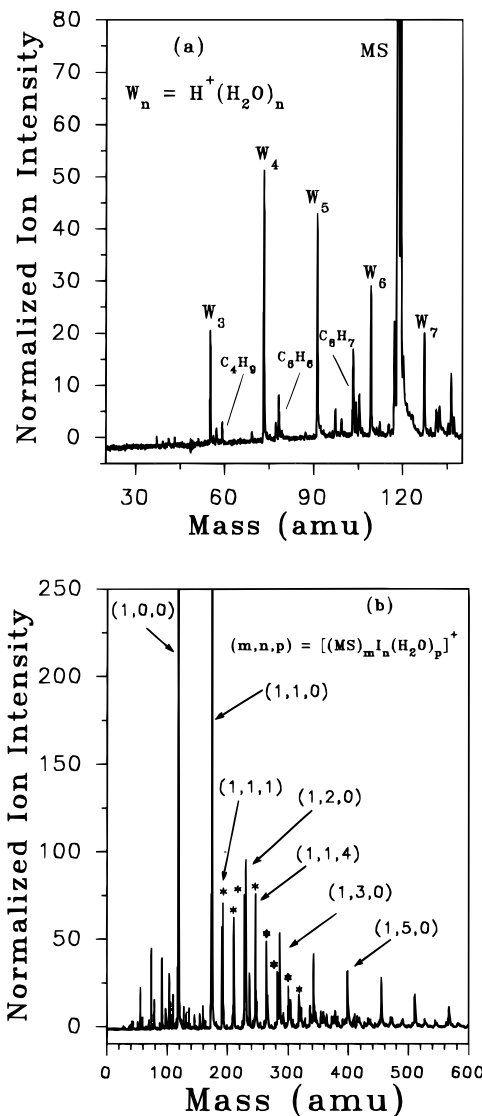
suggested by Gross.<sup>34</sup> This dimer is capable of undergoing both cationic and radical propagation independently in the conventional manner. We assume that isobutene molecules are added by cationic propagation on the charge site while styrene molecules can join the chain by the addition on the radical site. This is consistent with the well-established result that isobutene can only be polymerized by a cationic mechanism while styrene is readily polymerized by free radical, cationic, and anionic mechanisms.<sup>1-3</sup>

The observed maxima in the ion intensities of the  $SI_n^{*+}$  and  $MSI_n^{*+}$  sequences at  $n = 1$  are explained by cyclization of the corresponding distonic ions according to:



Here we assume that the  $SI^{*+}$  (or  $MSI^{*+}$ ) isomer with the  $-\text{CH}_2^+$  end group cyclizes much faster than the isomer with the dimethyl carbocation ( $\text{>C}^+$ ) end group owing to strong steric interaction among the phenyl and methyl groups of the latter. Therefore, the dimethyl carbocation isomer tends to propagate as an open chain distonic ion resulting in the oligomer structure shown in I. It is worth noting that a similar situation has been verified in the spontaneous polymerization of styrene where the Diels-Alder (DA) reaction between two molecules of styrene does not yield one single DA intermediate only but leads to two stereoisomers (with different stabilities) at rates of comparable order of magnitude.<sup>35</sup> Only one of these isomers is capable, when partnered with a further monomer molecule, to enter into a radical formation process which is the basis of the spontaneous initiation of styrene polymerization.<sup>35</sup> In the present system, the proposed 1,4-radical cation initiator possesses two active sites where cationic and radical propagations can take place during the growth of the styrene/isobutene copolymer. We also note a higher tendency to generate larger  $MSI_n^{*+}$  as compared to the  $SI_n^{*+}$  oligomers in spite of the fact that the relative concentration of isobutene in the styrene and  $\alpha$ -methylstyrene binary expansions is kept the same. This appears to be consistent with the known higher reactivity of ionic copolymerization of  $\alpha$ -methylstyrene-isobutene as compared to the styrene-isobutene system.<sup>1</sup> This is usually explained in terms of the inductive effect of the methyl group which increases the stability of the  $\alpha$ -methylstyrene cation just enough to sustain the propagation of the chain. Also,  $\alpha$ -methylstyrene and isobutene exhibit close similarity in structure and may therefore represent a more ideal copolymerization system than styrene-isobutene.

To further support the proposed structure of the styrene-isobutene or  $\alpha$ -methylstyrene-isobutene dimer cation radical and its role as the initiator of the copolymerization, we investigated the effect of adding a small amount of water on the ionic distribution displayed in Figure 10 for  $\alpha$ -methylstyrene/isobutene system. In Figure 11, parts a and b exhibit the mass



**Figure 11.** Mass spectra of  $\alpha$ -methylstyrene-isobutene-water ternary clusters ( $MS_mI_nW_p$ ) taken at 248 nm: (a) low mass region and (b) overall mass range. \* denotes the series  $MS_1I_1W_p$  with  $p = 1-8$ .

spectra obtained under conditions identical with the spectrum shown in Figure 10 [same concentrations of isobutene (270 mbar) and  $\alpha$ -methylstyrene (50 mbar) in the pre-expansion mixture and the same stagnation pressure of He (2500 mbar)] except of the small amount of water (20 mbar added to the expansion mixture of the mass spectrum of Figure 11. Several new features can clearly be identified in Figure 11, a and b, and are summarized as follows.

(i) The enhanced distribution of the  $MSI_n^{*+}$  sequence is greatly reduced in comparison with the data of Figure 10 obtained in the absence of water.

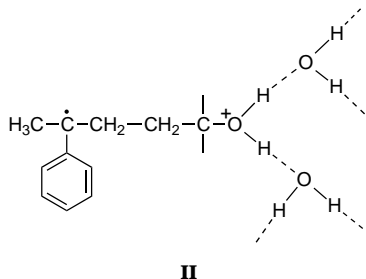
(ii) The most predominant ion sequence containing water is ( $\alpha$ -methylstyrene) (isobutene) (water)<sub>p</sub>,  $[(MS)(I)(H_2O)_p]^+$ , with  $p = 1-12$ .

(iii) Protonated water clusters  $H^+(H_2O)_p$  are observed only with  $p \geq 3$  with some particular enhancement of the ion intensities corresponding to  $p = 4$  and 5 (Figure 11a).

These features can be explained in terms of the well-known inhibition effect of water and other H-bonded solvents such as methanol on the cationic polymerization of styrene and isobutene.<sup>1-3</sup> For example, it is widely recognized that cationic polymerization is the predominant mechanism in the radiation

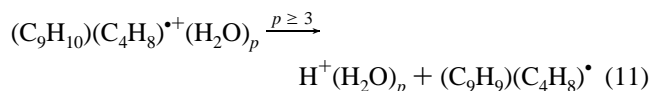
(35) Olaj, O. F.; Kauffmann, H. F.; Breitenbach, J. W. *Makromol. Chem.* **1977**, 178, 2707; **1976**, 177, 939, 3065. Buchholz, K.; Kirchner, K. *Makromol. Chem.* **1976**, 177, 935.

induced polymerization of styrene under very dry conditions.<sup>3</sup> On the other hand, the presence of a small amount of water and methanol is known to suppress cationic polymerization and enhance dimerization and free radical polymerization.<sup>36</sup> Based on our proposed structure of the  $\alpha$ -methylstyrene<sup>•</sup>–isobutene<sup>+</sup> dimer radical cation, it is very likely that the addition of water will take place on the charge site according to structure II.



It is clear that the attachment of water can inhibit the cationic addition of isobutene, and this explains the significant reduction in the population of the  $MSI_n^{•+}$  ions. Therefore, the data shown in Figure 11b could be taken as evidence for the cationic addition of isobutene on the  $\alpha$ -methylstyrene<sup>•</sup>–isobutene<sup>+</sup> distonic ion. Note that the attachment of water to the cationic site should not affect the reactivity of the radical site. However, since isobutene tends to propagate only by a cationic mechanism, the availability of the radical site is not expected to lead to more isobutene additions, but it could enhance the addition of a monomer that is likely to propagate by a radical mechanism. In fact, we have carried out experiments on styrene–isobutene clusters in the presence of water and observed significant intensity of the series (styrene)<sub>m</sub>(isobutene)<sub>n</sub>(water)<sub>p</sub> with  $m \leq 12$ ,  $n = 1$  or 2, and  $p \leq 15$ . We observed a strong propensity for the enhancement of ions with  $m > n$ , even in pre-expansion mixtures containing more isobutene than styrene, which implies that while the addition of isobutene on the cationic site is inhibited by the presence of water, the propagation of styrene can still occur on the radical site.

Another important result from the  $\alpha$ -methylstyrene–isobutene–water experiment is the evidence for an intracuster proton transfer reaction producing the protonated water clusters  $H^+(H_2O)_p$  with  $p \geq 3$  according to reaction 11.



We have observed a similar reaction in the styrene–water system and verified, by isotopic experiments involving  $D_2O$ , that the origin of the proton is the styrene molecule.<sup>37</sup> In the styrene<sup>•+</sup>(water)<sub>n</sub> clusters, the proton transfer reaction becomes energetically allowed at  $n = 3$  which is the same result obtained here for  $\alpha$ -methylstyrene/isobutene/water clusters. In the present work, we also observe a parallel correlation between the ion intensities corresponding to the  $(MS)(I)^{•+}(H_2O)_p$  and the  $H^+(H_2O)_p$  sequences which indicates that the  $(MS)(I)(H_2O)_p$  series

is the precursor of the protonated water clusters. Because of the distonic nature of the  $\alpha$ -methylstyrene–isobutene radical cation, the attachment of water to the charge site is expected to release significant amount of energy which could make the proton transfer more energetically allowed. This is also supported by the very weak ion intensity corresponding to the  $(MS)(H_2O)_p$  sequence.

The observation of enhanced ion intensities corresponding to  $H^+(H_2O)_4$  and  $H^+(H_2O)_5$  may reflect the closing of the first solvent shell around  $H_3O^+$  in  $H^+(H_2O)_4$  and the formation of a cyclic structure in  $H^+(H_2O)_5$ . These structures are commonly observed in the gas phase and cluster studies of ionic hydrogen bonding systems.<sup>38</sup>

#### 4. Conclusions

The combination of gas phase<sup>18</sup> and cluster studies of the isobutene system leads to some important conclusions which can improve our understanding of the early stages of cationic polymerization. These conclusions are summarized as follows.

1. The present work provides evidence for a concerted mechanism that leads to the generation of isobutene dimer cation upon photoionization of an aromatic precursor such as toluene that has an ionization potential greater than or equal to that of the isobutene dimer. A similar reaction mechanism has been established for the benzene<sup>•+</sup>/propene system where propene dimer cation and higher order propene oligomers have been observed following the selective photoionization of benzene in the gas phase and also within preformed binary clusters. These results will be presented in a forthcoming report.<sup>39</sup>

2. The observation of the concerted process in the gas phase<sup>18</sup> and within clusters suggests that a similar mechanism may actually be operative in solution. Since benzene and toluene are often used as polymerization solvents, the observation of the concerted process in solution may open the possibility for a “Solvent as Initiator Approach” which would eliminate the need for chemical initiators or additives. Experiments are underway to investigate the possibility of initiating radical cation polymerization by laser photoionization of appropriate aromatics in olefin solutions.

3. Evidence has been presented that points to the successive covalent additions of isobutene molecules on styrene and  $\alpha$ -methylstyrene radical cations within gas phase clusters. The intracuster reactions appear to yield two intermediate isomers. The first has an acyclic 1,4-radical cation structure which can initiate further polymerization via cationic or radical propagation depending on the nature of available monomers in the cluster. The structure of the second isomer is consistent with a cyclic form in which the ionic and the radical sites are interacting, and this gives rise to a stable product which manifests itself in the appearance of an enhanced ion intensity for the styrene–isobutene or the  $\alpha$ -methylstyrene–isobutene radical cations. Future work will address further structural characterizations of these species by photodissociation experiments on mass selected ions.

(36) Silverman, J.; Tagawa, S.; Kobayashi, H.; Katsumura, Y.; Washio, M.; Tabata, Y. *Radiat. Phys. Chem.* **1983**, *22*, 1039. Gotoh, T.; Yamamoto, M.; Nishijima, Y. *J. Polym. Sci.* **1981**, A-1, *19*, 1047. Machi, S.; Silverman, J.; Metz, D. J. *J. Phys. Chem.* **1972**, *76*, 730. Tagawa, S.; Schnabel, W. *Makromol. Chem., Rapid. Commun.* **1980**, *1*, 345. Tagawa, S.; Schnabel, W. *Chem. Phys. Lett.* **1980**, *72*, 120.

(37) El-Shall, M. S. *Polym. Preprints* **1996**, *37*, 367. Pithawalla, Y. B.; Gao, J.; Yu, Z.; El-Shall, M. S. *Macromolecules*, in press.

(38) El-Shall, M. S.; Daly, G. M.; Gao, J.; Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1992**, *96*, 507. El-Shall, M. S.; Marks, C.; Sieck, L. W.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1992**, *96*, 2045. Daly, G. M.; Gao, J.; El-Shall, M. S. *Chem. Phys. Lett.* **1993**, *206*, 500. Wei, S.; Shi, Z.; Castleman, A. W., Jr. *J. Chem. Phys.* **1991**, *95*, 585. Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1989**, *106*, 1265. Deakyn, C. A.; Meot-Ner (Mautner), M.; Campbell, C. L.; Hughes, M. G.; Murphy, S. P. *J. Chem. Phys.* **1986**, *84*, 4958. Newton, M. D. *J. Chem. Phys.* **1977**, *67*, 5535. Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971.

(39) El-Shall, M. S.; Pithawalla, Y. B.; Gao, J.; Meot-Ner (Mautner), M., in preparation.

4. Water has a detrimental effect on the cationic addition of isobutene onto the  $\alpha$ -methylstyrene–isobutene radical cation within gas phase clusters. Significant reduction in the number of isobutene units within the sequence  $\alpha$ -methylstyrene-(isobutene)<sub>n</sub> has been observed upon the addition of a small amount of water in the pre-expansion mixture. Intracluster proton transfer reactions within ( $\alpha$ -methylstyrene)(isobutene)-(water)<sub>p</sub> with  $p \geq 3$  producing protonated water clusters have been observed. The results are consistent with the distonic structure of the  $\alpha$ -methylstyrene–isobutene radical

cation which can initiate both cationic and radical propagations.

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