Photoinduced Polymerization of Haloaniline Studied by Liquid Beam-Multiphoton Ionization-Mass Spectroscopy

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An alcohol (ROH) solution of *p*-haloaniline, *p*-$NH_2C_6H_4X$ (X = Cl, Br, I), was introduced into vacuum as a continuous liquid flow (liquid beam) and was irradiated with a UV nanosecond laser having a pulse width of ∼5 ns or a UV femtosecond laser having a pulse width of ∼200 fs. Ions produced by multiphoton ionization in the liquid beam and ejected from it were analyzed by a time-of-flight mass spectrometer. The mass spectrum of ions ejected from the liquid beam exhibits peaks assignable to $H(-NHC_6H_4-)_nH^+$, $H(-NHC_6H_4-)_nOR^+$, and $H(-NHC_6H_4-)_nX^+$. The spectral features change significantly when the pulse width of the excitation laser is elongated from the femtosecond to the nanosecond range: (1) significant reduction of the $H(-NHC_6H_4-)_nBr^+$ intensities and (2) increase of the degree of polymerization in $H(-NHC_6H_4-)_nH^+$ and $H(-NHC_6H_4-)_nOC_2H_5^+$. These findings indicate that a sequential polymerization of *p*-$NH_2C_6H_4X$ is driven by photoabsorption. The degree of polymerization is explained in terms of rate equations of the polymerization.

Introduction

An intense laser facilitates exploration of novel photochemical reactions initiated by multiphoton absorption.[1−5] When a molecule in a solution is irradiated with an intense laser, the molecule is excited to an upper electronic state by absorbing one photon and further excited to a higher excited state or an ionization continuum by absorbing more photons. The excited or ionized molecule tends to react with solvent or solute molecules through reaction paths that are different from those of a conventional photochemical reaction. To elucidate the reaction mechanism in the solution, chemical species emerging during the reaction should be detected. To this end, a transient optical spectroscopy has been employed to detect transient chemical species being generated during a given chemical reaction.[3,4] A liquid chromatograph in combination with mass spectroscopy, etc., have been used for the product analysis, as well.[6]

It is more straightforward to directly observe reactants, products, and reaction intermediates including ionic species simultaneously by a mass spectroscopic technique, etc. To interface a liquid medium with such techniques, the medium should be placed in a vacuum at a reasonably low pressure. One of the most appropriate methods is the liquid beam technique which enables us to prepare a liquid surface in a vacuum at a pressure of $10^{-5}-10^{-6}$ Torr.[7−13] One can initiate a chemical reaction by multiphoton ionization on the liquid surface by laser irradiation on it and detect ionic species produced by the reaction and then ejected from the liquid surface into vacuum by means of mass spectroscopy, etc.

In fact, we have discovered novel multiphoton-induced reactions occurring in the vicinity of solution surfaces.[14,15] It has been revealed that in some reactions the precursor is either
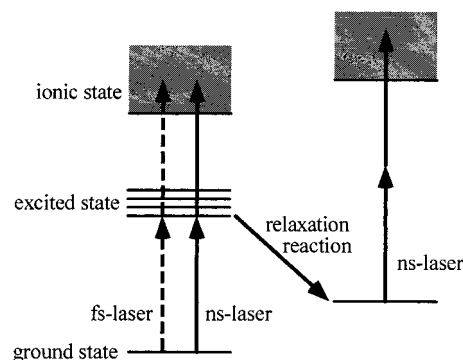

Figure 1. Excitation and relaxation paths to ionization continuum by the ns- (solid lines) and fs-lasers (dotted lines).

an ionic or an electronically excited species produced by multiphoton excitation. To identify the precursor of a given reaction, one has to prepare preferentially a desired precursor (see Figure 1). A laser having a pulse width of femtoseconds (fs-laser) can be employed for preparing an ionic precursor, since the fs-laser excites a molecule to its ionization continuum with high efficiency. On the other hand, a laser having a pulse width of nanoseconds (ns-laser) can be employed to prepare both a neutral and an ionic precursor.[16−19]

In the present work, a liquid beam of an alcohol solution of haloaniline was irradiated with ns- and fs-lasers, and chemical reactions initiated by multiphoton excitation were observed by measuring ionic species ejected from the liquid beam surface.[20−23] In an electronically excited state of the solute molecule, homolytic cleavage of a carbon−hydrogen bond, nucleophilic substitution, and hydrogen abstraction are known to proceed, while nucleophilic substitution is expected to occur through its ion as well because electrophilicity of the molecule increases with its ionization (abstraction of an electron).[24−26] In addition, haloaniline has two functional groups; the halogen atom is released upon photoexcitation, and the radical site is produced accordingly, while the NH_2 group is vulnerable by electrophilic attack. This feature predicts polymerization of haloaniline by
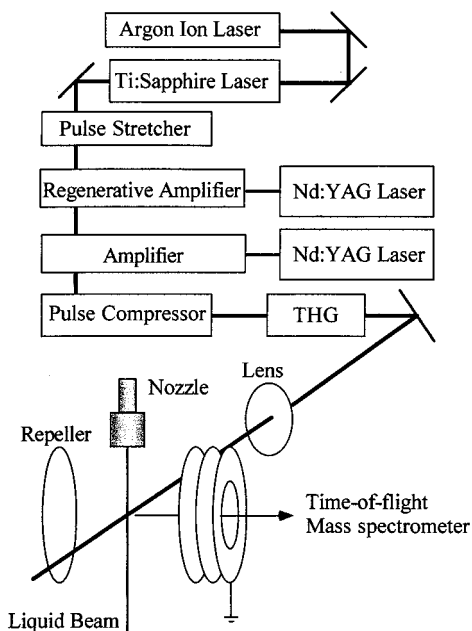
Figure 2. Schematic diagram of the liquid beam apparatus and the fs-laser for detection of product ions. The ns-laser was tightly focused and the fs-laser was defocused onto the liquid beam, so as to provide almost identical laser fluence of 10^8 W/cm^2.

Figure 3. Mass spectra of ions produced from 0.75 M solutions of *p*-PBA in ethanol (a) and 1-propanol (b) by irradiation of a 272 nm ns-laser. Ions, $[H-(NHC_6H_5)_n-H]^+$, do not shift, but $H-(NHC_6H_5)_n-OR^+$ (R = Et, Pr) shift by $m/z = 14$ with increase in the chain length of R.

the photoexcitation. Inhomogeneous solvation of halonaniline on the liquid beam surface elucidated so far may play an important role for the polymerization reaction.[10] The reactions initiated by the excited molecule and its ion were separately observed by irradiation of the ns- and fs-lasers, and a sequential polymerization of p-NH$_2$C$_6$H$_4$X was found to be driven by multiphoton excitation. The polymerization scheme was successfully explained by a simple kinematic model.

Experimental Section

A schematic diagram of the experimental setup is shown in Figure 2. A laminar flow of an alcohol solution of *p*-haloaniline (liquid beam) was prepared in a vacuum chamber by introducing the solution through a nozzle having an aperture with a diameter of 20 μm; the solution was pressurized by a pump designed for a liquid chromatograph, and its flow rate was maintained at 0.2 mL/min. The liquid beam was captured in a cylindrical trap cooled by liquid N$_2$ located 5 cm downstream from the nozzle. The pumping speed of the liquid N$_2$ trap was estimated to be 5000 L s^{-1}. The liquid-beam chamber was additionally evacuated by a 1200 L s^{-1} diffusion pump. The ambient pressure was kept at 10^{-5}–10^{-6} Torr, even when the liquid beam was injected into the main vacuum chamber.

After traveling a distance of 5 mm from the nozzle, the liquid beam was crossed with a UV laser beam at the acceleration region of the TOF mass spectrometer. Two lasers having different pulse widths were used for this experiment. A laser with a pulse width of ~5 ns (ns-laser) was obtained by frequency-doubling the output of a Quanta-Ray PDL-3 dye laser pumped by the third harmonics of a Quanta-Ray GCR-3 Nd: YAG laser. A laser with a pulse width of ~200 fs (fs-laser) and an output power of 100 μJ/pulse was obtained as follows: The output of a Ti:sapphire laser (Tsunami) pumped by an Ar ion laser was amplified. The third harmonic of the output was made by mixing the second harmonic and the fundamental in a KDP crystal. The pulse width of the fs-laser was measured to be typically 200 fs from interference between separated two laser beams; two spatially and temporally overlapped laser
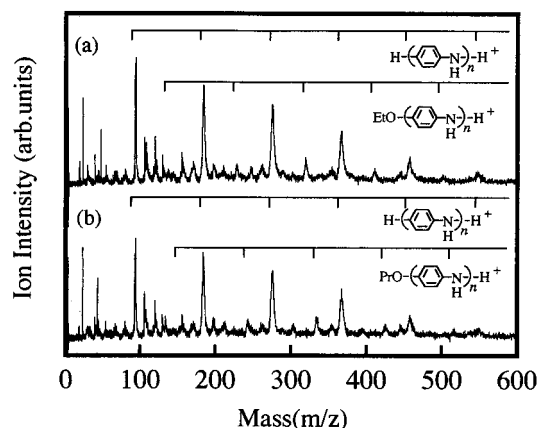
pulses interfere with each other, and the interference was monitored as a function of the optical delay between the two laser pulses. The ns-laser was tightly focused, and the fs-laser was defocused onto the liquid beam, so as to provide almost identical laser fluence of 10^8 W/cm^2.

Ions produced by the laser photoionization were mass-analyzed by a reflectron TOF mass spectrometer. Ions ejected from the liquid beam were accelerated by a pulsed electric field in the direction perpendicular to both the liquid and the laser beams. A delay time from the ionization to the ion extraction was varied in the range of 0–1.0 μs in order to obtain a higher mass resolution: This delayed extraction enables us to prevent the mass peaks from being broadened owing to delayed ion ejection from the liquid surface and metastable decay of the ejected ions with a lifetime shorter than 10^{-6} s. The ions were steered and focused by a set of vertical and horizontal deflectors and an einzel lens and then were reversed in a reflectron that provides a reversing field titled by 2° off the incoming beam axis. After traveling a 0.5 m field-free region, the ions were detected by a Murata EMS-6081B Ceratron electron multiplier. Time-of-flight signals from the multiplier were amplified and processed by a Yokogawa DL 1200E transient digitizer based on an NEC 9801 microcomputer. The mass resolution, defined as $m/\Delta m$, was 100 at $m = 150$ under the present experimental conditions.

Commercially available *p*-bromoaniline (PBA, p-NH$_2$C$_6$H$_4$-Br), *p*-chloroaniline (PCA, p-NH$_2$C$_6$H$_4$Cl) and *p*-iodoaniline (PIA, p-NH$_2$C$_6$H$_4$I) (Wako Pure Chemical Industries Ltd., 99% purity) were used without further purification.

Results

Figure 3a shows a typical mass spectrum of ions produced from a 0.75 M ethanol solution of *p*-bromoaniline under irradiation of the ns-laser at the wavelength of 272 nm. In this spectrum, a series of intense peaks appears at $m/z \geq 90$ with the equal mass difference of 91. Ions containing one bromine, $H(-NHC_6H_4-)_nBr^+$, are slightly discernible, as well. To identify these peaks, ethanol is replaced with 1-propanol, and m/z values are observed as shown in Figure 3b. In this spectrum, one series of peaks having the mass of $93 + 91n$ does not shift by the replacement of the solvent, while the other shifts by 14, where n is an integer. The peak shift corresponds to the mass difference between ethanol and 1-propanol. This result indicates that the former series of ions does not include any alcohol

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molecule, while the latter includes one alcohol molecule. Therefore, the former series of ions ($m/z = 93 + 91n$) is assigned to aniline polymer ions, $H(-NHC_6H_4-)_nH^+$, and the latter with $m/z = 137 + 91n$ and $151 + 91n$ are assigned to alcohol-substituted ions, $H(-NHC_6H_4-)_nOR^+$ with R = Et and Pr and $H(-NHC_6H_4-)_nH^+$, respectively.

The intensities of $H(-NHC_6H_4-)_nH^+$ and $H(-NHC_6H_4-)_n$-OEt^+ were measured as a function of the incident laser power; with increasing the laser power, the intensities are found to rise at a threshold value. As discussed in our previous papers, an ion is ejected from the liquid beam surface by a repulsive force exerted by neighboring cations generated by multiphoton excitation, when the charge density of the cations exceeds a threshold value, above which the Coulomb repulsive energy surpasses the solvation energy.[7]

Parts a, b, and c of Figure 4 show typical mass spectra of ions produced from 0.75 M ethanol solution of *p*-bromoaniline, *p*-chloroaniline and *p*-iodoaniline, respectively. The mass spectrum for the *p*-iodoaniline solution resembles most closely that for the *p*-bromoaniline solution, where aniline polymer ions and alcohol-substituted ions are observed. The intensities of the ions containing bromine and iodine are very weak, while those containing chlorine are intense.

Figure 5 shows a typical mass spectrum of ions produced from 0.75 M 1-propanol solution of *p*-bromoaniline by irradiation of the fs-laser at 272 nm. In this spectrum, aniline polymer ions, $H(-NHC_6H_4-)_nH^+$, $H(-NHC_6H_4-)_nBr^+$, and $H(-NHC_6H_4-)_nOPr^+$, are discernible. The peaks of $H(-NHC_6H_4-)_nBr^+$ in the fs-mass spectrum are more prominent than the corresponding peaks in the ns-mass spectrum.

Discussion

Product Ions. As described previously, $H(-NHC_6H_4-)_nH^+$, $H(-NHC_6H_4-)_nOR^+$, and $H(-NHC_6H_4-)_nBr^+$ are produced from a *p*-bromoaniline (PBA) solution in alcohol. These ions consist of chemically bonded $-NHC_6H_4-$, which is regarded as the building block, and are produced by chemical reactions initiated by multiphoton excitation on the liquid beam surface. If the solute ion or molecule does not react with the solute or the solvent molecules, it must be ejected from the surface, being accompanied by the solvent molecules. For example, C_6H_5-$OH^+(H_2O)_n$ is ejected from the surface of an aqueous solution of phenol by multiphoton excitation, where the solute ion, C_6H_5-OH^+, is known to be nonreactive with solvent H_2O molecule.[27]

In the previous study, we have proposed a mechanism of ion ejection from a liquid beam after laser irradiation:[7,9] Upon irradiation of the laser on the liquid beam surface, electrons are released at first from the region as deep as ~2 nm, and then, ions are repelled from the electron-depleted surface region. As the escape depth of the photoelectrons is in a range of ~2 nm, the escape depth of the ions is considered to be less than that of the photoelectrons. This implies that the reactions occur in the close vicinity of the liquid beam surface where haloaniline is inhomogeneously solvated.[10] The inhomogeneous solvation will be discussed in the following section.

Ion−Molecule Reactions Initiated by fs-Laser. Under irradiation by the fs-laser, a solute molecule is ionized by absorbing photons resonantly without any relaxation in the intermediate states involved, because the laser pulse is much shorter than the relaxation time. Therefore, the parent ion, $NH_2C_6H_4Br^+$ (PBA^+), is the most plausible candidate for the reaction precursor. The dimer ion, $H(-NHC_6H_4-)_2Br^+$, is considered to be produced by the reaction of PBA^+ with PBA, where the positively charged carbon atom of PBA^+ is attacked
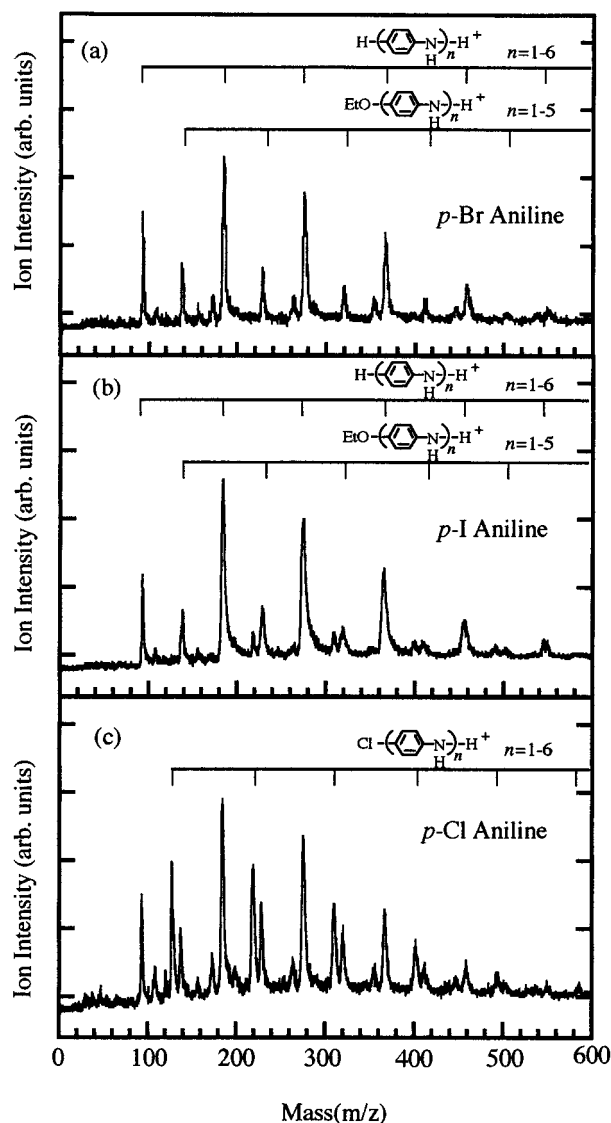

Figure 4. Mass spectra of ions produced from a 0.75 M PBA (*p*-PBA) solution in ethanol (a), a 0.75 M PIA (*p*-iodoaniline) solution in ethanol (b), and a 0.75 M PCA (*p*-chloroaniline) solution in ethanol (c).
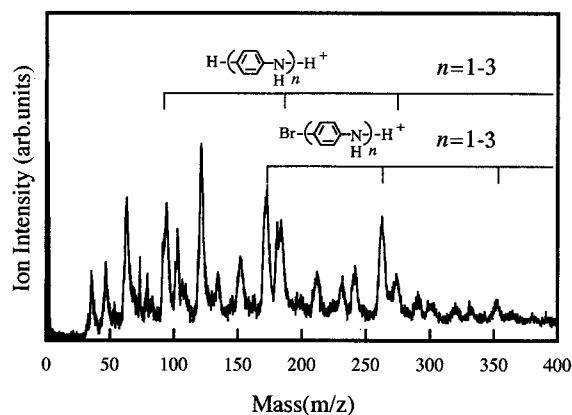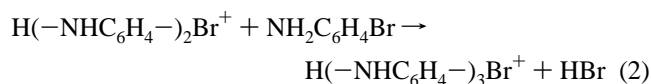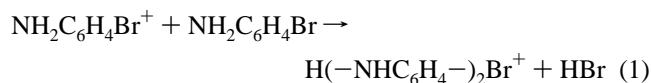

Figure 5. Mass spectrum of ions produced from a 0.75 M *p*-PBA solution in 1-propanol by irradiation of the fs-laser, where $H-(-NHC_6H_5-)_n-Br^+$ ($1 \leq n \leq 3$) are observed.
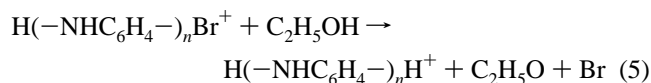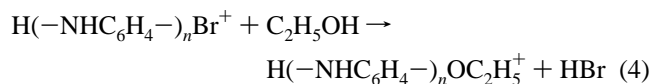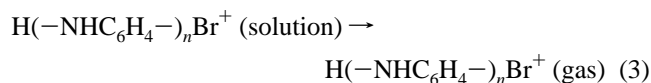
by a lone-pair electron of the nitrogen atom in the amino group of PBA. The dimer ion reacts further with another PBA. This reaction continues to generate a larger polymer ion, $H(-NHC_6H_4-)_nBr^+$ (propagation reaction), and is terminated

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when the ion is ejected into vacuum. Thus, $H(-NHC_6H_4-)_n$-Br^+ is produced as observed in the gas phase. On the other hand, nucleophilic substitution of alcohol to the polymer PBA ion should occur as termination of the propagation reaction, although the nucleophilic substitution has not been reported so far. The termination results in formation of $H(-NHC_6H_4-)_n$-OR^+ and $H(-NHC_6H_4-)_nH^+$. Neutralization of the ions is not taken into account, since only ions are detected in the present measurement. In summary, the polymerization propagates as
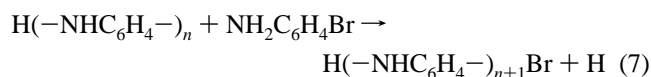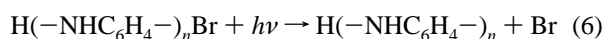
$$NH_2C_6H_4Br^+ + NH_2C_6H_4Br \rightarrow$$
$$H(-NHC_6H_4-)_2Br^+ + HBr \quad (1)$$

$$H(-NHC_6H_4-)_2Br^+ + NH_2C_6H_4Br \rightarrow$$
$$H(-NHC_6H_4-)_3Br^+ + HBr \quad (2)$$

$$...$$

and is terminated as

$$H(-NHC_6H_4-)_nBr^+ \text{ (solution)} \rightarrow$$
$$H(-NHC_6H_4-)_nBr^+ \text{ (gas)} \quad (3)$$

$$H(-NHC_6H_4-)_nBr^+ + C_2H_5OH \rightarrow$$
$$H(-NHC_6H_4-)_nOC_2H_5^+ + HBr \quad (4)$$

$$H(-NHC_6H_4-)_nBr^+ + C_2H_5OH \rightarrow$$
$$H(-NHC_6H_4-)_nH^+ + C_2H_5O + Br \quad (5)$$

The degree of polymerization of the product ions by the fs-laser excitation is much smaller than that by the ns-laser excitation.
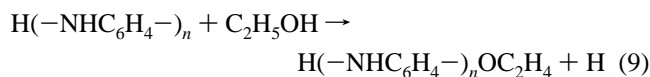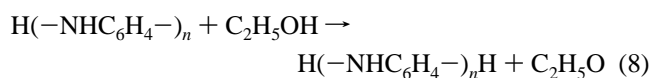
Reactions through Excited State by ns-Laser. The ion distribution changes significantly when the pulse width of the excitation laser is elongated from a fs- to a ns-range: (1) significant reduction of the $H(-NHC_6H_4-)_nBr^+$ intensities and (2) increase in the degree of polymerization for $H(-NHC_6H_4-)_nH^+$ and $H(-NHC_6H_4-)_nOC_2H_5^+$. These findings indicate that the precursor of the polymerization reaction initiated by the ns-laser excitation has a characteristic reaction time longer than 200 fs but shorter than 5 ns; the first excited state of the solute PBA molecule is considered to be the precursor, as the lifetime of halobenzene is reported to be less than 50 ps.[28] Note that interval two-photon absorption is longer than 50 ps in the laser-fluence range of the ns-laser used.

A PBA molecule in the first excited state is known to dissociate into an aryl radical and a bromine atom. It is highly likely that the radical reacts further with one additional PBA molecule to form a dimer product, $H(-NHC_6H_4-)_2Br$. The laser is sufficiently intense that this bromine-containing dimer is dissociated into a dimer radical, $H(NHC_6H_4-)_2$, and a Br atom by absorbing one more photon during the same laser pulse. This reaction is repeated until a polymer radical, $H(NHC_6H_4-)_n$, is produced in the same pulse. The reaction (propagation reaction) is expressed as

$$H(-NHC_6H_4-)_nBr + h\nu \rightarrow H(-NHC_6H_4-)_n + Br \quad (6)$$

$$H(-NHC_6H_4-)_n + NH_2C_6H_4Br \rightarrow$$
$$H(-NHC_6H_4-)_{n+1}Br + H \quad (7)$$

The propagation is terminated by reacting with an ethanol molecule as

$$H(-NHC_6H_4-)_n + C_2H_5OH \rightarrow$$
$$H(-NHC_6H_4-)_nH + C_2H_5O \quad (8)$$

$$H(-NHC_6H_4-)_n + C_2H_5OH \rightarrow$$
$$H(-NHC_6H_4-)_nOC_2H_4 + H \quad (9)$$

These neutral products are ionized by absorbing photons and then are ejected into vacuum.

The polymer ions might be produced through PBA^+ produced by the ns-laser excitation. However, this reaction process is ruled out because no appreciable amount of ions containing a Br atom such as $NH_2C_6H_4Br^+$ is produced (see Figure 3). It is concluded, therefore, that all the ions are produced after dissociation through the excited state.

Degree of Polymerization. As described above, the polymerization propagates through reaction 7 with a rate constant of k_{n1} and is terminated by reactions 8 and 9 with the rate constants of k_{n2} and k_{n3}, respectively, where n represents the degree of polymerization. The branching ratio for the polymerization, η_n, is given by

$$\eta_n = \frac{k_{n1}C}{k_{n1}C + k_{n2} + k_{n3}} = \frac{\kappa_n C}{1 + \kappa_n C} \quad (10)$$

$$\kappa_n = \frac{k_{n1}}{k_{n2} + k_{n3}} \quad (11)$$

where C is the concentration of PBA in the solution. In deriving the above relations, reactions 8 and 9 are treated as a quasi-first-order reaction because an excess amount of ethanol is present, while the rate of reaction 7 depends linearly on the PBA concentration on the liquid beam surface.

The branching ratio is obtained from the intensities of the relevant ions as

$$\eta_n =$$

$$\frac{\displaystyle\sum_{i=n+1}^{\infty} \{[H(-NHC_6H_4-)_iH] + [H(-NHC_6H_4-)_iOC_2H_5]\}}{\displaystyle\sum_{i=n}^{\infty} \{[H(-NHC_6H_4-)_iH] + [H(-NHC_6H_4-)_iOC_2H5]\}}$$

$$(12)$$

where [ ] designates the intensity of the ion shown in the parentheses. The branching ratio for a given n ($n = 1-4$) is plotted as a function of the PBA concentration in Figure 6. The dotted lines show the calculated branching ratios with assuming one best-fitted κ_n:; $\kappa_1 = 7.0 \pm 1.3$, $\kappa_2 = 1.8 \pm 0.2$, $\kappa_3 = 1.1 \pm 0.1$, and $\kappa_4 = 0.63 \pm 0.13$. The decreasing tendency of κ_n with n implies that the rate of the propagation or the polymerization decreases with increasing the length of the polymer chain. As a result of increasing reduction in a propagation rate with degree of polymerization (n), the abundance of a polymer ion decreases with n. The tendency is explained in terms of less electrophilicity of $H(-NHC_6H_4-)_n$ with a larger n owing to the intramolecular electronic polarization toward the radical site. In addition, the steric hindrance of the polymer chain prevents a reagent molecule from approaching the radical site.

Figure 7 shows the plots of η_n against n for three different systems, ethanol solutions of p-bromoaniline (PBA), p-chloroaniline (PCA), and p-iodoaniline (PIA) as a comparison at
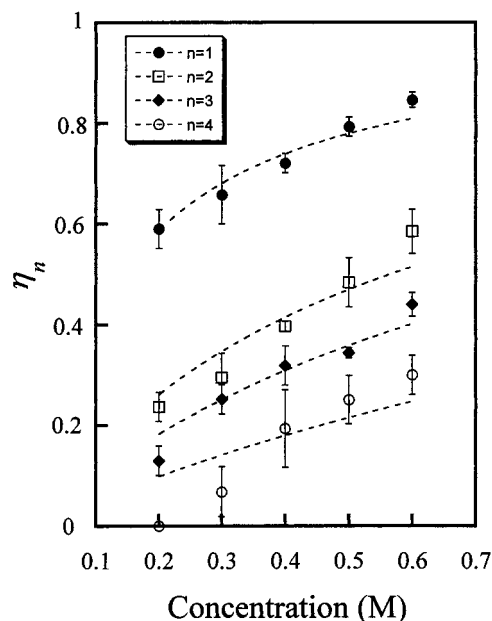
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Figure 6. Branching ratio, η_n, plotted as a function of the degree of polymerization, n.
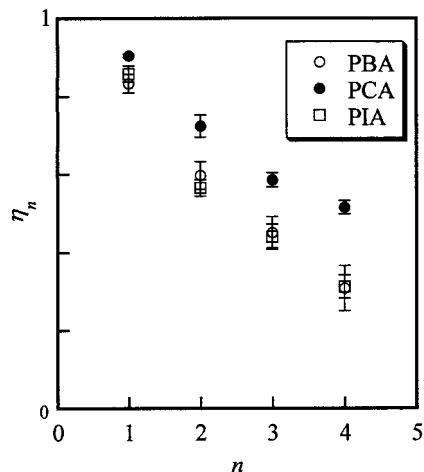

Figure 7. Branching ratio plotted as a function of the PBA concentration. Dotted lines are the least-squares fittings obtained by using eq 10.

0.5 M. In the evaluation of η_n for the system of the PCA solution, the intensity of the chlorine-containing species, $H(-NHC_6H_4-)_nCl^+$, is included as shown below:

$$\eta_n = \frac{\sum_{i=n+1}^{\infty} \{[H(-NHC_6H_4-)_iH] + [H(-NHC_6H_4-)_iOC_2H_5] + [H(-NHC_6H_4-)_iCl]\}}{\sum_{i=n}^{\infty} \{[H(-NHC_6H_4-)_iH] + [H(-NHC_6H_4-)_iOC_2H_5]\} + \sum_{i=n+1}^{\infty} [H(-NHC_6H_4-)_iCl]}$$

(13)

The decreasing tendency with n is also observed in the PCA and the PIA systems as well as the PBA system. The agreement of the PBA with the PIA data implies that the rate of the propagation or the polymerization is almost equal in the PBA and PIA systems, since a given termination reaction for these systems should have the same reaction rate (see reactions 8 and 9). It is concluded that the larger branching ratio for the PCA system is attributed to a larger rate of the propagation in the PCA system. This reaction scheme also explains a decreasing

intensity of $H(-NHC_6H_4-)_nX^+$ in the order of Cl, Br, and I (see Figure 4), since the lifetime of the first excited state of $H_2NC_6H_4X$ is longer in this order.

Inhomogeneous Solvation of Haloaniline. The polymerization reaction is shown to proceed in a time scale less than 10^{-10} s. Then, the reaction would be diffusion-controlled, as a characteristic time of diffusion is considered to be comparable with that of the polymerization reaction. However, reactions 7, 8, and 9 cannot be diffusion-controlled, because the κ_n value remains unchanged by replacing ethanol with 1-propanol; note that the viscosity coefficients increase from 1.19 to 2.20 m Pa s at 20 ° C, respectively, by this replacement. This finding indicates that haloaniline is inhomogeneously solvated in the surface region where the reaction proceeds and the concentration of haloaniline in the region is higher than the bulk concentration. In addition, as the concentration dependences of η_n are well-reproduced by the simple rate equations in Figure 6, the surface concentration must still increase linearly with bulk concentration. This conjecture is also supported by the scheme of the Langmuir adsorption isotherm: The surface concentration linearly increases with the bulk concentration in a lower concentration region.

Conclusion

In our series of works, we have demonstrated that the liquid beam provides a unique opportunity for studying solvation and reactions of ions on a liquid beam surface by combining mass spectrometry and laser photoionization. In the present study, an ultrashort-pulse laser was introduced for ionization and following rapid reactions of molecules on the liquid beam surface of alcohol−haloaniline solutions. It was discovered that a stepwise polymerization proceeds specifically on on the liquid beam surface, where the haloaniline is inhomogeneously solvated. Our results demonstrate a possibility of undertaking the polymerization reaction, molecule by molecule, with changing the pulse width, the power, the wavelength etc., of the excitation laser. This technique can be extended to a study on formation of a peptide from amino acids that have two functional groups, −COOH and −NH$_2$.

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