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Even/Odd Alternation in Styrene Cluster Ions. Evidence for Multiple Cyclization during the Early Stages of Polymerization and the Inhibition Effect of Water

Y. B. Pithawalla, J. Gao, Zhongde Yu, and M. Samy El-Shall*

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

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The fundamental mechanism that governs ionic polymerization is an important question in a number of scientific disciplines as well as practical applications including industrial processes, radiation chemistry, and interstellar synthesis.[1−3] Despite significant progress, detailed understanding of the complex reactions in solution, which include initiation, propagation, chain transfer, inhibition, termination, and solvent effects, remains limited. Information regarding the exact nature of each mechanistic step and the elementary events occurring in the course of polymerization remains largely unavailable.

In order to elucidate the mechanisms of initiation and the early stages of polymerization reactions, studies of gas phase and cluster polymerization are desirable and are being pursued by several groups.[4−13] The overall long-sought goal of this activity is to initiate a close dialogue between gas phase, clusters, and condensed phase polymer chemistry with the implicit assumption that this dialogue will provide a molecular-level understanding of the competitive reaction channels in a typical polymerization system. Of particular interest is the ability to identify the unique features associated with the early reaction steps including the structure and reactivity of the small growing oligomers. Herein, we report evidence for a remarkable alternation in the reactivity of styrene radical cations with a unique tendency of the species containing an even number of styrene molecules to form multiple cyclic oligomers during the early steps of propagation.

In the condensed phase, styrene is known to undergo polymerization in bulk monomer or in solution by free radical, cationic, and anionic mechanisms. Although the crucial role played by the presence of trace amounts of water and other protic impurities on the mechanism and rate of polymerization is widely recognized,[2] the fundamental understanding of the role of water in inhibiting or initiating the polymerization remains limited. In this communication, we also report the observation of intracluster proton transfer reactions in styrene−water and styrene−methanol clusters which provide direct evidence for the inhibition effects of water and methanol on the cationic reactions and for the enhancement of the free-radical polymerization.

In cluster polymerization, neutral clusters of the monomer molecules are produced in the gas phase by supersonic cluster beam techniques.[5,8,13] Polymerization is initiated following the cluster's ionization either by electrons, by photons, or by the interaction with metal cations. One can also form binary clusters of two selected monomers or a monomer with a deliberately added inhibitor such as water or methanol. In favorable cases, photofragmentation spectroscopy is employed to characterize the structures of the polymerization intermediates and hence measure the extent of propagation.

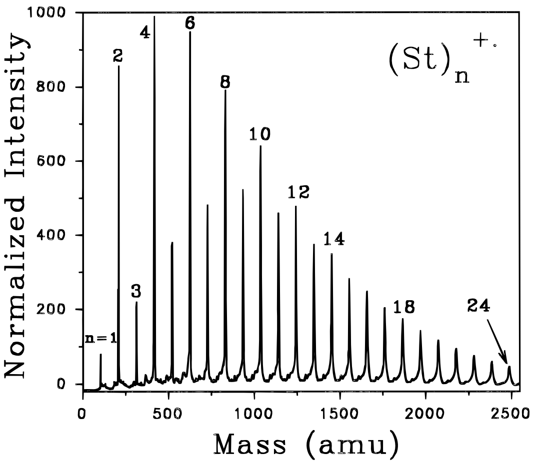

Figure 1. Mass spectrum of styrene clusters $(St)_n$ ionized with two-photon ionization taken at $\lambda = 248$ nm.

Information regarding the kinetics and thermochemistry of the individual reaction steps can by obtained by examining the ionic reactions in the gas phase with high-pressure mass spectrometry (HPMS).[9,12] In this work, we demonstrate the application of these techniques to study the radical cations of styrene and α-methylstyrene oligomers, their reactions with isobutene, and the effect of water on the cluster polymerization.

Styrene clusters are generated by pulsed adiabatic expansion in a supersonic cluster beam apparatus.[13] The essential elements of the apparatus are jet and beam chambers coupled to a pulsed time-of-flight (TOF) mass spectrometer. During operation, a vapor mixture of 2−7% styrene (Aldrich, 99% purity) in He (ultrahigh purity, Spectra Gases 99.99%) at a pressure of 2−4 bar is expanded through a conical nozzle (500 μm diameter) in pulses of 200−300 μs duration at repetition rates of 6−10 Hz. The jet is skimmed and passed into the ionization region of a pulsed TOF mass spectrometer where it intersects a laser pulse from a 248 nm radiation provided by an excimer laser (KrF, Lumonics Hyper Ex-400). The cluster ions are electrostatically accelerated in a two-stage acceleration region (3000 V/cm), travel a field-free region ($\approx$170 cm in length), and are then accelerated to a two-stage microchannel-plate detector. The TOF spectrum is recorded by digitizing the amplified current output of the detector by a 350 MHz digitizer (LeCroy 9450) and averaged over 500 pulses.

Figure 1 displays a typical mass spectrum obtained following the two-photon (248 nm) ionization of styrene clusters produced under intense clustering conditions. The mass spectrum shows an enhanced intensity for the dimer with a remarkable even/odd alternation in the ion intensities: the even-numbered ions are systematically more intense than the odd-numbered ions, up to $n = 12$. This behavior is more pronounced under intense expansion conditions which produce large neutral clusters. The even/odd alternation has also been observed for α-methylstyrene ions, although to a much weaker extent with a clear periodicity only up to $n = 6$. We note that these distributions (for styrene and α-methylstyrene) are quite different from those of other aromatic cluster ions such as benzene, toluene, ethylbenzene, *p*-xylene, fluorobenzene, and other substituted benzenes where a smooth ion population with intensity decreasing monotonically for $n < 10$ and no evidence for a discontinuity or a sharp drop in intensity have

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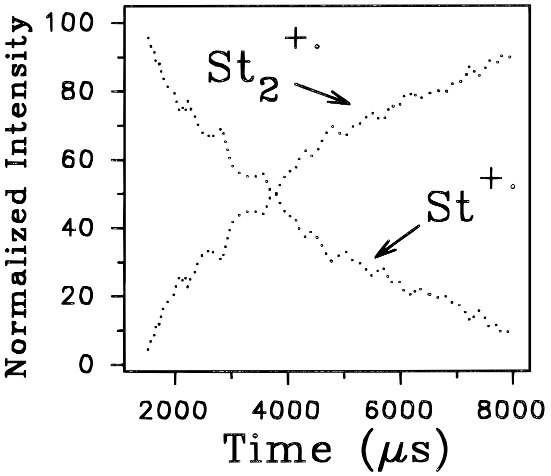


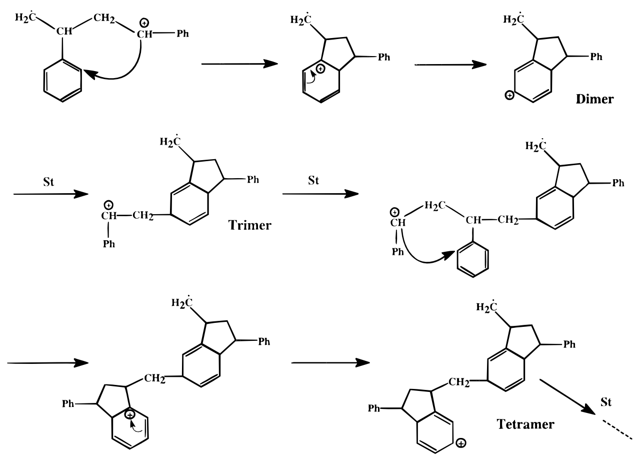
Figure 2. Normalized ion profiles for the reaction of styrene radical cation ($St^{\bullet+}$) with styrene neutral to generate the styrene dimer radical cation ($St_2^{\bullet+}$).

been observed. Similarly, we are not able to observe periodicity in the ion intensities of several olefin clusters such as ethylene, propene, isobutene, vinyl chloride, and acrylonitrile. In these systems, enhanced ion intensities corresponding to some stable ions such as $(\text{propene})_3^{\bullet+}$ and $(\text{isobutene})_3^{\bullet+}$ have been observed under cold beam expansion conditions and attributed to the formation of cyclic oligomers.[13] However, no evidence for periodicity has been reported in such systems. The only exception is the recent work of Bohme et al., who observed periodicity in the addition reactions of allene to C_{60}^{2+} and proposed a mechanism for the sequential reactions with an alternating formation of acyclic and cyclic oligomers.[14]

To characterize the reaction system, we have examined the gas phase reaction of styrene radical cation ($St^{\bullet+}$) with neutral styrene (St) using HPMS.[15] In this experiment, benzene cations are generated by resonant-two-photon ionization in a HPMS source containing styrene vapor (0.1%) in Ar carrier gas at a total pressure of 0.5–2 Torr.[15] The styrene radical cation is generated via the exothermic charge transfer from $\text{benzene}^{\bullet+}$ (the ionization potentials of benzene and styrene are 9.25 and 8.42 eV, respectively).[16] The time profiles corresponding to the reaction of $St^{\bullet+}$ and the formation of $St_2^{\bullet+}$ (according to the reaction $St^{\bullet+} + St \rightarrow St_2^{\bullet+}$) are shown in Figure 2. Since the number density of St neutral is much greater than the ion number density $St^{\bullet+}$, pseudo-first-order kinetics applies. The slope of the ln $[St^{\bullet+}]$ vs time plot gives the pseudo-first-order rate coefficient (k_1), and the apparent second-order rate coefficient (k_2) for the formation of $St_2^{\bullet+}$ is then calculated from $k_2 = k_1/[St]$, where [St] is the styrene number density. The results indicate that the formation of the styrene dimer cation radical is irreversible in the gas phase and proceeds with a rate coefficient of 7.0×10^{-11} $cm^3\ s^{-1}$ at 300 K. We estimate the rate coefficient of the second reaction step after the formation of the dimer to be several orders of magnitude slower.

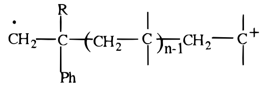
Our results are consistent with the work of Gross and co-workers, who established that the adduct produced in the reaction of the styrene radical cation with neutral styrene is covalently bonded and could possess a cyclic structure.[17] On the other hand, it is well known that indan derivatives are formed during the cationic polymerization of styrene, and the cyclic dimer 1-methyl-3-phenylindan and oligomers have been isolated.[18,19] We believe that the observed periodicity in the intensity of the styrene ions is a direct manifestation of the formation of indan end groups which occur preferentially for the even-numbered ions. This means that because of the cyclic structures, the even-numbered ions would be less reactive toward further addition of styrene and therefore more abundant. The difference between styrene and α-methylstyrene in the extent of the even/odd periodicity is ascribable to steric factors which would favor the linear carbocation terminus over the indan cyclization. Scheme 1 outlines a possible mechanism for the multiple cyclization reactions of the styrene radical cation oligomers.

Scheme 1



Several additional observations on the cluster polymerization are summarized below:

(i) We have also examined the binary clusters of styrene–isobutene ($S_m{\cdot}I_n$) and α-methylstyrene–isobutene ($MS_m{\cdot}I_n$) following the 248 nm photoionization. The covalent addition of isobutene on the styrene or α-methylstyrene radical cations is evident from the observation of dissociation products corresponding to the loss of alkyl fragments such as $CH_3^{\bullet}$, $C_2H_5^{\bullet}$, C_3H_6, and $C_3H_7^{\bullet}$ from the styrene–isobutene or the α-methylstyrene–isobutene adducts. In this system, we observe periodicity within the series containing several styrene molecules and only one isobutene, i.e. $(S_m{\cdot}I)^{\bullet+}$ with enhanced intensity for $m = 1, 3, 5$, etc. On the other hand, the species containing several isobutene molecules and only one styrene, i.e. $(S{\cdot}I_n)^{\bullet+}$ do not show even/odd alternation. This suggests that cyclization can occur if isobutene occupies the terminal site of the polystyrene oligomer chain. This also suggests that isobutene molecules can sequentially add into styrene or α-methylstyrene cations with no evidence for cyclization according to



$$\dot{C}H_2-\overset{R}{\underset{Ph}{C}}\!-\!\left(CH_2-\overset{|}{\underset{|}{C}}\right)_{n-1}\!CH_2-\overset{|}{\underset{|}{C}}{}^{+} \qquad \text{(I)}$$

[R = H (styrene), CH_3 (α-methylstyrene)]

(ii) Consistent with a cationic mechanism, much larger α-methylstyrene $(\text{isobutene})_n^{+}$ ions are observed (more than $n = 40$) as compared to $\text{styrene}(\text{isobutene})_n^{+}$ ions under similar conditions. This is consistent with the reactivity of α-methylstyrene being higher than styrene in reactions involving the intermediacy of carbocations.[1]

(iii) Following the ionization of the binary styrene–water clusters, protonated water clusters $H^+(H_2O)_n$ are

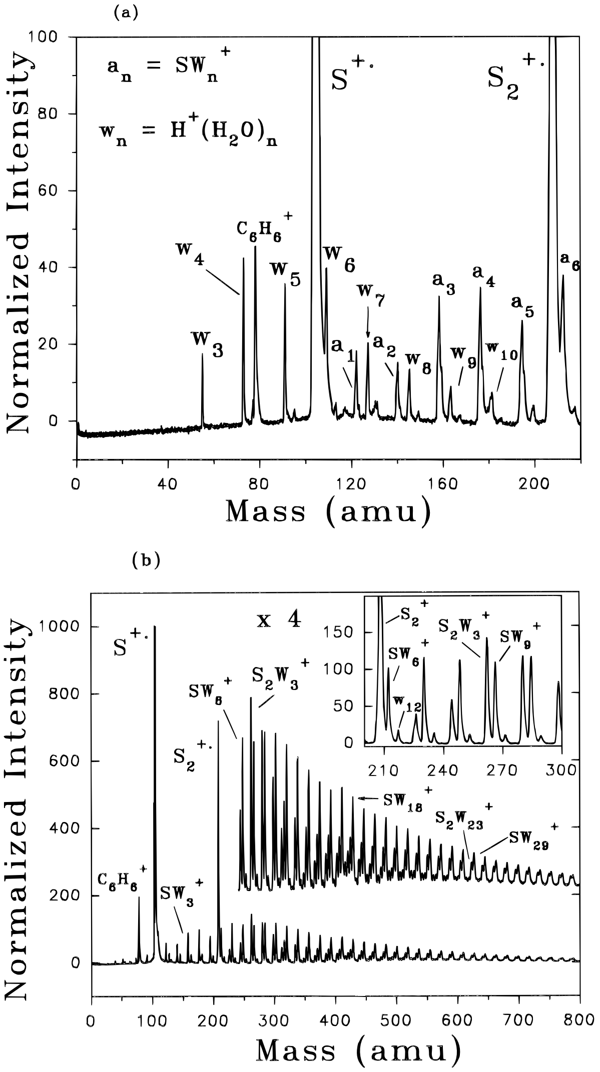


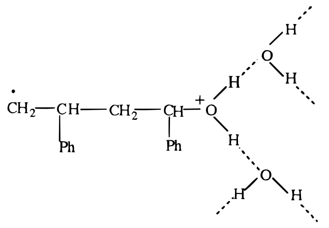
Figure 3. Mass spectra of styrene–water clusters ($S_n \cdot W_m$) ionized with two-photon ionization taken at $\lambda = 248$ nm: (a) low-mass region; (b) overall mass range.

observed starting from $n \geq 3$. It should be noted that in the absence of styrene, water clusters could not be ionized with the same laser power used to ionize the styrene–water clusters. We have also verified, by isotopic experiments involving D_2O, that the origin of the proton in the protonated water clusters is the styrene molecule. This indicates the occurrence of intracluster proton transfer reactions according to

$$(C_8H_8)_mC_8H_8^+(H_2O)_n \rightarrow H^+(H_2O)_n + (C_8H_8)_mC_8H_7^{\bullet},\ n \geq 3$$

Another intriguing feature of the styrene–water clusters is the observation of a very large number of water molecules (more than 50) on styrene$^{\bullet+}$ and (styrene)$_2^{\bullet+}$ ions. Typical examples are shown in Figures 3a,b. Based on structure I proposed for the styrene$^{\bullet}$(isobutene)$_n^+$ oligomers, it is likely that the addition of water will take place on the charge site according to structure II.

The distonic structure of the styrene dimer radical cation provides unique capability for undergoing both radical and cationic propagation independently in the conventional manner. It is clear that the attachment of water inhibits the cationic addition of styrene but it



(II)

should not affect the reactivity of the radical site. This suggests that the styrene oligomers are most likely formed by a radical mechanism in the presence of water. This is also consistent with the absence of higher ions of α-methylstyrene oligomers in the presence of water since this monomer tends to propagate mostly by a cationic mechanism.

Similar behavior has been observed in styrene–methanol clusters. In this case, the proton transfer channel requires only two methanol molecules, and consequently protonated methanol clusters $H^+(CH_3OH)_n$ have been observed starting from $n \geq 2$. This can be understood in terms of the relative proton affinities of water and methanol clusters.[15]

The observed intracluster proton transfer reactions are consistent with the detrimental effects of water and methanol on the bulk cationic polymerization of styrene. For example, in radiation-induced polymerization of the bulk monomer free cations are largely responsible for the polymerization under very dry conditions. On the other hand, under "wet" conditions where the water concentration $[H_2O] > 10^{-3}$ M, a slower polymerization takes place and is believed to be an entirely free radical process .[20] These observations can be fully accounted for by the present results.

In summary, we have observed a novel and remarkable periodicity in the reactivity of styrene radical cations which is attributed to size-dependent indan cyclization during the early stages of cationic propagation. We have also demonstrated that intracluster polymerization is important not only for a fundamental understanding of the initiation mechanisms and the early stages of propagation, but also for the elucidation of the effects of inhibitors and retarders on the efficiency of different polymerization channels such as cationic vs free-radical mechanisms.

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