Size-Dependent Intracluster Reactions in Metal-Vinyl Molecule Clusters: Anionic Oligomerization Initiated by Electron Transfer

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As a microscopic model of anionic polymerization systems, clusters of an alkali metal atom (M) with vinyl molecules (VM), $M(VM)_n$, have been investigated systematically for various combinations of M and VM by photoionization mass spectrometry. For the systems of VM = acrylonitrile, acrylic ester molecules, and methacrylic ester molecules, the magic number at $n=3$ is commonly observed in the mass spectra. Fragmented ions with the loss of ROH, $[M(VM)_n\text{-ROH}]$, are also detected at specific cluster sizes for the latter two systems. These results are explained by intracluster oligomerization reaction initiated by electron transfer from the metal atom. The magic number trimer is concluded to have a ring structure of cyclohexane derivatives as a result of oligomerization. The fragmentation reaction is explained by Dieckmann cyclization and lactonization reaction after anionic oligomerization.

Key words: cluster, electron transfer, anionic polymerization, intracluster reaction, alkali metal

1. INTRODUCTION

Ionic polymerization of vinyl compounds has been one of the important reaction to produce various useful materials in the past several decades. Although the polymerization reaction mechanisms were fully discussed in the condensed phase [1], the detailed mechanism in the molecular level has also recently been investigated in the gas phase [2-22]. Especially for the studies of anionic polymerization, three approaches were investigated so far in the gas phase. As one of such studies, a flowing ion-molecule reaction was studied to obtain information on the kinetics in the reaction processes of anionic oligomerization. As for the oligomerization of acrylonitrile (AN, $CH_2=CHCN$) and methyl acrylate (MA, $CH_2=CHCO_2CH_3$), McDonald and Chowdhury investigated the ion-molecule reactions between the vinyl molecules and several negative ions as reaction initiators [2,3]. They found the termination of the oligomerization reaction at the MA trimer and also the existence of several side-reactions. The second approach to the study of anionic oligomerization in the gas phase was done more recently by observing intracluster reactions in the anionic clusters by Kondow and his coworkers [4-12]. They investigated extensively the anion mass spectrometry of various vinyl compounds such as AN combined with the techniques of electron transfer from high-Rydberg atoms [4-7], photodissociation [8,9], collision-induced dissociation [10], and photoelectron spectroscopy [11,12]. They also found the trimeric terminations for the cluster anions of AN and its derivatives, and concluded that the trimer is a stable anion radical having a cyclohexane-ring structure. $(AN)_6^-$ and $(AN)_9^-$ were also found to be efficiently produced, which indicates the plural trimeric units are formed in the intracluster reaction. However, such magic number behavior did not observed for the $(MA)_n^-$ clusters [5].

As a third approach to the anionic oligomerization in the gas phase, the authors have investigated the intracluster reaction of the neutral $M(VM)_n$ cluster (M; alkali metal atom, VM; vinyl molecule) by photoionization mass spectrometry [13-15]. Because the alkali metal atom is known to be one of the initiator of the anionic polymerization in the condensed phase, the above cluster is expected to be a microscopic model of the polymerization reaction. In fact, the same magic numbers at $n=3k$ ($k=1,2,3,...$) were observed in the photoionization mass spectra of $M(AN)_n$ [13,15] as those in the anion mass spectra of $(AN)_n$ by Kondow and coworkers [7]. Furthermore, the same $n=3k$ magic numbers were observed for $M(\text{acrylic ester})_n$ clusters [14], whereas they were not observed in the anion mass spectra [5].

In the present study, we present the results of systematic investigation for several vinyl monomers which have various reactivity of anionic polymerization. As vinyl molecules which cause anionic polymerization, we have investigated AN, two acrilyc ester molecules ($CH_2=CHCO_2R$) [methyl acrylate (MA, $R=CH_3$) and ethyl acrylate (EA, $R=C_2H_5$)], and two methacrylic ester molecules ($CH_2=C(CH_3)CO_2R$) [methyl methacrylate (MMA, $R=CH_3$) and ethyl methacrylate (EMA, $R=C_2H_5$)]. Firstly we discuss the interpretation of the magic numbers observed in the photoionization mass spectra of $M(VM)_n$ clusters. Next the intracluster oligomerization reaction and the competing side-reaction are discussed mainly for the $M(AN)_n$, $M(\text{acrylic ester})_n$ and $M(\text{methacylic ester})_n$ clusters.

2. EXPERIMENT

The present experiments were performed by using an apparatus described elsewhere [13]. Briefly, the system is composed of two-stage differentially evacuated chambers which contain a cluster beam source and a time-of-flight mass spectrometer (TOF-MS). The clusters of an alkali metal atom, M (M=Li, Na and K), and vinyl molecules, VM, $M(VM)_n$ were produced by a pickup source [23-25] consisting of a combination of laser vaporization and pulsed supersonic expansion. A sample gas mixed with helium was expanded from a pulsed valve with a stagnation pressure of 4 atm. The second harmonic output of a Nd:YAG laser was focused onto a sample metal rod placed at about 10 mm down-

stream from the nozzle. In this source, the vaporized metal atoms immediately collide and react with the molecular clusters formed in the pulsed jet, although subsequent collisional relaxation with buffer gas cannot be ruled out. The resultant neutral species were introduced to the TOF-MS chamber after collimated with a conical skimmer. One-photon ionization of the neutral clusters were then performed by irradiation with a pulsed laser beam in the source region of the TOF-MS. The fluence of the ionization laser was kept under 4 mJcm^{-2} during the measurement, to avoid multiphoton ionization process. The cluster ions formed by photoionization were accelerated to about 3.0 keV and were detected by a dual microchannel plate at the end of the TOF tube. The sample rods of sodium (Rare metallic, 99.9 % pure) and potassium (Aldrich, 99.5 % pure) were made from lump under nitrogen atmosphere in a vacuum dry box to avoid the reaction with water in the air. Chemicals were purchased at the minimum percent impurities and used without further purification.

3. RESULTS AND DISCUSSION

3.1 Phtoionization Mass Spectra

Typical photoionization mass spectra of Na(VM)$_n$ (VM=AN, EA, MA, EMA, and MMA) are shown in Fig. 1. These mass spectra were obtained by irradiation with a fourth harmonic (266 nm, 4.66 eV) of a Nd:YAG laser or the frequency-doubled output of a dye laser. All of the ions appeared in the figure were found to be produced by one-photon absorption from the experiment of laser power dependence. There found a typical feature which is common to all systems, along with some additional features characteristic to each species. The common feature is that the appearance of the magic number at $n=3$. Also for AN, EA, and MA systems, the ions with $n=6$ is also observed as a magic number. For acrylic ester (MA and EA), the dissociative cluster ions with the loss of ROH, [Na(acrylic ester)$_n$ - ROH]$^+$, are observed only for $n=3$. This type of fragmented cluster ions are also detected for the sizes of $n=2$ and 3 in the systems of methacrylic ester (MMA and EMA). All of these features are also observed for K(VM)$_n$ clusters.

3.2 Cyclization Oligomerization Initiated by Electron Transfer from the Metal Atom

In our previous papers, the observed magic numbers at $n=3k$ were fully discussed for AN [13,15] and for MA and EA systems [14] and concluded that they originate from the stability of the neutral M(VM)$_{3k}$ cluster. The arguments of the conclusion are briefly summarized here. First, following three factors can be considered as possibilities to generate the magic numbers; (1) size-dependent evaporation efficiency after photoionization which reflects the relative stability of cluster ions, (2) size-dependent photoionization efficiency at the given ionization energy, and (3) relative abundance of the neutral clusters which reflects the relative stability. Among these, we can safely exclude the possibility (2), from the measurements of photoionization mass spectrometry at various photon energies. In fact, the magic numbers at $n=3k$ are observed at all photon energies higher than ionization thresholds. Therefore we can assume that the ionization efficiency is not sensitively
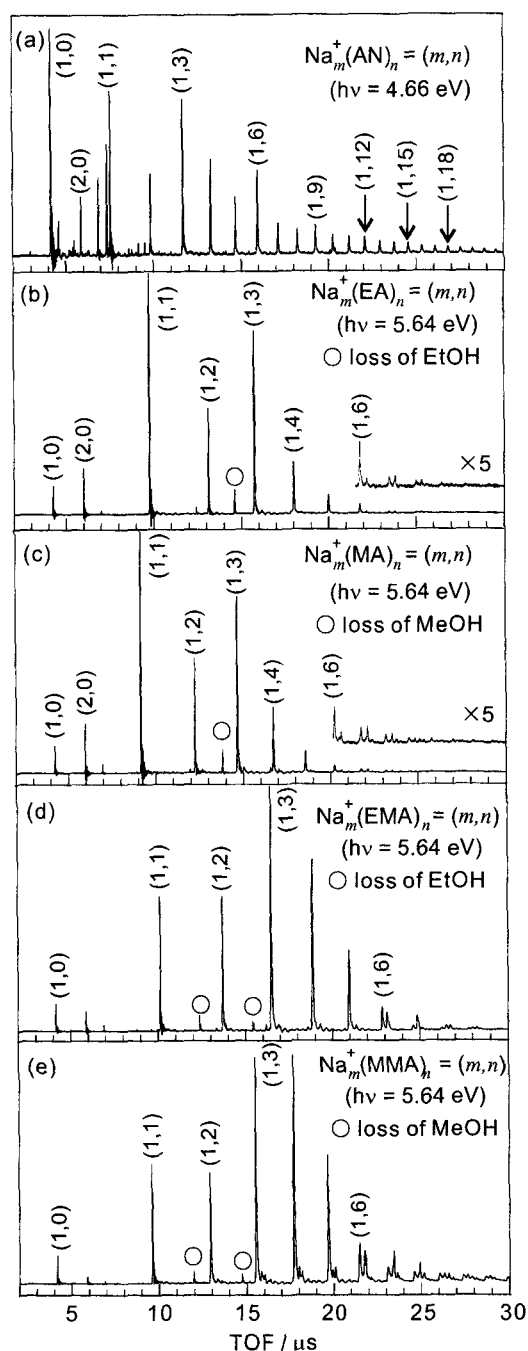

Fig. 1. Photoionization mass spectra of (a) Na$_m$(AN)$_n$, (b) Na$_m$(EA)$_n$, (c) Na$_m$(MA)$_n$, (d) Na$_m$(EMA)$_n$, and Na$_m$(MMA)$_n$. The fragment ions with the loss of ROH in (b)-(e) are assigned as circles. Unassigned peaks in (b)-(e) are the ions containing water molecules.

dependent on n for all clusters in the present study. From the photoionization experiment with the photon energy just above the ionization threshold, the size-dependent evaporation process after ionization (possibility (1)) is also ruled out. Furthermore, mass spectrometry of the cluster ions nascently produced in the source also supports the insignificance of the relative stability of ions in the formation of the magic numbers; no magic number behavior was observed for the cluster ion mass spectra. As a result, the possibility of the relative stability of neutral clusters (possibility (3)) is
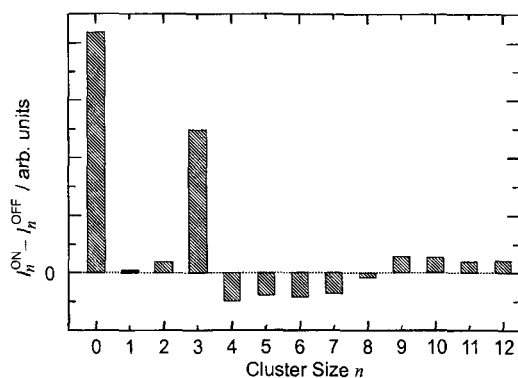
Fig. 2.   The differnce between ion intensities, I_n^{ON} (dissociation and ionization) I_n^{OFF} (ionization only), $I_n^{ON} - I_n^{OFF}$, in $K^+(AN)_n$.

most probable. This possibility is also supported from the photodissociation experiment of the $K(AN)_n$ neutral clusters [15]. In this experiment, the second harmonic of a Nd:YAG laser was irradiated 100 ns prior to photoionization. We have obtained the difference of each ion intensity with the photodissociation laser (I_n^{ON}) and that without the laser (I_n^{OFF}). Photon absorption by the clusters induces the evaporation process in the neutral clusters, and as a result, the population of the stable neutral species is expected to increase. The difference between I_n^{ON} and I_n^{OFF} are plotted as a function of n in Fig. 2. The ion intensities at K^+ and $K^+(AN)_3$ are found to be enhanced in the photoionization after dissociation. This result indicates that the neutral $K(AN)_3$ has a distinguished stability relative to other sizes of clusters.

Next we discuss the structure of $M(VM)_3$ that exhibits anomalous stability. First, the stable structure does not come from the solvation structure around the metal atom, from the results that the magic number is common to the three alkali metal atoms having different van der Waals radii. Furthermore, this discussion is also supported from the observation that the magic number is observed only for the vinyl molecular systems. In fact, no magic number is observed for propionitrile (CH_3CH_2CN) [15] nor the propionate ester molecules $(CH_3CH_2CO_2R)$ systems [14], which have similar structures with AN and the acrylic ester molecules, respectively. Therefore it is expected that the stable structure is attributed to the formation of chemical bonds as a result of intracluster reactions. The ns valence electron of the alkali metal atom and the C=C bond of the vinyl molecules are presumed to play a crucial role in such reactions. Now we consider the possibility of intracluster electron transfer from the alkali metal atom to vinyl molecules. In the condensed phase, vinyl molecules are known to easily be polymerized by electron transfer from initiators such as alkali metals. Also in the present clusters, the alkali metal atom is expected to act as an electron donor to the VM cluster. It is also informative to compare the present results with the detailed studies on the cluster negative ions of vinyl molecules by Kondow and his coworkers [4-12]. In their studies, the ions with $n = 3$ and 6 are found to be stable for $(AN)_n^-$ clusters [7], whereas such stability was not observed for $(MA)_n^-$ [5]. They concluded that the stable species in $(AN)_n^-$ are formed by intracluster anionic oligomerization after
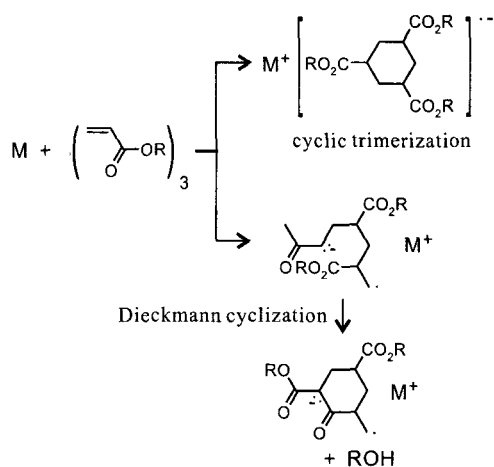
electron attachment, which can be related with anionic polymerization in the condensed phase. Therefore the common magic numbers at $n = 3k$ in the present photoionization mass spectra of $M(VM)_n$ are also expected to indicate the intracluster anionic oligomerization reaction initiated by electron transfer from the metal atom. As for $M(MA)_n$, we have obtained an evidence that one of the optimized structures of $Na(MA)$ has in fact an ion-pair character, and that in the isomer the Na atom suppress the nucleophilicity of the O atom in the carbonyl group, which causes side reactions other than oligomerization [14]. Therefore, the fact that the magic numbers for $M(MA)_n$ in the present study was not observed in the cluster negative ions by Kondow and coworkers can be explained by the absence of the initiator. It is concluded that such site-specific effect on the electron transfer reaction are crucial to promote the following oligomerization.
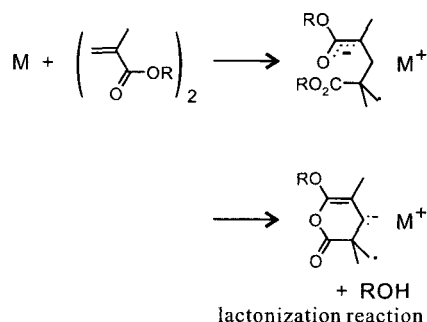
3.3 Alcohol Fragmentation Reactions

In the systems of acrylic ester and methacrylic ester, fragment ions assignable to the loss of an alcohol molecule from the clusters are observed at specific cluster sizes ($n=3$ for acrylic ester and $n=2$ and 3 for methacrylic ester). Results of the appearance potential measurements of the fragment ions indicate that the fragmentation occurs in the neutral clusters before ionization rather than in the photoions [14]. Thus, the fragments are expected to be the products of side-reactions of anionic oligomerization. As for the MA system, a flowing ion-molecule reaction was investigated using negative ions of F_3C^-, $NCCH_2^-$ and $C_3H_5^-$ as the polymerization initiators by McDonald and Chowdhury [3]. They found the formation of the fragment ions with the loss of CH_3OH only from the trimer and assigned the ions to be the product of Dieckmann cyclization reaction that is a side-reaction of the polymerization. Dieckmann cyclization is a condensation reaction of the compounds having more than one ester groups, and is known as one of the termination reaction in the polymerization. In the present M-MA clusters, we considered another fragmentation process from the cyclic trimer after exothermic trimerization reaction. However, this process was ruled out in the present cluster formation condition that efficient relaxation proceeds by collision with background buffer gas as noted in the experimental section [14]. After all we concluded that the fragment is produced by the Dieckmann cyclization reaction for the M-acrylic ester clusters. We can summarize the intracluster reaction in the $M(acrylic\ ester)_3$ cluster as Scheme 1.

In the M-methacrylic ester systems, the same Dieckmann cyclization is expected to produce the fragments from $n=3$. By contrast, another fragmentation reaction should be considered for the formation of fragments with loss of ROH from $n=2$ cluster. In this case, Dieckmann cyclization reaction can hardly be considered because of the ring strain in the product (four-membered ring). As another reaction process, it is expected that the nucleophilic substuitution by the O atom in the carbonyl group is promoted in the methacrylic ester systems. Thus we concluded that the fragments from the $M(methacrylic\ ester)_2$ are produced by the lactonization reaction shown in Scheme 2 [26].

Scheme 1

$$M + \left(\begin{array}{c} \\ \end{array} \right)_3 \text{-OR}$$

$$M^+ \left[RO_2C \diagdown CO_2R \atop CO_2R \right]^{\cdot-}$$

cyclic trimerization

$$M^+$$

CO_2R O RO_2C

Dieckmann cyclization ↓

$$M^+$$

$RO \diagdown CO_2R$ O

+ ROH

Scheme 2

$$M + \left(\begin{array}{c} \\ \end{array} \right)_2 \text{-OR} \longrightarrow M^+$$

RO O RO_2C

$$\longrightarrow M^+$$

RO O O

+ ROH

lactonization reaction

4. CONCLUSION

The photoionization mass spectra of clusters of an alkali metal atom (M, M=Na and K) with AN, acrylic ester molecules (MA and EA), and methacrylic molecules (MMA and EMA) have been measured systematically. For all systems examined, the magic number at $n=3$ is clearly observed. The result of photodissociation experiment of the $K(AN)_n$ neutral clusters reveals that the $n=3$ has an anomalous stability relative to other sizes of clusters. Based on the polymerization reaction in the condensed phase and the observations in the studies of $(AN)_n^-$, it is concluded that the observed magic number is generated by intracluster anionic oligomerization induced by electron transfer from the alkali metal atom. The observation of the fragment ions with the loss of ROH for the acrylic ester and the methacrylic ester systems also supports the intracluster oligomerization reaction. In these systems, the existence of the counter ion (reaction initiator) has been proven to have an important role in the promotion of the oligomerization reaction. Therefore, in comparison with the former approaches to the anionic polymerization in the gas phase using molecular anions or free electrons as reaction initiators, the present systems of an alkali metal atom with VM clusters are expected to be more suitable as microscopic models to simulate the anionic polymerization reaction in the condensed phase.

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